

[54] TOBACCO COMPOSITION

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[56] **References Cited**

UNITED STATES PATENTS			
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3,003,895	10/1961	Grunwald.....	131/17 R
3,251,368	5/1966	Neurath	131/17 R
3,380,458	4/1968	Touey et al.	131/17 R
3,720,214	3/1973	Norman et al.	131/17 R

3,807,416 4/1974 Hedge et al. 131/17 R

FOREIGN PATENTS OR APPLICATIONS

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OTHER PUBLICATIONS

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[57] **ABSTRACT**

The concentration of polycyclic aromatic hydrocarbons in tobacco smoke is reduced by incorporating zinc oxide and a nitrate of a Group IIa and IIb metal into tobacco.

8 Claims, No Drawings

TOBACCO COMPOSITION

This invention relates to a smoking composition containing tobacco and having a combination of a catalytic agent and an additive releasing nitric oxide associated with the tobacco for reducing the concentration of polycyclic aromatic hydrocarbons in tobacco smoke. More particularly it relates to such compositions wherein the catalytic agent is zinc oxide and the nitric oxide releasing additive is selected from the group consisting of magnesium, calcium and zinc nitrates.

BACKGROUND

Observations of the mechanism of combustion in tobacco compositions such as cigarettes, indicate that the smoke components responsible for biological activity of smoke are formed in pyrolysis zone of the cigarette cone. It is widely accepted that much of the biological activity observed in connection with cigarette smoke condensate resides in the neutral smoke fraction and more specifically within the subfraction which contains the polycyclic aromatic hydrocarbons (PAH).

It has been generally accepted that it would be desirable to decrease the levels of PAH compounds in cigarette smoke and this has led to a substantial amount of research aimed at reducing the proportion of such compounds in cigarette smoke.

It has been postulated that there are several pathways by which the tobacco components are converted into polycyclic aromatic hydrocarbons. One major route is the thermal degradation of various organic materials such as, e.g., cellulose into unsaturated free radical structures consisting of two, four or five carbon atoms and, in case of the longer fragments, of conjugated double bonds. The free radical structures subsequently participate in the pyrogenesis of aromatic ring structures, the two and four carbon fragments giving rise to unsubstituted PAH and the five carbon branched structure giving rise to methyl substituted PAH. Another major route is the formation of PAH from pre-extant skeletal structures already present in tobacco such as steroids. In the latter case only minor thermally induced modifications are necessary to produce PAH molecules. Many other routes, such as ring closures of side-chains are possible.

Since the possible pathways of PAH formation are widely different it is highly unlikely that any one catalytic agent or other additive would interfere with all of the different formation processes. For instance, in US Patent 3,720,214 there is disclosed a smoking composition comprising tobacco in association with finely divided zinc oxide. This material is disclosed to result in a tobacco composition wherein the polycyclic aromatic hydrocarbon (PAH) content arising from the pyrolytic reactions within this composition is substantially reduced when compared to a control cigarette. It has now been found, however, that zinc oxide catalyst alone, while apparently very efficient in eliminating the production of PAH by some of the pyrosynthetic routes, has its limitations and does not affect all of the pathways.

The addition of nitrates and nitrites to tobacco has been previously described in various patents and publications. Thus French Pat. No. 1,180,320 teaches the addition of unspecified amounts of nitrites to tobacco and cigarette paper to reduce the PAH yield and U.S. Pat. No. 3,121,433 describes the addition of potassium nitrate to reconstituted tobacco sheet to improve its

burning characteristics. U.S. Pat. No. 3,380,458 teaches the addition of 5.5 to 10% of potassium and sodium nitrates to tobacco (NaNO_3 : 0.91–1.65% nitrate nitrogen, KNO_3 : 0.76–1.39% nitrate nitrogen) and it discloses a reduction in cigarette tar yield which is caused by the concomitant increased burn rate of the cigarette.

Bentley and Burgan (Analyst 85, 727–730, 1960) describe the addition of various nitrates to tobacco in an attempt to reduce the yield of 3,4-benzopyrene. They achieved a reduction only with copper and potassium nitrates and increases with lead, silver and zinc nitrates.

Wynder and Hoffman (*Acta Pathol. Microbiol. Scand.* 52, 119–132, 1961 and *Deutch. Med. Wochenschr.* 88, 623–628, 1963) using cigarettes treated with 5% copper nitrate (0.50% nitrate nitrogen) confirmed Bentley and Burgan's finding that copper nitrate reduced the 3,4-benzopyrene yield of cigarettes. Hoffmann and Wynder also demonstrated (*Cancer Res.* 27, 172–174, 1967) that the addition of 8.3% of sodium nitrate (1.37% nitrate nitrogen) resulted in a significant reduction of cigarette 3,4-benzopyrene yield as well as in a reduction of the biological activity of the smoke condensate. Pyriki et al. (*Ber. Inst. Tabakforsch. Dresden*, 12, 37–55, 1965), on the other hand, have shown that the addition of 4% of potassium nitrate (0.55% nitrate nitrogen) increased the level of 3,4-benzopyrene in cigarette smoke by 40%.

While most of the past investigators have expressed their research results in terms of the effect of the additive on cigarette 3,4-benzopyrene yield, it is now becoming widely recognized that this compound probably plays at most only a minor role in the biological activity of tobacco smoke condensate. It is also now recognized that the yield of 3,4-benzopyrene, which is a very minor constituent of the PAH fraction, is not necessarily a reliable indicator of the additives' effect on the bulk of the PAH.

It has been postulated that the effect of nitrates on the composition of cigarette smoke stems from two properties of nitrates: a) their capacity to oxidize, and b) their capacity to form the unpaired electron species, nitric oxide, in the pyrolysis zone of the cigarette that acts as a free radical scavenger. Provided a sufficiently high level is added, all nitrates tend to lower the PAH yield of cigarettes to some degree, but depending on the particular cation, not necessarily the concentration of PAH in the smoke condensate.

The nitrates' capacity to reduce PAH concentration is particularly dependent on the ability of the salt to form nitric oxide in the appropriate temperature region of the combustion zone. Many of the nitrates and, in particular, nitrates of Group Ia metals are good combustion promoters. When they are added to tobacco the burn rate of cigarettes is accelerated and the total smoke yield is decreased. The concentration of PAH within the smoke condensate is, however, not necessarily decreased and is at times increased. The nitric oxide yield from such nitrates is relatively low. Hence, nitrates of Group Ia metals have to be added at relatively high levels to reduce the concentration of PAH in tobacco smoke.

All added nitrates, and in particular those that accelerate burn rate impart a disagreeable taste to the main stream smoke and an obnoxious odor to the side stream aroma. For this reason, additive levels such as have claimed to show beneficial effects in some of the previ-

ous work (5-10%) are unacceptable from the point of view of a palatable cigarette. In sum, nitrate, like zinc oxide, even though being an efficient agent for disrupting some of the pathways of PCAH formation, has not proven to be a universal eliminator of PCAH, particularly at levels compatible with acceptable taste and smell of cigarette smoke.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, the concentration of PCAH is substantially reduced without adverse organoleptic effect on tobacco smoke by incorporating both zinc oxide and a Group IIa or IIb nitrate in tobacco. Unlike the Group Ia metal nitrates, the Group IIa and IIb metal nitrates do not accelerate cigarette burn rate. In addition they yield more nitric oxide per mole under the conditions extant in the cigarette cone. Hence, they effect more efficient reductions in the PCAH concentration in smoke condensate.

The incorporation of the nitrate compound enables reduction of the PCAH concentration to levels below those achieved with zinc oxide alone. This effect is achieved with nitrate concentrations well below the levels having objectionable effects on the organoleptic properties of smoke. In particular, substantial reductions in PCAH concentrations are achieved at nitrate levels below 0.8% nitrate nitrogen, based upon the weight of tobacco.

The zinc oxide which has been found to be particularly effective in combination with tobacco to provide the smoking composition of this invention is A.C.S. grade zinc oxide which contains (on a weight basis) less than about 0.005% lead, 0.004% sulfate ion, 0.002% nitrate ion and 0.001% chloride ion. The particle size of the zinc oxide is finer than about 50 U.S. mesh. Generally, the particle size is within the range of 60-200 U.S. mesh with the greater portion of the material being preferably finer than 100 U.S. mesh.

The catalytic amount of zinc oxide associated with the tobacco in the smoking composition is in the range of between about 0.1% to about 15% by weight of the tobacco used to prepare the smoking composition. Although the reduced yield of polycyclic compounds arising from pyrolytic reactions of the composition have been achieved at these levels, it has been found that the best results are obtained when the zinc oxide is in the preferred range of from about 0.5% to about 8% based upon the weight of the tobacco.

The nitrates which are employed in accordance with this invention are the Group IIa and IIb metal nitrates, with calcium, magnesium, and zinc nitrates being preferred. A nitrate which has been particularly effective in combination with zinc oxide and tobacco to provide the smoking composition of this invention is A.C.S. grade $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ which contains (on a weight basis) less than about 0.0005% chloride ion, 0.005% sulfate ion and 0.004% heavy metals (calculated as lead).

As noted above, the proportion of nitrate associated with zinc oxide and tobacco in the smoking composition is below 0.8%, and preferably is in the range of from about 0.25% to about 0.75%, calculated as nitrate nitrogen. Although the amount of reduction of PCAH yield that is due to the nitrate can be increased as the level of nitrate is increased, the taste and aroma of smoke becomes progressively more obnoxious as the nitrate level is increased. Hence, in combination with

zinc oxide we prefer to operate in the 0.25 to 0.60% nitrate nitrogen range.

The additives should be well dispersed throughout the tobacco so that they will be uniformly effective during the entire period during which the composition is smoked. Furthermore, it is important to ensure that the dispersion effectively contacts a maximum volume of smoke which is inhaled by the user. Since the catalytic activity of the zinc oxide is most likely a surface phenomenon, the greatest likelihood of maximum contact between the smoke being drawn in by the user and the zinc oxide is obtained when the area/volume ratio of the zinc oxide particles is maximized for a given weight of zinc oxide. For this reason, it is employed as a fine powder of particle size, preferably smaller than about 100 U.S. mesh.

The calcium, magnesium, and zinc nitrates are very soluble in water and can be applied as a relatively concentrated solution which avoids the excessive wetting of tobacco and yet assures good distribution throughout the tobacco mass.

We have found that the combination of zinc oxide and nitrate compound is most efficiently applied in a conventional casing solution of glycerin and propylene glycol wherein the zinc oxide crystals have been suspended and by adding a sufficient amount of water to solubilize the requisite amount of nitrate compound. Such a suspension-solution can be conveniently atomized on uncut tobacco strip by conventional casing apparatus.

Another method of application of the additives to the tobacco is to dry blend the zinc oxide, ground tobacco, a fibrous material and a binder. Dry blending, as in a conventional double cone blender effectively distributes the zinc oxide over the surface of the tobacco, including the pores within the tobacco surface which are large enough to accept the zinc oxide particles.

When required, dry blending is followed by wet mixing with water and casing materials in proportions sufficient to provide the resulting mixture with the appropriate consistency for conventional reconstituted tobacco sheet manufacturing operations. The sheet is then cut into strips and a solution of nitrate compound in water is applied to the strips. This is followed by a drying step if the tobacco moisture level needs to be adjusted. This material can be used in cigarette manufacture as such or it can be blended in any desired proportion with regular tobacco.

The fibrous material which is a constituent of the dry blend can be, for example, α -cellulose or fibrous tobacco stem material. The binder portion of the dry blend may be sodium carboxymethyl cellulose, or a natural gum such as guar gum. The casing materials used in the wet mixing step are usually glycerin and propylene glycol. Of course, any other known fibrous material, binder or casing materials known to be useful in combination with tobacco products can be used in combination with or in place of those herein set forth.

The weight proportions of the additives described above for use in reconstituted tobacco sheets are within the following approximate weight ranges. The proportions shown are within the usual range required to provide useful tobacco products.

Material	Weight %
Fibrous	4-8
Binder	1-20
Casing	3-9
Comprising:	
a) glycerin	4-6
b) propylene glycol	0.5-2
Tobacco	balance to 100%

The smoking composition may be further processed and formed into any desired shape or used loosely e.g., cigars, cigarettes, and pipe tobacco in a manner well-known to those skilled in the tobacco art.

The following Example is illustrative:

EXAMPLE

30.58 lbs. of ZnO and 28.52 lbs. of $Mg(NO_3)_2 \cdot 6H_2O$ were suspended and dissolved respectively in a mixture of glycerinpropylene glycol casing solution and water and sprayed in a conventional casing applicator onto 294 lbs. of uncut strip tobacco blend. The treated tobacco was blended with 38.5 lbs. of reconstituted tobacco sheet and 17.5 lbs. of stems. The resulting blend was cut at 32 cuts per inch.

Blends containing only the zinc oxide and only the magnesium nitrate as well as a control blend containing neither additive were prepared in a similar manner.

All four samples were pyrolyzed in a special pyrolysis reactor consisting of a steel cylinder about 4 inches in diameter and 5 inches along with an annular space at the central perimeter covered with a stainless steel screen. Cut tobacco was packed into this reactor at densities similar to cigarette densities and the tobacco was lit at the exposed perimeter. The burning tobacco itself thus produced the necessary heat for pyrolysis and the reactor closely approximated on a large scale the conditions extant in a burning cigarette cone. The combustion and pyrolysis products were pumped out through a small tube positioned concentrically with the cylinder and the dry solids in the smoke were analyzed for PCAH content. The concentrations of PCAH in the test tobaccos, as a per cent of the concentration of PCAH in the control tobacco are tabulated below for a typical run:

Sample	Additive, wt.%		Concentration of PCAH Relative to Control	
	ZnO	$Mg(NO_3)_2^*$	Weight Basis	IR Analysis**
1	5.0	—	83	71
2	—	0.55	78	78
3	5.0	0.55	68	65
Control	—	—	100	100

*As nitrate nitrogen.

**From infrared spectral absorption in the region of aromatic C-H bonding vibrations. (11.9-14.0 u)

As is evident, Sample No. 3 illustrative of this invention, afforded materially lower concentrations of PCAH than were obtained with either zinc oxide or magnesium nitrate alone.

What is claimed is:

1. A smoking composition comprising:

a. tobacco;

b. finely divided zinc oxide in a catalytic amount of from about 0.1 to about 15 weight percent sufficient to reduce the amount of polycyclic aromatic compounds in tobacco smoke; and

c. a nitrate of calcium, magnesium or zinc in an amount of from about 0.25 to about 0.75 weight percent calculated as nitrate nitrogen, based upon the weight of said tobacco, said amount being sufficient to effect a further reduction in the amount of polycyclic aromatic compounds in said smoke.

2. The composition of claim 1 wherein the concentration of zinc oxide is from about 0.5 to about 8 weight per cent and the concentration of said nitrate is from about 0.25 to about 0.6 weight per cent calculated as nitrate nitrogen, based upon the weight of said tobacco.

3. The composition of claim 1 wherein said nitrate is magnesium nitrate.

4. The composition of claim 2 wherein said nitrate is magnesium nitrate.

5. A cigarette containing the tobacco composition of claim 1.

6. A cigar containing the tobacco composition of claim 1.

7. A pipe tobacco containing the composition of claim 1.

8. The process for making the composition of claim 1 comprising admixing catalytic quantities of zinc oxide, said nitrate and tobacco to provide a uniform dispersion of said zinc oxide and nitrate throughout said tobacco.

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