A cigarette or other tobacco smoke filter is disclosed which has a filamentary or fibrous cellulose acetate support carrying a stabilized mixture of zinc oxide and an alkali carbonate salt. The zinc oxide and the carbonate salt are dispersed in a plasticizer to form the stabilized mixture by a milling operation.

7 Claims, 3 Drawing Figures
FIG. 2

ZINC OXIDE
EXPECTED
SODIUM CARBONATE
ACTUAL MIXTURE

% REMOVAL HYDROGEN SULFIDE

0 10 20 30 40 50 60 70 80 90 100

m^2

0 1 2 3 4 5 6 7 8 9 10

11 12
FILTER EFFICIENCY CONTOURS V.S. AMOUNT & RATIO OF ADDITIVE

EXPECTED EFFICIENCY FOR HYDROGEN CYANIDE (EQUATION II)

EXPERIMENTAL EFFICIENCY

ZINCOXIDE/SODIUM CARBONATE
8:1 MOLAR RATIO LINE

ZINC OXIDE/SODIUM CARBONATE
1.5 MOLAR RATIO LINE

FIG.3
BACKGROUND OF THE INVENTION

The invention is directed to improvements relating to filters for tobacco smoke. The filters are intended for use attached either to cigarettes, cigars, or cigarillos, or as a separate cartridge filter for pipes, cigarettes, or cigar holders. Further, the filters may be employed attached to smoking articles formed from reconstituted tobacco.

As is well known, tobacco smoke consists of a gaseous or vapor phase in which are suspended liquid or semi-liquid droplets or solid particles, which form the visible smoke stream. Conventional cigarette filters are formed fromcellulosic fibers or convoluted creped paper formed into a cylindrical plug to remove varying proportions of the droplets passing therethrough. For the most part, they do not effectively remove gaseous molecules.

Such gaseous molecules, including hydrogen cyanide and hydrogen sulfide can be considered as gases or highly volatile liquids. In the brief period of time in which they are carried from the tobacco combustion zone to the smoker’s mouth, there is relatively little time for the gases to condense into droplets. Consequently, these materials are almost entirely found in the vaporized state as they leave the smoking article and enter the smoker’s mouth. The smooth and generally non-porous nature of commonly used fibrous filtering materials may capture tobacco smoke droplets, but do not present a sufficient surface area to effectively adsorb gaseous molecules.

In an attempt to improve the adsorptive properties of conventional tobacco smoke filters, various adsorbents have been proposed for ordinary filtering materials. In U. S. Pats. No. 3,251,365 and 3,460,543, it is disclosed that zinc oxide particles may be added to a filter for a smoking article. However, zinc oxide particles, per se, are not efficient in removing gaseous components, particularly hydrogen cyanide and hydrogen sulfide from tobacco smoke, except at unacceptably high levels.

Various carbonates, including sodium carbonate, are described as being useful to reduce the temperature of burning tobacco in various prior art patents, such as U. S. Pat. No. 3,034,932. Tests have shown, however, that sodium carbonate, magnesium carbonate and calcium carbonate in either the hydrous or anhydrous form, have very limited effectiveness in removing volatile components from smoke, particularly hydrogen cyanide. Sodium carbonate has proven particularly inefficient in removing hydrogen sulfide from tobacco smoke.

In U.S. Pat. No. 3,550,600 it is disclosed that a mixture of hydrated zinc acetate and sodium acetate removes volatile compounds from tobacco smoke, including hydrogen cyanide and hydrogen sulfide. While the above metal organic salts provide satisfactory selective removal of volatile constituents, there remains an additional need for providing selective removal of volatile smoke constituents, employing inexpensive and readily available additives, such as inorganic salts. It is well known that inorganic salts are difficult to admix with the organic plasticizers commonly employed to deposit additives on cellulose acetate filter material. As illustrated hereinbelow, attempts to substitute sodium carbonate for the sodium acetate of the 600 Patent described above have proved unsatisfactory. Severe reductions in selective removal of gaseous components, particularly hydrogen sulfide are noted.

SUMMARY OF THE INVENTION

It is, therefore, a primary object of the present invention to provide an improved filter additive adapted to be combined with a filter material for removing substantial quantities of volatile constituents, particularly hydrogen cyanide and hydrogen sulfide from the smoke of burning tobacco.

It is another object of the invention to provide an improved filter employing inexpensive additive material for removing volatile or gaseous tobacco smoke constituents.

The above, and other beneficial objects and advantages are obtained in accordance with the present invention by a tobacco smoke filter comprising a support or carrier of fibrous, filamentary or sheet filtering material, carrying a mixture comprising zinc oxide and a carbonate salt selected from the group consisting of sodium carbonate, potassium carbonate or mixtures thereof. Such filter may be connected at one end to an outer wrapper having a charge of tobacco therein. To produce the filter a stable suspension of zinc oxide, sodium or potassium carbonate and a liquid plasticizer is formed and the suspension is thereafter sprayed on the filter support.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph illustrating the unexpected selective filtration property with respect to hydrogen cyanide, of the filter of the invention;

FIG. 2 is a graph depicting the unexpected selective filtration characteristic with respect to hydrogen sulfide, of the filter of the invention; and

FIG. 3 is a graph illustrating the unexpected selective filtration properties with respect to hydrogen cyanide of the improved filter material as compared to expected efficiencies for predetermined loadings of additive.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The tobacco smoke filter of the invention is produced by treating a tobacco smoke filtering material formed from, for example, fibrous, filamentary or sheet material with a mixture of zinc oxide and either sodium carbonate, potassium carbonate or mixtures thereof. In order to facilitate application of the additive mixture onto conventional cigarette filtering material, such as cellulose acetate tow, a stable suspension of the mixture is formed.

Although the following discussion is directed to zinc oxide and sodium carbonate additives, it is also applicable to potassium carbonate and zinc oxide additives and other carbonate and zinc oxide mixtures. In general, the stable suspension is formed by intimately combining, with agitation, zinc oxide and sodium carbonate solids and a liquid plasticizer. Conventional liquid plasticizers may be employed such as triethyleneglycol diacetate, triethylenecitrate, triacetin, and glycerol derivatives.

For practical use, generally, the concentration of solids in the dispersed plasticizer is from about 10 to 40 per cent of the combined weight of the solids and plasticizer. In preparing the stable suspension, the additive
solids and liquid plasticizer are introduced into a ball mill, and milled for a sufficient period of time to form a sprayable dispersion stable for at least four to five days. The milling step is carried on for at least about 16 hours to insure that a sufficiently reduced solids particle size is obtained.

The stable additive plasticizer dispersion permits both deposition of the additive on tobacco smoke filter material, such as conventional cellulose acetate tow, and also simultaneous addition of a plasticizer to the tow, which causes a fiber-to-fiber bond to form. Previously, organic water-soluble zinc acetate and sodium acetate salts were added to creped paper in an aqueous solution. It is a feature of the present invention that a stable, sprayable dispersion containing a filter additive and a plasticizer is applied to conventional cellulose acetate tow, both to enhance the selective filtration properties of the resulting filter, and also to provide a strengthened and more resilient filter as a result of the plasticizing action of the dispersion.

Although the molar ratio of zinc oxide to sodium and/or potassium carbonate in the additive mixture may be varied widely, nevertheless, the described ranges are deemed to be most practical and efficient. In general, the molar ratio of zinc oxide to sodium and/or potassium carbonate in the filter additive is from about 25:1 to 1:25. Enhanced selective removal characteristics are obtained when the molar ratio of zinc oxide to sodium carbonate is from about 8:1 to 1:5 as is shown by FIG. 3.

The following discussion demonstrates the unpredicted selective removal efficiencies obtained with the tobacco smoke filter of the invention. The expected filter efficiency for hydrogen cyanide is derived as follows:

\[ A = E_a, B = E_s, C = E_d, D \]

where \( E_f \) = Fractional efficiency of acetate tow only.

\[ E_s = \text{Fractional efficiency of zinc oxide only.} \]

\[ E_d = \text{Fractional efficiency of sodium carbonate only.} \]

\[ A = \text{Amount of hydrogen cyanide presented to the filter.} \]

\[ B = \text{Amount of hydrogen cyanide left after acetate filtration.} \]

\[ C = \text{Amount of hydrogen cyanide left after zinc oxide filtration.} \]

\[ D = \text{Amount of hydrogen cyanide delivered to the smoker, after sodium carbonate filtration.} \]

Considering which is filtered by one component cannot be filtered by the other component, the following is derived:

\[ \text{I. } E_f = A(1 - E_d) = C(1 - E_n) = B(1 - E_s) = E_f(1 - E_s) = E_f(1 - E_n) = E_f E_s + E_f E_d - E_f E_s - E_f E_n \]

Therefore, the total filter efficiency, \( E_n \), is:

\[ \text{II. } E_f = E_f E_s + E_f E_d + E_f E_s E_d - E_f E_s - E_f E_d - E_f E_s - E_f E_d \]

Since \( E_f \) is a mechanical filtration, it is assumed that \( E_f \) is a constant independent of the chemical filtration, \( E_s \) and \( E_n \). Thus values for only \( E_s \) or \( E_n \) are found from the equation:

\[ E_f = E_f(1 - E_s) = E_f(1 - E_n) = E_f \]

where \( t = z \) or \( n \) and \( E_f \) is the total filtration with \( z \) or \( n \).

Once the values for \( E_s \) and \( E_n \) versus the amount of zinc oxide and sodium carbonate are known, then total efficiency contours can be plotted for any mixture on the filter. This is shown in FIG. No. 3. The experimental \( E_f E_s E_d \) term has been found to be much greater than predicted and the total efficiency ratio is raised proportional to

\[ \{E_f E_s E_d \text{ experimental} - (E_f E_s E_d \text{ calculated})\] FIG. No. 3 also shows why the molar ratio range of 8:1 to 1:5, zinc oxide to sodium carbonate, is preferred. Obtaining a filter efficiency of 80 percent and more is simple. One merely adds sufficient zinc oxide and sodium carbonate to stay above and right of the 80 percent contour.

Controlling the filter efficiency between 50 percent and 80 percent is difficult. FIG. 3 shows the greatest separation of the 50 percent and 80 percent contours when the above molar ratios are within 8:1 to 1:5. A 1% variation in additive amount or ratio causes relatively small changes in total filter efficiency in the preferred molar ratio range. A 1 percent variation outside the preferred range results in greater variations in efficiency. Thus, the preferred molar ratio range allows better control over the 50 percent −80 percent filter efficiency range.

Furthermore, with regard to filter efficiencies beyond the 25:1 to 1:25 molar ratio range, the required amount of mixture is near the predicted requirements. Within the 25:1 to 1:25 molar ratio range, high efficiencies are achieved with much reduced amounts of additive on the filter tow.

In general, sufficient zinc oxide and sodium and/or potassium carbonate are employed in the tobacco smoke filter to provide from about 2 to 25 milligrams (mgs.) of solids mixture per cigarette. It is particularly preferred to employ from about 3 to 10 mgs. of the zinc oxide-sodium carbonate mixture per cigarette. As illustrated in FIG. 3, generally at least about 30 micromoles of additive are preferably employed in a filter section.

Comparative tests with mixtures of zinc oxide and calcium or magnesium carbonate illustrate the criticality of employing Group IA metal carbonates. Selective removal efficiencies for hydrogen cyanide and hydrogen sulfide were only a fraction of those obtained with Group IA metal carbonates, especially sodium and potassium carbonate.

The following examples are illustrative only, and are not limiting of scope:

**EXAMPLE I**

In order to demonstrate the efficiency with which the improved filter selectively removes volatile smoke constituents, particularly hydrogen cyanide and hydrogen sulfide, a 30 centimeter (cm.) length of unbleached 3.3Y−44,000 cellulose acetate tow was bloomed by hand. The end of the tow was squared, and 6-centimeter lengths were cut off. The tow weights were adjusted by end-trimming to 400 mgs.
The above-described, bloomed, tow was then sprayed using a conventional laboratory atomizer with a stable dispersion formed by mixing a mixture of 200 grams of zinc oxide, 50 grams sodium carbonate and 550 grams of plasticizer for 24 hours. The molar ratio of zinc oxide to sodium carbonate in the dispersion was 5:1. The plasticizer employed was a mixture of 6 parts by weight triethylene glycol diacetate and 5 parts by weight polyethylene glycol.

The sprayed tow was then gathered, and placed into the tobacco cavity of a manual cigarette making machine. The cigarette-maker employed was the revolutionary LAREDO cigarette-maker, described in U.S. Pat. No. 3,491,768 issued Jan. 27, 1970. The filter-rod of the invention was fabricated as one would fabricate a cigarette in the LAREDO cigarette-maker. The resulting rods were cured for at least four hours, and thereafter severed into 21 mm. segments. The 21 mm. filters were inserted in the tipping cavity of a standard 84 mm. cigarette.

Cigarettes made by the above procedures were smoked mechanically, using a conventional smoking machine which smoked the cigarettes to tipping plus 3 mm., employing FTC procedures.

The filters fabricated by the above procedures contained 4 mgs. of zinc oxide and 0.9 mgs. of sodium carbonate. The proportions of hydrogen cyanide and hydrogen sulfide removed from the smoke were determined by standard analytical methods.

Analysis of the tobacco smoke shows an 80 per cent reduction of hydrogen cyanide, and an 89 percent reduction of hydrogen sulfide, as compared to a control filter-rod fabricated by the above procedures, but formed without the filter additive.

EXAMPLE II

In order to demonstrate the synergistic interaction between the zinc oxide and sodium carbonate, resulting in an unexpectedly enhanced selective removal of hydrogen sulfide and hydrogen cyanide, filter-rods were produced and tested according to the procedure of Example I. A first series of rods was formed containing zinc oxide only as the filter additive. A second series of rods was formed containing sodium carbonate only as the filter additive. A third series of rods contained a mixture of zinc oxide and sodium carbonate. The filter-rods were formed into cigarettes, and tested according to the procedure of Example I.

The results of the tests are illustrated in the graphs of FIGS. 1 and 2. The weight per cent of cyanide or sulfide removed [as compared to untreated smoke] is plotted against weight loading in milligrams of zinc oxide and/or sodium carbonate in the filter section. As illustrated in FIG. 1, typical removal levels for hydrogen cyanide by zinc oxide range from 23 to 58 per cent, while the removal levels for sodium carbonate range from 48 to 62 per cent. As further illustrated in FIG. 1, the expected additive effects of a filter section containing equal loadings by weight of zinc oxide and sodium carbonate is represented by a median line. Since the Gram Molecular Weight for zinc oxide and sodium carbonate is almost identical, the graph also represents the expected smoke selective removal properties at equimolar concentrations.

As seen in FIG. 1, the actual removal efficiency for the filter additive with respect to hydrogen cyanide was over 30 per cent greater than the expected additive result. The theory behind the synergistic interaction is not presently understood. It is postulated, however, that the more uniform deposition of finely divided additive on the filter section provided by the stable dispersion initially formed is at least partially responsible. However, dusted mixtures of additive have yielded somewhat unexpected selective removal efficiencies also. As depicted in FIG. 2, the actual removal efficiency with respect to hydrogen sulfide is found to be 70 per cent better than that expected by the combination of individual ingredients. Again, while the nature of the interaction between the additives is not presently understood, it is postulated that the uniform fine particle dispersion formed allows a more uniform deposition of additive on the filter plug, resulting in a greater surface area of particles presented to the tobacco smoke stream passing therethrough. Prior art methods of introducing solid particles onto filter plugs tended to produce aggregates or agglomerates thereon, thus reducing the surface area of the particles and their selective removal efficiency.

The data graphically presented in FIGS. 1 and 2 is presented in tabular form in Table 1.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Amount mg</th>
<th>Per Filter micro moles</th>
<th>HCN %</th>
<th>H₂S %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc Oxide</td>
<td>2.1</td>
<td>26</td>
<td>23</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>61</td>
<td>37</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>88</td>
<td>38</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>123</td>
<td>58</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>14.2</td>
<td>163</td>
<td>62</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>18.8</td>
<td>206</td>
<td>65</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>24.0</td>
<td>256</td>
<td>70</td>
<td>13</td>
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<td></td>
<td>29.8</td>
<td>306</td>
<td>75</td>
<td>9</td>
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<td></td>
<td>35.0</td>
<td>356</td>
<td>80</td>
<td>5</td>
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<td></td>
<td>42.0</td>
<td>426</td>
<td>85</td>
<td>2</td>
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<td></td>
<td>50.0</td>
<td>506</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>60.0</td>
<td>606</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>3.2</td>
<td>45</td>
<td>48</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>68</td>
<td>51</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>6.8</td>
<td>83</td>
<td>55</td>
<td>17</td>
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<td></td>
<td>9.0</td>
<td>94</td>
<td>59</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td>124</td>
<td>63</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>18.1</td>
<td>184</td>
<td>68</td>
<td>8</td>
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<tr>
<td></td>
<td>25.0</td>
<td>254</td>
<td>72</td>
<td>6</td>
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<tr>
<td></td>
<td>35.0</td>
<td>354</td>
<td>76</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>47.0</td>
<td>474</td>
<td>79</td>
<td>1</td>
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<td></td>
<td>62.0</td>
<td>624</td>
<td>83</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>80.0</td>
<td>804</td>
<td>85</td>
<td>0</td>
</tr>
<tr>
<td>Zinc Oxide/Sodium Carbonate</td>
<td>3.8/0.2</td>
<td>47/2</td>
<td>63</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>4.0/0.9</td>
<td>49/9</td>
<td>68</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>3.3/1.7</td>
<td>40/16</td>
<td>79</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>2.0/2.7</td>
<td>23/23</td>
<td>76</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>1.5/5.0</td>
<td>31/47</td>
<td>86</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>1.8/5.6</td>
<td>22/53</td>
<td>81</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>1.2/6.4</td>
<td>15/60</td>
<td>77</td>
<td>7</td>
</tr>
</tbody>
</table>

EXAMPLE III

In U.S. Pat. No. 3,550,600 there are presented data showing satisfactory properties of a filter formed from zinc acetate and sodium acetate. A test was conducted substituting sodium carbonate monohydrate for the sodium acetate. The filters were formed, attached to the cigarettes, and smoked as described in U.S. Pat. No. 3,550,600. Table 2 summarizes the results obtained.

<table>
<thead>
<tr>
<th>Test Run</th>
<th>Additive</th>
<th>Wt % in filter</th>
<th>Smoke Component component removed %</th>
<th>HCN</th>
<th>H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>zinc acetate</td>
<td>5</td>
<td>60</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>sodium acetate</td>
<td>5</td>
<td>62</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>zinc acetate</td>
<td>5</td>
<td>53</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>sodium carbonate</td>
<td>5</td>
<td>53</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>monohydrate zinc acetate</td>
<td>5</td>
<td>53</td>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>

The results indicate that the substitution of sodium carbonate for sodium acetate causes a 71 percent drop in selective removal efficiency with respect to hydrogen sulfide, and a 7 percent drop with respect to hydrogen cyanide. Notwithstanding the adverse test results, it has been discovered that the further substitution of zinc oxide for zinc acetate provides unexpectedly en-
enhanced smoke-removal properties. Test results have indicated that at substantially identical addition levels, the filter of the invention provides in the order of 20 percent increased hydrogen cyanide removal and in the order of 6 percent increased hydrogen sulfide removal as compared to cigarettes containing zinc and sodium acetate filter additives. As compared to the cigarettes containing a filter plug formed from zinc acetate and sodium carbonate, the present filter provides increased selective removal properties in the order of 30 percent for hydrogen cyanide, and 70 percent for hydrogen sulfide.

**EXAMPLE IV**

A stable dispersion of 74.8 parts plasticizer, 19.8 parts zinc oxide and 6.8 parts potassium carbonate (parts by weight) was formed in accordance with the procedures set forth in Example I.

Filters containing 6 mg of zinc oxide and 2 mg of potassium carbonate (molar ratio of 4.4/1) were formed and tested as per Example I. The removal efficiencies, 73% for HCN and 82% for H_2S, are comparable to an equivalent zinc oxide/sodium carbonate treated filter.

**COMPARATIVE EXAMPLE I**

A stable dispersion of 73.5 parts plasticizer, 20.2 parts zinc oxide and 5.0 parts calcium carbonate was formed and tested as per Example I. Filters containing 6 mg zinc oxide and 1.6 mg calcium carbonate (molar ratio of 4.6/1) were substantially ineffective for removing hydrogen cyanide or hydrogen sulfide. Selective removal efficiencies for hydrogen cyanide and hydrogen sulfide were 22% and 12% respectively.

**COMPARATIVE EXAMPLE II**

A stable dispersion of 74.6 parts plasticizer, 20.3 parts zinc oxide and 5.1 parts magnesium carbonate were formed and tested according to Example I. Filters containing 6 mg zinc oxide and 1.5 mg of magnesium carbonate (molar ratio of 4.1/1) were not effective for removing hydrogen cyanide or hydrogen sulfide with removal efficiencies of 28% and 2% respectively.

This invention is not to be limited except as set forth in the following claims.

Having thus described my invention, what is claimed is:

1. An improved tobacco smoke filter comprising a carrier of fibrous or filamentary cellulose acetate on which is supported a stabilized mixture comprising a plasticizer, zinc oxide and a carbonate salt selected from the group consisting of sodium carbonate, potassium carbonate or mixtures thereof, and said molar ratio of zinc oxide to said carbonate salt being from about 25 to 1 to 1 to 25, said mixture resulting from the intimate dispersion of said zinc oxide and carbonate salt in said plasticizer by a milling operation.

2. The invention in accordance with claim 1, in which the molar ratio of zinc oxide to sodium carbonate is from about 8:1 to 1.5.

3. The invention in accordance with claim 1 in which said mixture comprises from about 90 to 60 percent by weight liquid plasticizer and from about 10 to 40 percent by weight of said mixture of zinc oxide and carbonate salt, said weights based on the combined weight of said mixture and plasticizer.

4. A smoking article comprising a charge of tobacco enrobed in an outer wrapper and a filter connected to one end of said wrapper, wherein said filter comprises a carrier of fibrous or filamentary cellulose acetate on which is supported a stabilized mixture comprising a plasticizer, zinc oxide and a carbonate salt selected from the group consisting of potassium carbonate, sodium carbonate or mixtures thereof, and said molar ratio of said zinc oxide to said carbonate salt being from about 25 to 1 to 1 to 25, said mixture resulting from the intimate dispersion of said zinc oxide and carbonate salt in said plasticizer by a milling operation.

5. The invention in accordance with claim 4 in which the molar ratio of zinc oxide to sodium carbonate is from about 8:1 to 1.5.

6. The invention in accordance with claim 4 wherein at least about 30 micromoles of said mixture is deposited on said filter carrier.

7. The invention in accordance with claim 4 in which said mixture comprises from about 90 to 60 percent by weight liquid plasticizer and from about 10 to 40 percent by weight of said mixture of zinc oxide and carbonate salt, said weights based on the combined weight of said mixture and plasticizer.