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# CIGARETTE WRAPPER MATERIAL AND METHOD FOR PRODUCING SAME

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The present invention relates generally to novel cellulosic compositions having special desirable combustion characteristics and with a method which enables control over cellulose combustion processes and the nature of the resulting products. More particularly, this invention is directed to a novel cigarette wrapper material which, during the combustion or charring thereof occurring during smoking of cigarettes made with such cellulosic or paper wrappers, does not evolve or produce a known carcinogenic substance.

Studies dating back many years as to the causes of cancer have led to the generally accepted conclusion that 3,4 benzpyrene is one of the most potent carcinogenic substances. More recently, studies relating particularly to the causes of bronchogenic carcinoma have revealed that 3,4 benzpyrene is commonly present in substantial and highly dangerous quantities in the combustion products of cellulosic materials such as rags and papers. It has also been determined that 3,4 benzpyrene is a normal constituent of cigarette smoke and, accordingly, many authorities are of the opinion that this fact accounts for the newly discovered link between the prolonged heavy use of cigarettes and malignant primary neoplasms of the lungs.

With the steady increase of 3,4 benzpyrene content in the atmosphere of our cities due in part to the general practice of incinerating all combustible refuse, alarm as to the health hazard involved has been expressed. The smog problem is already well recognized, and health authorities regard smog as a definite health hazard, pointing to the fact that a number of deaths occur whenever the concentration of smog reaches certain high levels. However, some of these same experts are inclined to fear the invisible 3,4 benzpyrene which lurks in the smog as much more dangerous than the visible part of the smog itself. The death rate of asthmatics rises sharply during periods of heavy smog concentration, apparently because of the high solids contents of the atmosphere or because of the presence of large amounts of irritating gases, as in the case of the Donora disaster. But, if cancer may result from the inhalation of contaminated atmosphere with 3,4 benzpyrene, the number of deaths which could eventually be attributed to smogs will be thousands of times greater than the number of acute asthmatic fatalities.

It is also believed that while the substantial elimination of visible smog will save the lives of some asthmatics, the lung cancer problem hazard will not be eliminated unless something is done beyond merely reducing the solids content of metropolitan atmospheres. Apparently, the 3,4 benzpyrene content of combustion products is largely independent of the solids content thereof. Consequently, improvement in combustion conditions does not seem to offer a complete solution to the problem. Smoke abatement, in other words, only scratches the surface of the real smog problem and leaves the greatest danger undiminished.

Similarly, the screening or filtering of cigarette smoke does not and can not provide an answer to the problem



of guarding the smoker against 3,4 benzpyrene. The invisible carcinogen travels through the filter to reach the lungs, while some of the associated constituents of the smoke are caught and collected as visible deposits for the smoker's reassurance.

It is, accordingly, an important object of this invention to provide means by which the 3,4 benzpyrene content of cigarette smoke can be reduced to a negligible amount. With respect to this phase of the invention, it is to be understood that the incorporation in the paper of the compound to be specifically referred to hereinafter results in a decrease in production of the involved carcinogenic substance of at least 85%.

It is a further object of this invention to provide control over certain combustion processes so that the 3,4 benzpyrene content of the products of such processes will be substantially limited.

It is still another object of this invention to enable the realization of the foregoing advantages in a manner which is inexpensive and which requires a minimum of labor, technological knowledge and skill.

A further object of this invention is the provision of means whereby the foregoing objectives can be realized while affording the operator a choice of the several alternatives as to the manner in which the control over the combustion processes involved in the smoking of cigarettes is established and maintained.

Another object of this invention is the accomplishment of the foregoing objectives relative to cigarettes without alteration of the form or appearance of conventional cigarettes and without materially increasing the cost of cigarette production.

An additional objective of the invention is the production of cigarettes in a manner to substantially and effectively reduce the production of 3,4 benzpyrene during the burning thereof while at the same time retaining the same characteristic taste of the cigarette and the same typical ash resultant from combustion of both paper and tobacco. With respect to this objective, it is to be understood that if the resultant ash from paper or tobacco is so altered as to make it adhere to the unburned portion of the cigarette, or results in an unpleasant odor or taste or both, the cigarette will, for all practical purposes, lack utility. As stated, the procedure herein involved and described eliminates the possibility of any such undesirable results. In the practice of our invention, the resultant ash is of the usual sort—a white, formless and friable ash that is readily detachable from the unburned portion of the cigarette.

It is an additional object of the invention to provide a procedure for the addition of compounds substantially reducing the total carcinogenic substances produced in the burning of cigarettes while at the same time reducing the irritating effects of the combustion products normally present in known types of cigarette wrappers.

The foregoing objectives and additional advantages are obtained in accordance with this invention through the use of a certain substance in certain quantity, the substance being incorporated in a suitable manner in cellulose, or, more particularly, as referred to herein, cigarette paper, so that it is available during the combustion of the said cellulose. Accordingly, this invention has both composition and method aspects.

A composition of this invention, described briefly, comprises combustible material containing cellulose and an amount of an ammonia containing substance which will release ammonia upon heating in the amount of 1.2% to 2.1% of the weight of the cellulose, thereby effectively limiting the 3,4 benzpyrene content of the combustion products of this combustible material. Stated in another way, tests have indicated that, in the combustion or charring of ordinary untreated cigarette paper, approxi-

mately one part of 3,4 benzpyrene is produced per million parts of paper. In contrast, combustion of paper treated in our preferred manner, described herein, results in a reduction of at least 85% in the amount of 3,4 benzpyrene formed during the burning or charring of untreated paper. As a matter of fact, in following the briefed procedure and ranges as above described, the benzpyrene reduction normally approaches 100%.

In its method aspect, this invention, in general, involves heating a substance in the presence of the cellulose containing material and thereby substantially and effectively decreasing the 3,4 benzpyrene content of the combustion products of cellulose under most conditions.

In view of the foregoing brief descriptions, it will be understood that the fundamental discovery which we have made and which underlies our present invention in all its phases and aspects relates to the novel and unexpected effect which certain substances have under certain conditions upon the processes of combustion of cellulosic materials. Under ordinary combustion conditions, particularly under smoldering, slow combustion, paper materials, such as conventional untreated cigarette wrappers, yield combustion products in which the 3,4 benzpyrene level is dangerously high. By smoldering we mean an oxidation process which takes place with visible light but without open flame. Optical pyrometer measurement indicate temperatures, at such smoldering conditions, to run between 500° and 900° centigrade.

We have found that no matter how combustion is carried out and no matter what the conditions of the combustion operation may be as to such factors as rates, temperatures and oxygen supplies, the amount of 3,4 benzpyrene in the combustion products of cellulose materials can be consistently and substantially limited.

As a result of our original discovery and the results of the exploratory work following it, we formulated a theory as to what occurs in a combustion operation conducted in accordance with this invention. Subsequent experimental work tends to support our original assumptions and has enabled us to determine to a large extent the metes and bounds of this invention as well as to accurately predict the utility of any substance for our purposes. Thus, we have found that there are certain substances, sharing a single common property, which are effective to inhibit 3,4 benzpyrene formation during the combustion of cigarette wrapper papers and the like.

There may be one or several chemical mechanisms accounting for the action of these effective substances. It is, accordingly, possible that these substances may act in different ways to accomplish the results of this invention, and it is also possible that one substance will function in different ways at the same time through different molecules released under the combustion conditions for action directly upon 3,4 benzpyrene or upon the building blocks necessarily present in the construction of the 3,4 benzpyrene molecule.

In accordance with the theory which we have evolved as a result of our observations and our experimental work up to the present time, 3,4 benzpyrene is present in combustion products because of a reaction which takes place at an elevated temperature between intermediate combustion products of cellulose. A material such as the conventional cigarette wrapper does not normally contain any detectable amount of 3,4 benzpyrene. Furthermore, there does not appear to be any 3,4 benzpyrene derivative in these cellulose containing substances. Consequently, a molecular breakdown mechanism does appear to explain the presence of this carcinogen in cigarette smoke.

Synthesis of 3,4 benzpyrene would be effectively prevented in accordance with our theory if the chemical building blocks required either were not created or were not released in the combustion process, or if they were destroyed or neutralized before they could combine to produce this substance. As we envision it, the molecules which might reasonably be expected to combine under the relatively high temperature circumstances of cellulose combustion to produce 3,4 benzpyrene react instead in the preferred embodiment of our invention with ammonia which is probably made available in the surrounding atmosphere to prevent the formation of benzpyrene. In any event, our factual observation is that certain ammonium salts, in which the ammonium content is at a certain level, inhibit to a substantial degree the formation of the involved carcinogen=3,4 benzpyrene.

The essence of our invention is the discovery that certain ammonium containing compounds, incorporated into the cigarette paper, have the ability to release ammonia under smoldering or slow-burning conditions and that it is this released ammonia which substantially precludes the formation of 3,4 benzpyrene. The preferred substances that we employ in accordance with the instant invention, and which so preclude this formation of benzpyrene, are as follows: ammonia sulfamate, ammonium persulfate and ammonium perchlorate.

These substances may be used in combination, if preferred, to gain other advantages such as rate of burning or preferred ashing qualities, the factor of importance being the available ammonia. It is obvious that the actual weight percent of the salt will vary depending on the weight percent of contained available ammonia in the salt.

Examples of successful combinations are listed below which will provide a reduction of approximately 95% of the 3,4 benzpyrene in the tars.

| Salts | Wt. Percent | Wt. Percent $NH_3$ |
|---|---|---|
| Ammonium sulfamate | 5 | 1.5 |
| Ammonium sulfamate<br>Ammonium persulfate | 3<br>4 | .90<br>.60 |
| Ammonium sulfamate<br>Ammonium persulfate | 4.75<br>.54 | 1.42<br>.08 |
| Ammonium sulfamate<br>Ammonium perchlorate | 3<br>4.15 | .90<br>.60 |

In addition to the above, we have found that the following additional compositions may be successfully employed to release ammonia in such amount as to substantially reduce production of benzpyrene during smoldering or slow burning conditions: ammonium chloride, nickel hexammino sulfate, nickel hexammino chloride, cobalt hexammino sulfate, cobalt hexammino chloride, ammonium aluminum sulfate, calcium ammonium sulfate, ammonium perchlorate, ammonium persulfate, ammonium sulfamate, sulfamide and urea sulfate.

The above pairings in the percentage amounts indicated produce excellent results. As stated, the use of a single one of these will also attain the stated objectives of this invention. For example, an 8.3% inclusion in cigarette paper of ammonium perchlorate provides 1.2% available $NH_3$ and therefore results in a satisfactory product.

It is to be observed that not all ammonium containing substances are capable of producing the desired results. Undoubtedly the reason for this is the inability of such compounds to properly decompose and interfere with formation of the carcinogen under the combustion conditions of the type herein contemplated. For example, many organic amines are inoperable in a sense herein used; typically, amides, glycine, acedamid, ammonium nitrate and an organic ammonium salt, such as ammonium acetate. In any event, the ammonium sulfamates, perchlorates and persulfates do effectively prevent 3,4 benzpyrene build-up

The preferred substances for use in the wrapper which substantially completely eliminate production of benzpyrene have been set forth in the foregoing. However, the other alternate materials named may be used in

varying amounts, the percentage by weight with respect to the paper being readily calculable. As an example, it can be shown, with respect to ammonium sulfamate, that this salt decomposes under smoldering conditions in cigarette paper in accordance with the following equation:

$$2(NH_4)SO_3NH_2+2CaCO_3 \rightarrow 4NH_3+2CaSO_4+2CO_2$$

From the above equation, those skilled in the art will appreciate that 4.25% of ammonium sulfamate is required to provide 1.2% of available $NH_3$. Such a calculation follows the customary method of computing the known molecular weights of the starting substances and solving the usual arithmetical equation for the percentage amount of released ammonia that is desired. In similar fashion, those skilled in the art can compute the amount of any of the other ammonia releasing salts to be added to the paper to obtain released ammonia within the stated range of 1.2 to 2.1%.

Those skilled in the art will understand that it is also possible to use other substances or mixtures of substances which are normally regarded as the equivalents of these substances for the purposes of this invention, the measure and guide of equivalency being our theory as expressed above.

The amount of the control agent added is determined by the weight percent of contained available ammonia. We have found experimentally that 1.2% available $NH_3$ will provide a 90% reduction, that 1.5% will provide approximately a 95% reduction, that 2.1% available $NH_3$ will provide approximately a 98% reduction. Thus, it can be easily seen that the amount of control agent to provide a specified reduction will vary inversely as the percent of $NH_3$.

As an example:

| Agent | Percent Contained $NH_3$ | Percent Salt Necessary for 90 Percent Reduction |
|---|---|---|
| Ammonium sulfamate | 33.5 | 4.25 |
| Ammonium persulfate | 15 | 8 |
| Ammonium perchlorate | 14.5 | 8.3 |

The proportion of the active ingredient in these substances is the determining factor in all cases. The quantity of available ammonia therein determines the amount of the agent to be incorporated in the paper or to be associated with it in such a way as to provide the requisite quantity of ammonia for 3,4 benzpyrene control within predetermined limits. Those skilled in the art can, accordingly, readily determine the relative amounts of the various substances to be used in accordance with this invention and they will be able to adjust the mixtures with respect to these agents to balance reagent cost against other factors to obtain the desired results with a minimum of expense and difficulty.

The method of this invention involves, in the case of cigarette papers, the impregnation or coating of a conventional cigarette paper with a substance capable during the smoking process of controlling 3,4 benzpyrene production. Thus, in treating cigarette papers where distribution of the control agent is highly critical, we prefer to spray the finished web prior to the time that it is introduced into the cigarette machine. Here, again, however, there are alternatives which may better suit the needs of the individual users and these are contemplated by the present invention and are within the scope of the appended claims. For example, a solution or suspension of a control agent or substance may be brushed on a cigarette paper web in the latter stages of its production, or the web may be dipped into such a solution or suspension. Alternatively, the pulp from which the web is to be made may be treated with one of our control substances so that when the web is formed it will contain the requisite amounts of such substance in uniform distribution.

The following examples are offered by way of illustration and not limitation to acquaint those skilled in the art further with our preferences as to the practice of the present invention. It is, of course, to be understood in the practice of the following examples that reference to the amount of control substances in the paper treated is directly proportional to the strength of the treating solution and retention thereof by the paper. Thus, a paper treated with a 5% solution and having 100% retention or "pickup" of the solution, would, upon drying of the solution, have impregnated or incorporated upon it 5% of the given substance.

*Example I*

A strip of commercial cigarette paper, 5" long and weighing 0.945 gm., is dipped into a 5% aqueous $NH_4$ sulfamate solution and is removed, the excess solution being squeezed out between rolls to about 100% pickup. It is then dried. The paper after drying shows an increase in weight of approximately 0.047 gm. indicating an increase in weight of approximately 5% representing the ammonium sulfamate content. This will provide approximately 1.5% available $NH_3$. On combustion, or by charring in the smoking of a cigarette, it was found that the composition products from the burning of this treated paper contained approximately 5% of the amount of 3,4 benzpyrene present in the combustion product of untreated paper. In other words, as a result of this treatment, there was a 95% reduction in the amount of 3,4 benzpyrene normally evolved in the combustion of untreated paper.

*Example II*

A commercial size roll of cigarette paper is passed over an absorbent roll that dips into a water solution containing 2½% of ammonium sulfamate and 2½% of ammonium persulfate in order to saturate the paper to approximately 105 to 110% by weight retention of the solution. This will provide approximately 1.2% available $NH_3$ The saturated paper then passes over a series of steam heated drying rolls to evaporate the water. The treated paper is made up into cigarettes in the usual manner. When smoked, such cigarettes produce 3,4 benzpyrene in the combustion products thereof only in an amount which is approximately 90% less than the amounts normally present in the combustion products of the untreated paper—1 part of 3,4 benzpyrene per one million parts of paper burned.

*Example III*

As the paper stock leaves the driers, it is passed through a series of sprays. These apply a nearly saturated solution of equal parts of ammonium sulfamate and ammonium perchlorate. A sufficient amount of the solution is applied so as to result in adherence of a 6.7% total of these reagents on the paper. This will provide approximately 1.5% available $NH_3$. When such paper is burned, the 3,4 benzpyrene content of the combustion products thereof was found to be approximately 95% less than the amount of the same carcinogen normally present in the combustion products of untreated paper.

*Example IV*

An absorbent roll is dipped into a water solution containing 8.5% ammonium perchlorate. The roll is subsequently compressed sufficiently to remove the excess solution. It is then placed in contact with a sheet of cigarette paper prior to the final drying stage in the commercial preparation of the paper. The roll, or a series of such rolls, is maintained in contact sufficiently long with the paper to impregnate the latter to 100% by weight retention or pickup. The paper is then dried.

Adequate uniformity of impregnation may be obtained in the above suggested manner without wetting the dry

paper to the extent of 100% pickup. Thus, as the concentration of the ammonium perchlorate in the water is increased the amount of this solution applied to the paper may be reduced. Those skilled in the art can readily make the adjustment. When nearly saturated solutions are used, the amount will be small and better uniformity of impregnation is obtained by applying part of the total to one side of the paper and with another roll applying the balance to the other side.

With respect to all of the foregoing examples, it should be obvious that the control of certain variables to obtain the desired percentage incorporation of the active ingredients of this invention in the paper is well within the skill of the art. Thus, such factors as the concentration of the solution, length of time under the sprays or in contact with dipped or saturated rolls, stage of paper processing where impregnation of the aforesaid ammonium containing compounds occurs, among others, can be easily determined by those skilled in the art to obtain the required percentage of retention or pickup by the paper.

Having thus described the present invention so that others skilled in the art may be able to understand and practice the same, we state that what we desire to secure by Letters Patent is defined in the following claims. This is a continuation-in-part of application Serial No. 510,857, filed May 24, 1955, on Cigarette Wrapper Material and Method for Producing Same now abandoned.

We claim:

1. A cigarette wrapper material having added thereto a compound which releases free ammonia under smoldering combustion conditions in an amount not less than about 1.2% to about 2.1% by weight of said wrapper, said compound being effective to eliminate not less than about 85% of the 3,4 benzpyrene content normally present in the combustion products of said cigarette wrapper material before addition of said compound.

2. A cigarette paper having added thereto a compound sufficient to release free ammonia under smoldering combustion conditions in an amount not less than about 1.2% to about 2.1% by weight of said paper, said compound being effective to eliminate not less than about 85% of the 3,4 benzpyrene content normally present in the combustion products of said cigarette paper.

3. A cigarette paper having added thereto a compound which releases free ammonia under smoldering combustion conditions in an amount not less than about 1.2% by weight of said paper and effective to eliminate not less than about 90% of the 3,4 benzpyrene content normally present in the combustion products of said cigarette paper.

4. A cigarette paper having added thereto a compound which releases free ammonia under smoldering combustion conditions in an amount not less than about 1.5% by weight of said paper and effective to eliminate not less than about 95% of the 3,4 benzpyrene content normally present in the combustion products of said cigarette paper.

5. A cigarette paper having added thereto a compound which releases free ammonia under smoldering combustion conditions in an amount not less than about 2.1% by weight of said paper and effective to eliminate not less than about 98% of the 3,4 benzpyrene content normally present in the combustion products of said cigarette paper.

6. A paper cigarette wrapper having added thereto a substance selected from the group consisting of ammonium sulfamate, ammonium persulfate and ammonium perchlorate, said substance being incorporated in said paper and releasing free ammonia, under slow burning, smoldering conditions, the amount of said substance being sufficient to release from about 1.2% to about 2.1% by weight of said wrapper of ammonia, whereby the benzpyrene content existing in the combusion products of said cigarette wrapper is reduced not less than about 85%.

7. A cigarette wrapper material having added thereto that amount of ammonium persulfate distributed substantially uniformly through the material which is sufficient to release from about 1.2% to about 2.1% by weight of said material of ammonia during smoldering conditions of said material.

8. A cigarette wrapper material having added thereto that amount of ammonium perchlorate distributed substantially uniformly through the material which is sufficient to release from about 1.2% to about 2.1% by weight of said material of ammonia during smoldering conditions of said material.

9. A cigarette wrapper material having added thereto that amount of ammonium sulfamate distributed substantially uniformly through the material which is sufficient to release from about 1.2% to about 2.1% by weight of said material of ammonia during smoldering conditions of said material.

10. A sheet of natural fibers for use in cigarette wrappers which contains a substance selected from the group consisting of ammonium sulfamate, ammonium persulfate and ammonium perchlorate, said substance being present in said fibers in an amount sufficient to release at least 1.2% of free ammonia under smoldering conditions of said fibers, said fibers yielding, under smoldering conditions, approximately 90% less of 3,4 benzpyrene than is produced during smoldering of said natural fibers.

11. A method of converting cigarette wrapper material into combustion products containing a negligible amount of 3,4 benzpyrene which comprises the step of adding to said material ammonium sulfamate in an amount sufficient to release between about 1.2% and about 2.1% by weight of said material of free ammonia, heating the ammonium sulfamate and smoldering said material in the presence of said sulfamate, whereby the 3,4 benzpyrene production, during said smoldering conditions, is reduced in an amount not less than about 85% of the amount normally released during the combustion of said wrapper material.

12. The method of converting cigarette paper into combustion products from which at least 85% of the normal 3,4 benzpyrene content has been removed, comprising the steps of subjecting a substance selected from the group consisting of ammonium sulfamate, ammonium persulfate and ammonium perchlorate to a temperature between about 500° C. and about 900° C. and smoldering said paper in the presence of the atmosphere resulting from the heating of said substance, said substance having been added to said paper in an amount sufficient to release from 1.2% to about 2.1% of ammonia by weight of said paper.

13. A cigarette wrapper containing a compound which releases free ammonia under smoldering combustion conditions in an amount not less than about 1.2% to about 2.1% by weight of said wrapper; said compound being effective to eliminate not less than about 85% of the 3,4 benzpyrene content normally present in the combustion products of the said wrapper which does not contain said compound.

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