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TREATMENT OF TOBACCO SMOKE TO REDUCE METAL CARBONYL CONTENT THEREOF

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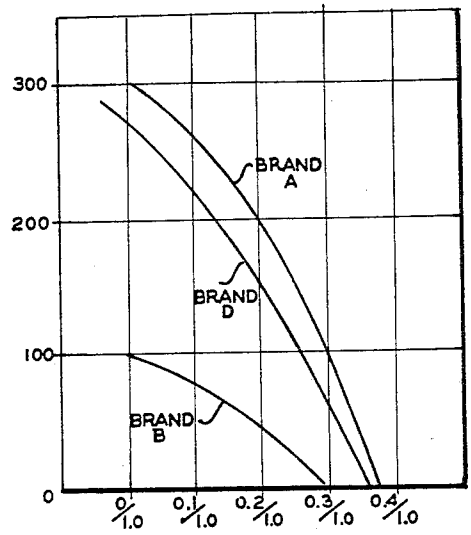
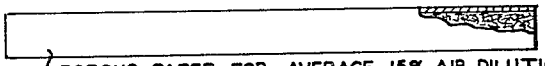
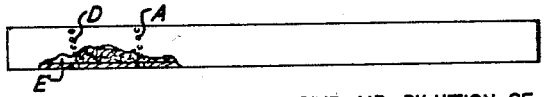


FIG. 1



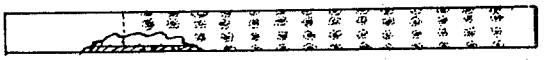
POROUS PAPER FOR AVERAGE 15% AIR DILUTION (CIGARETTE BRAND A) TO TOBACCO TREATED WITH UREA PEROXIDE

FIG. 2



HOLES D & A SIZED TO GIVE AIR DILUTION OF 0.4 VOLS PER VOL SMOKE

FIG. 3



HOLES SEALED WITH A FUSIBLE MATERIAL. HOLES OPEN UP ABOUT 1 CM BEHIND THE BURNING ZONE

FIG. 4



POROUS PAPER COVERING B AND C ADMITS INITIAL AIR FOR 0.25 DILUTION

FIG. 5

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TREATMENT OF TOBACCO SMOKE TO REDUCE METAL CARBONYL CONTENT THEREOF

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Continuation-in-part of application Ser. No. 303,929, Aug. 22, 1963. This application Oct. 7, 1968, Ser. No. 765,589

Int. Cl. A24d 1/04, 1/06, 1/02

U.S. Cl. 131—9 1 Claim

ABSTRACT OF THE DISCLOSURE

Highly toxic metallic carbonyls are removed from tobacco smoke by oxidation by extraneously introduced oxygen derived in part from heat decomposable peroxy compounds with which the tobacco is impregnated and in part from air introduced through pores or perforations in the tobacco wrapper of a smoking device such as cigarettes, pipes, cigars, or the like.

The present invention is a continuation-in-part of my copending application, Ser. No. 303,929, filed Aug. 22, 1963, now abandoned, entitled Cigarette Air Dilution for Oxidation of Carbonyls.

This invention relates to a method of improving tobacco smoke by reducing the metal carbonyl content of the smoke. More particularly, this invention relates to controlled introduction of oxygen into tobacco smoke in smoking devices, e.g., cigarettes, cigars, and pipes, the oxygen being derived both from air and other chemical sources, the oxygen serving to oxidize and destroy metal carbonyls, to produce smoke which is free of metal carbonyls.

The term "metal carbonyls" as used herein refers to compounds of a metal and carbon monoxide and, in addition, to compounds containing only a metal and CO, including metal nitrosyl carbonyls and metal hydrocarbonyls, wherein the metal-carbonyl combination also contains nitrosyl (NO) and/or hydrocarbonyl (COH) groups respectively.

Objects of the invention severally and interdependently are to provide an improved tobacco smoke free of metal carbonyls; provide an improved cigarette smoke free of metal carbonyl as compared to conventional cigarettes; improved cigar and pipe smoke as compared to conventional cigar and pipe smoke; an improved method for conventional smoking devices which will provide an improved tobacco smoke from which the nickel carbonyls are substantially eliminated to meet standards set by government hygienists for maximum atmospheric concentrations of nickel carbonyl; and an improved tobacco smoke from which the metal carbonyls are substantially eliminated by introduction of both air and a material which releases oxygen to dilute the tobacco smoke.

In combustion of tobacco in conventional smoking devices, some carbon monoxide is formed. The carbon monoxide contents of tobacco smoke have been found to vary from 4 to 11 volume percent, in spite of an apparent sufficiency of air for complete oxidation of CO to CO_2. The amount of CO present is presumably dependent in part on the ratio of oxygen to tobacco in the combustion zone. The carbon monoxide will not be oxidized further outside the combustion zone in the absence of a catalyst, and hence is always present in significant amounts in the smoke in the unburned portions of the cigarette.

Metal carbonyl formation appears to be dependent on the reaction of the carbon monoxide with metal compounds or complexes present in the tobacco in the cooler, unburned portions of the tobacco because, as is known, iron, cobalt, and nickel carbonyls completely dissociate at 150° C. to 200° C., and could not form in the much hoter, burning ember. Thus these volatile metal carbonyls form behind or below the combustion zone of a cigarette, cigar or pipe. To demonstrate such formation of metal carbonyls, a gas containing 7 percent carbon monoxide was passed over cigarette tobacco at a temperature of 50° C. and it was found that the nickel content of the tobacco was reduced from 10 micrograms per gram to 1 microgram per gram; cobalt content from 1.3 micrograms to 0.1 microgram per gram; and iron from 330 to 170 micrograms per gram of tobacco.

Conventional tobacco smoke, more particularly, conventional cigarette, cigar and pipe tobacco smoke, contains substantial traces of metal carbonyls, especially of nickel, cobalt and iron carbonyls which are removed from the smoke by the present invention.

The present invention removes metal carbonyls from tobacco smoke by introducing air lateraly through the side walls of the smoking device such as the cigarette paper and simultaneously enriching the air with oxygen derived from an oxygen evolving chemical compound such as a peroxy compound which releases oxygen by warming by the smoke.

The invention is further described with relation to the drawing wherein:

FIG. 1 shows graphically the effect on carbonyls by equivalent air dilution;

FIG. 2 illustrates a cigarette having porous paper in which the tobacco has been impregnated with urea peroxide as a typical peroxy compound;

FIG. 3 shows a paper having perforations and a filter at the left hand end near the uppermost perforations;

FIG. 4 illustrates a cigarette having sealed perforations to impart a relatively constant air dilution during smoking; and

FIG. 5 illustrates a filter cigarette having only a limited portion, such as one-third to two-thirds filled with tobacco treated with a peroxy compound and the balance comprising both empty space and filter.

As shown in the drawings, FIG. 1 illustrates that the carbonyl content of smoke is reduced rapidly by introducing an oxidizing agent air and oxygen released by a peroxy compound which may approach 0 at about 0.3 part of air per part of smoke. As equivalent air dilution, the same effect will result if the oxygen is supplied chemically by the peroxy compound or the oxygen in the air, both being preferred herein. That is, oxygen preferably is supplied by a combination of oxygen-releasing peroxy compound and air. It is obvious that at least 0.3 equivalent air dilution parts per part of smoke is needed to completely destroy the carbonyls in the smoke.

Introduction of air laterally through the walls tends to destroy the smoking pleasure and the resistance to the drawing through a cigarette. Obviously the dilution by air should be held to a minimum, a practical limit being about 1 part of air per part of smoke and preferably the introduced air is not over 0.5 part of air per part of smoke. As the oxygen is also supplied by the tobacco impregnated peroxy compound, the quantity of laterally introduced air as a source of oxygen may be progressively reduced. The combination of both, however, allows more accurate control of the quantity of oxygen released since the use of the

peroxy salt alone can release all of the oxygen required to oxidize carbonyl in the smoke.

FIG. 2 illustrates a cigarette where 0.15 percent of air is drawn in laterally through a porous cigarette paper, and the tobacco is treated with sufficient urea peroxide to release the required remainder. It will be appreciated that the even distribution of the peroxy compound readily overcomes the reduction of porosity of the paper, progressively as the cigarette is consumed, and the lateral wall of cigarette paper becomes diminished thereby. The reduced quantity of air is supplemented at least to present an adequate quantity of oxygen to oxidize the carbonyls by oxygen released from the peroxy compound.

FIG. 3 shows a filter cigarette having a filter E and two rings of perforations D near the filter, and A, at an upper intermediate point. The body of the cigarette paper B may or may not be porous. However, the quantity of air introduced through A and D with a selected porosity, as desired of the paper in the area C, is sufficient in combination with the peroxy compound with which the tobacco is impregnated to adequately oxidize the carbonyls in the smoke as the cigarette is being consumed.

FIG. 4 illustrates another modification of a perforated cigarette paper about a cigarette having a filter. The perforations in this case are sealed with a low melting wax such as paraffin, tallow or stearin, whereby the perforations in the paper become progressively opened by melting of the wax therein, just behind the hot ember of the cigarette as the cigarette is being consumed.

FIG. 5 illustrates a cigarette in which a lower portion C of the cigarette contains tobacco, and an empty space B is, as well as the portion C, covered overall by porous paper. A cigarette filter A can be mounted on the end of B. At the beginning of smoking of the cigarette, air is introduced through the porous paper of both B and C sections. The tobacco present only in the C section is also impregnated with a peroxy compound. According to such modification the carbonyl content of the smoke is destroyed both in the tobacco section C and in the empty section B. This oxidation of carbonyls in the smoke is accomplished by introduction of at least the minimum volume of air and oxygen which I have found necessary to reduce the metal carbonyl contents. For example, the smoke behind the combustion zone, in either non-filter or filter cigarettes, cigars, or pipes, while it contains some unused air, requires a certain minimum additional oxygen supply thereto to eliminate the metal carbonyls from the smoke.

The procedure employed in demonstrating the present invention was: (1) the smoking of a group of sixty cigarettes, each of three brands (D, B and A) to serve as controls. The method of scrubbing of the smoke and analysis for nickel carbonyl was used by F. W. Sunderman, Sr., and F. W. Sunderman, Jr. (American Journal of Clinical Pathology, 35, pp. 203–209, 1961) wherein alcoholic iodine solution and nitric acid scrubbers absorbed carbonyls of iron, nickel and cobalt from the smoke; (2) sixty cigarettes were smoked for each example.

These values for metal carbonyl contents of the smoke were confirmed by analysis of tobacco of the unsmoked cigarette, together with the butt tobacco and ashes of the smoked cigarette; when filter cigarettes were tested the filter was analyzed before and after smoking to obtain contents of iron, nickel and cobalt. These analytical determinations on the tobacco, ashes and filters were made by a combination of chemical and spectrophotometric methods.

The smoking was accomplished by a mechanical smoking system wherein 35 ml. puffs were taken in, collecting about 350 ml. of smoke for control tests, and 500 ml. or more in the dilution tests utilizing my invention. The 35 ml. were made in a measured manner by use of a bulb which, on expansion, drew 35 ml. of smoke, and on compression passed the puff of smoke into the scrubbing system described by Doctors Sunderman (as cited above). Further details are given as required in the descriptions of the individual examples. Examples I through VI show the dilution which I have found necessary with the three brands of cigarettes identified above.

EXAMPLES I–VI.—AIR DILUTION vs. METAL CARBONYLS IN TOBACCO SMOKE

	Air dilution, vol. air/vol. smoke	O_2, mol percent	O_2/Co, mol. ratio (approx.)	Micrograms of metal carbonyls in smoke (total Fe, Co, Ni)		
				D	B	A
Example I	0/1.0	11.4	1.5	273	100	300
Example II	0.15/1.0	12.5	2.0	183	65	233
Example III	0.3/1.0	13.4	2.5	68	0	100
Example IV	0.4/1.0	13.9	2.8	0	0	0
Example V	0.8/1.0	15.2	3.9	0	0	0
Example VI	1.0/1.0	15.7	4.5	0	0	0

While variations in metal contents of tobacco may require provision of different minimum amounts of air dilution to eliminate the metal carbonyls from the tobacco smoke, my invention is based on a controlled dilution of the tobacco smoke with additional oxygen, so that all metal carbonyl contents are eliminated. The diluent with oxygen is effected by introduction of air into the smoking device and introduction of oxygen in a combination of air and oxygen.

Air and oxygen in controlled amounts are introduced into tobacco smoke behind the combustion zone of the tobacco. The air and oxygen are introduced in an amount sufficient to decompose the metal carbonyls already formed; or, if introduced immediately behind the combustion zone, the formation of the metal carbonyls can be prevented by the excess of air.

Such controlled introduction of air and oxygen in cigarettes is effected in the present invention in two ways:

(a) By providing openings in the cigarette paper, of controlled surface area from 10 to 20 mm. in front of the present conventional filter; or, for non-filter cigarettes, from 10 to 20 mm. from the mouth end of the cigarette, the mouth end being the end which enters the smoker's mouth, thus introducing a constant amount of air with each puff; and

(b) By incorporating a compound into the tobacco formulation which releases oxygen into the smoke as it is warmed to 60° C. to 200° C.

Each provision, (a) and (b) reduces the metal carbonyls in the smoke by a mechanism as discussed above.

The use of a uniformly porous paper alone is not successful for maintaining the required low metal carbonyl content of the smoke, because if the porosity is properly adjusted for the full unsmoked cigarette there is not sufficient air introduced in the partly smoked cigarette to maintain sufficiently low metal carbonyl content in the cigarette smoke.

Of course, excess air can be introduced by use of a high porosity paper, but smoking pleasure is correspondingly reduced as the air dilution exceeds 1 volume air per volume of smoke. By the data contained in Examples I–VI, at least 0.3 volumes of oxygen enriched air per 1.0 volume of smoke are provided. For pleasure not more than 1.0 volume of air per 1.0 volume of smoke is provided by my invention. The oxygen enrichment, 0.06 to 0.2 volumes of oxygen per 1.0 volumes of smoke, is provided via oxygen releasing additives.

The oxygen-releasing additives to be used in this invention must not deleteriously affect the tobacco or the tobacco smoke and, for this purpose, are preferably

peroxy compounds. Examples of useful peroxy additives are shown in the table below.

TABLE 1.—OXYGEN RELEASING ADDITIVES OF THIS INVENTION

Additive	Grams to produce 30 ml. oxygen	Weight percent available oxygen	Melt. pt., ° C.	Temp. of (° C.) for O_2 release
Sodium perborate:				
Monohydrate	0.27	15	100	100
Trihydrate	0.4	10	63	63
Lithium perborate	0.2	20	----------	100
Sodium phosphate peroxyhydrate	0.45	9	----------	100
Ammonium perborate	0.2	20	----------	100
Potassium superoxide [1]	0.12	34	380	[1] 100
Urea peroxide	0.24	17	80	80
Sodium carbonate peroxyhrydate	0.29	14	----------	----------
$K_2C_2O_6$	0.25	16	200	200
Na_2CO_4	0.31	13	----------	----------
Tertiary butyl hydroperoxide	0.25	16	(2)	200

[1] Releases oxygen upon contact with CO, CO^2, or H_2O.
[2] Liquid.

These agents or additives may be incorporated into the tobacco by one of the following methods: (1) impregnating from an aqueous solution and drying at temperatures below 50° C.; (2) addition in solution in the humectant which can be glycerin, propylene glycol, etc.; (3) painted on the inside of cigarette paper in aqueous or propylene glycol or glycerin solution; (4) mechanically mixing the powdered additive with the tobacco in the amount calculated for practice of my invention.

Potassium super oxide is most advantageously mixed with the tobacco for use in pipes, cigars or cigarettes by a mechanical blender, either batch or continuous. Since it reacts with moisture, the KO_2 particles must first be coated with a polymer from a non-aqueous solvent, e.g. cellulose triacetate solution in chloroform, so that moisture of the tobacco does not react with it during storage. It is less convenient to employ potassium superoxide than the other additives, but it has the advantage of release of large amounts of oxygen per unit weight. It is the only one of the above-listed additives which can oxidize the CO and convert it to CO_2 at temperatures below 100° C. By the present invention, the contents of the metal carbonyls in tobacco smoke are reduced and substantially eliminated, thereby helping to safeguard smokers against exposure to these volatile and toxic metal carbonyls. The following examples further demonstrate the reduction in metal carbonyls effected by my invention.

EXAMPLE VII

Non-filter cigarette brand D made with non-porous cigarette paper was selected to serve as control. Three cigarettes from each of 10 packs of the same carton were dismantled and the tobacco therefrom was combined and analyzed for iron, nickel and cobalt, and was found to be 330, 9.6 and 1.2 micrograms per cigarette respectively. Six cigarettes from each of 10 packages from the same carton were smoked, leaving about 16% of the tibacco as unsmoked butt tobacco. The butt tobacco from these sixty cigarettes was analyzed and found to have been reduced 25% in iron content, 25% in nickel content and 50% in cobalt content during smoking. Thus, the metal carbonyls were forming and entering the smoker.

EXAMPLE VIII

Filter cigarette brand A made with a uniformly porous paper was smoked to leave about 16% butt tobacco as in Example VII. From sixty cigarettes it was found that about 15% air was admitted through the paper, i.e. 15% based on the smoke volume obtained in Example VII, and of course this 15% constituted an average of an initially higher percent and a final lower percent, since the air admitted through the paper decreases during smoking as the amount of paper decreases with progress of smoking. The analysis showed 310 micrograms iron, 5.2 micrograms nickel, and 1.4 micrograms cobalt per cigarette.

The amount of air dilution was calculated from the increase in number of standard puffs required to smoke the cigarettes to 16% butts over that required with non-porous paper.

EXAMPLE IX

Filter cigarettes brand B were used in this test. Tiny holes were punched in the paper 20 mm. in front of the filter so that the smoke at the point of the perforation was diluted with an equal volume of air. The cigarettes were smoked down to the point of the perforations (about 16% butt tobacco). Analysis of the butt tobacco showed that instead of a reduction, an increase in metal content had occurred. Thus, nickel content of the butts showed an increase from 5.2 p.p.m. to 8.0 p.p.m. The amount of air dilution was calculated as in Example VIII from the comparative number of standard puffs to reach 16% butt tobacco. The nickel carbonyl of the smoke after dilution with air deposited the nickel metal in the butt tobacco.

EXAMPLE X

Forty non-filter brand D cigarettes were smoked as follows: Prior to each puff two holes were punched in the paper about 5 mm. back of the burning zone. Thus air was introduced into the smoke so that the smoke was diluted with 0.9 volume of air, and the air was introduced earlier in the smoke stream than in Example III. Smoking was stopped after 60% of the tobacco was combusted. Analysis of the butt tobacco remaining showed an increase in iron content of 31% and in nickel content of 50%. The degree of air dilution was calculated in the manner described in Examples II and III.

EXAMPLE XI

Sixty brand D non-filter cigarettes were smoked, leaving about 50% of original tobacco unsmoked. Air was introduced into the smoke as in Example IV via 1.0 mm. holes back of the burning zone. The smoke was thus diluted with 0.8 volume of air as calculated from the relative number of puffs required to smoke to a 30% butt both with and without the 1 mm. holes or perforations. A 40% increase in nickel content was found in the butt tobacco, a 20% increase in iron, and 100% increase in the cobalt content.

From Examples VII to XI it was calculated that air dilution of from 30 to 40% or more was essential to maintain a detectibly unchanged concentration of iron, nickel, and cobalt in the butt tobacco. This is the point at which no change in metal contents of the unburned tobacco occurs; hence no metal carbonyls can be carried to the smoker. Example XII was then run with 0.4 air dilution of the smoke.

EXAMPLE XII

Sixty brand B filter cigarettes were smoked after punching three holes 0.02 inch in diameter 2 cm. in front of the filter. This gives an approximate dilution of the smoke of 0.4 volume of air per volume of smoke. Analysis of butt tobacco showed the same content of iron, nickel and cobalt as a sample of the initial unsmoked cigarette tobacco from the same carton of cigarettes, i.e., 122 p.p.m. iron, 2.8 p.p.m. nickel and 0.5 p.p.m. cobalt. (Each cigarette contained about 1 gram of tobacco.)

A control test with sixty cigarettes of the same brand B cigarettes from the same carton, but without air dilution gave a butt tobacco containing 100 p.p.m. iron, 2 p.p.m. nickel, and 0.3 p.p.m. cobalt. This control test confirms that iron, nickel and cobalt carbonyls are formed (from the unsmoked tobacco) when air dilution is not employed in accordance with my invention.

EXAMPLE XIII

Example XII was repeated, using twice as many perforations to effect air dilution of the smoke so that two volumes of air were introduced behind the combustion zone. This effected the same results in depositing metals on the final butt tobacco via initial formation of the carbonyls behind the combustion zone. However, the taste of the smoke was noticeably altered. Thus, large amounts of air are unnecessary, and even undesirable. The smoking taste and flavor is not appreciably altered when from about 0.3 to 1.0 volume of air per volume of smoke is employed.

EXAMPLE XIV

Sixty-five brand B cigarettes were treated by carefully immersing in a concentrated sodium perborate solution for ten seconds, draining, and drying to constant weight at 40° C. in a stream of air passing at a rate of a cubic foot per minute containing moisture at 25 mm. Hg vapor pressure. Care was exercised to avoid tearing the cigarette papers. Dipping and drying were repeated until analysis of five cigarettes showed a sodium perborate trihydrate content of 0.4 grams per cigarette. These dried cigarettes were then smoked with a mechanical smoker, as in Example IV and XII. Analysis of the butt tobacco showed that the nickel, iron and cobalt content had not changed from the initial tobacco, and the scrubbing of the smoke showed no metal content of the smoke. This example shows the equivalence of 30 ml. of oxygen (released from the additive) and air containing 30 ml. of oxygen for eliminating metal carbonyls from tobacco smoke.

EXAMPLE XV

Brand A cigarettes made with porous paper accomplished an overall dilution of smoke with 15% air (0.15 vol. air/vol. smoke) which represents a decrease in dilution from 0.26 vol. air/vol. smoke for the first puff, to 0.04 vol. air/vol. smoke for the last puff (at least 16% butt tobacco). From air dilution required for the substantially complete removal of the metal carbonyls from the smoke of tobacco of brand A (0.4 vol./vol. of smoke) it is calculated that 0.08 volume of oxygen (20% of 0.4 vol.) is required for complete removal of iron, nickel and cobalt carbonyls from 0.1 volume of smoke, i.e., 40 ml. of oxygen for 500 ml. of smoke. Urea peroxide solution was prepared at about 10% concentration in water (i.e., one mol of urea H_2O_2 adduct per 900 ml. water). Sixty-five brand A cigarettes were dipped carefully to immerse about 85% of the column of tobacco by holding the filter tip in the fingers. The dipped cigarettes were dried as in Example XIV. The dipping and drying were repeated until analysis of five of the dipped cigarettes showed the presence of 0.28 gram of urea peroxide per cigarette. The smoke of sixty of these treated cigarettes showed no content of metal carbonyls. This was confirmed by analysis of the butt tobacco (16%) which showed no difference in content of iron, nickel and cobalt from that of the original tobacco. Thus the combination of air through the porous paper plus oxygen from the urea peroxide for the last puff equaled the effect obtained from equal

oxyfien dilution when obtained with air alone (Examples IV and XII) and when obtained from an oxygen-releasing additive alone (Example XIV). For a puff of 35 ml. volume, a total of 2.8 ml. of oxygen is required for the purpose of my invention. In the present example, 0.28 ml. were supplied through the paper and 2.52 were supplied by the urea peroxide (0.28+2.52=2.8).

EXAMPLE XVI

Ammonium perborate solution (15%) was employed to impregnate pipe smoking tobacco brand E containing 80 micrograms iron/gram of tobacco, 4 micrograms nickel per gram of tobacco, and 1.1 micrograms of cobalt per gram of tobacco. It was found more convenient to spray the tobacco with an aqueous solution than to dip it, spraying at the rate of 14 ml. of solution per gram of tobacco at about 40° C. at reduced pressure (1 mm. Hg mercury) so that 0.20 gram of the perborate were deposited per gram of tobacco. A pipe full (4 grams) was smoked by drawing air through the pipe and scrubbing system employing a water filter pump to draw the air through the pipe. The pipe was smoked to consume 3 grams of the tobacco. The ammonium perborate released 30 ml. O_2 (STP) in the pipe smoke per gram of tobacco. The remaining tobacco was analyzed, and analysis confirmed that no metal carbonyls were formed. The total smoke collected (following the scrubbers for removing the metal carbonyls) was measured at 1,500 ml. and showed no metal carbonyl formation. The dilution amounted to 90 ml. of oxygen per 1,500 ml. of smoke, or the equivalent of 0.3 volume of air per volume of smoke.

EXAMPLE XVII

The outer leaves i.e. the wrapper of a cigar C, were removed and the remainder of the cigar was sprayed with tertiary butyl hydroperoxide in acetone solution (50%) to obtain a uniform distriubtion of the peroxide in the amount of 0.25 gram per gram of cigar weight. After evacuation at 30° C. for an hour, the wrapper was replaced on the cigar and the latter was smoked—mechanically—by drawing two liters of air through the cigar until three quarters of the cigar was smoked. The gas was collected after scrubbing the smoke with the alcoholic iodine solution and nitric acid. Again metal carbonyl formation did not occur as found by analysis of the scrubbed solutions and of the remaining 25% cigar. The dilution with oxygen amounted to 0.06 volume per volume of smoke.

EXAMPLE XVIII

Cigarette tobacco was removed from 130 brand A cigarettes. One-half of this tobacco was sprayed with an 8% solution of lithium perborate and was dried in vacuo at 40° C. The spraying and drying operation was repeated until the lithium perborate content was about 0.2 grams per gram of tobacco and this was confirmed by analysis of 5 grams of treated tobacco. The other half of the tobacco was sprayed with distilled water and dried at 40° C. to serve as control tobacco. In a do-it-yourself cigarette-making machine the treated tobacco was used to roll 60 cigaretes using cigarette paper which had three holes of 2 cm. from one end. The diameter of the holes was 1 mm. The paper was 7 cm. long. Similarly, 60 controls were made with untreated tobacco. In smoking the controls, 30% air dilution of the smoke was provided by the holes in the paper for the first puff. For the last puff with 16% of the tobacco in the butt, the dilution was only 5%; the resistance of the column of tobacco was reduced to 16% of the original resistance so that there was corresponding decrease in the air drawn through the holes in the paper. The average air dilution for the total smoke was 18%. The dilution with oxygen was 3.6%. The results of analyses showed 200 micrograms total carbonyls (3 micrograms nickel carbonyl) in the smoke.

When the lithium perborate treated cigarettes were smoked, the smoke was completely free of detectible amounts of iron, nickel, and cobalt carbonyls. The oxygen dilution was calculated to be 12% for the first puff

(equivalent to 60% air dilution), 6% oxygen from air through the holes in the paper and 6% from the perborate additive; and 7% oxygen dilution was calculated for the last puff; 1% from air through the holes and 6% from the additive.

EXAMPLE XIX

Example XVIII was repeated using 0.25 gram of potassium peroxydicarbonate ($K_2C_2O_2$) instead of 0.2 gram lithium perborate per gram of tobacco. The results of the smoking test again showed no detectible amounts of metal carbonyls; the smallest detectible amount from 60 cigarettes being 0.1 microgram which is calculated to be less than 0.5 part per billion, or less than half the threshold value set by the government hygienists and also by the International Health Congress. The calculated oxygen dilution of the smoke was 8% (0.88 vol./vol. of smoke).

EXAMPLE XX

Sixty grams of pipe tobacco brand E was treated with sodium peroxy carbonate ($NaCO_4$) solution according to the procedure of Examples XVIII and XVI to deposit 0.31 gram of the carbonate per gram of tobacco. The dried tobacco was smoked in 20 pipefuls and the smoke was found to be free of metal carbonyls. The oxygen dilution of the smoke was calculated to be 8%.

The controlled introduction of air into tobacco smoke may be attained in various ways in accordance with the instant invention. For filter cigarettes, the wrapping may contain perforations at a point about 10 to 20 mm. ahead of the filter. For non-filter cigarettes, the perforations may be made about 10 to 20 mm. ahead of the mouth end. Again, porous papers can be used which permit 1/1 air dilution for the first puff, and which decrease to about 0.025/1 for the last puff at about 16% butt tobacco. Thus an overall average of about 50% and over dilution does not eliminate the carbonyls from tobacco smoke for the last puffs, and must be supplemented by oxygen-releasing additives for complete carbonyl elimination. A more porous paper may be used if the degree of porosity is controlled throughout the smoking of the cigarette. This control is possible to attain by coating the pores with a material that melts in the range of 100° C., so that the pores open for a limited and controlled area just behind the combustion zone. This would maintain a constant dilution by maintaining a constant open porous area in the cigarette. Cellulosic materials, such as alkyl cellulose, cellulose acetate, propionate, butyrate or mixed esters of cellulose, or waxes, such as carnauba, polyethylene, and the like, may serve to seal the pores. The selection of such materials would naturally be made on the basis of the pleasantness added to the smoke. Again, the filter length can be lengthened and the butt tobacco eliminated. Replacement of the tobacco, which normally remains unsmoked, with more filter material for the air and the smoke will avoid metal carbonyl formation from "traveling the smoke further" over tobacco at temperatures conductive to formation of metal carbonyls.

In pipe smoking, small air ducts can be built into the pipe, of the correct size to give the desired air dilution prior to inhalation by the smoker. In cigars, small holes running through the cigar diametrically an inch or more from the mouth end of the cigar can be utilized to give the desired air dilution constant throughout the smoking of the cigar.

It is not intended herein to decide which provision is optimum for use in controlling the air dilution of tobacco smoke, since the invention resides in eliminating the transition metal carbonyls, particularly of iron, nickel and cobalt, from tobacco smoke, prior to inhalation by the smoker, by controlled introduction of air into the tobacco smoke. It is preferred to make such air introduction at about 2 cm. from the mouth end of the cigars, cigarettes, or pipe.

Thus it has been demonstrated that harmful metal carbonyls can be eliminated from tobacco smoke by controlled air and/or oxygen dilution from about 0.3 to 1 volume of air (or 0.06 to 0.20 vols. of oxygen) per volume of smoke prior to inhalation by the smoker. Each manufacturer of each brand of cigarette must determine (1) what air dilution is required for his supply of tobacco (also for pipe or cigars); and (2) what porosity of paper plus amount of additive will give the required dilution for a given "draw" resistance, the draw resistance depending on the particle size and packing in the smoking device.

EXAMPLE XXI

The safest pleasant smoke free of metal carbonyls was obtained by eliminating the last one-third of the tobacco in the ordinary size cigarette and the last one-half of the king size cigarette and replacing it with cellulosic filter material to maintain the present normal draw resistance—about 20 mm. of water—for the whole cigarette. The removal of said tobacco eliminated a major portion of the source of the metal carbonyls by avoiding the "further travel" over tobacco of the smoke containing carbon monoxide. This elimination of butt tobacco accompanied by the use of a porous paper which permitted a 1/1 air dilution of the first puff and about 0.4/1 for the last puff. The cigarette paper was of the same length as for conventional cigarette B brand so that air introduction occurs through the paper and cellulosic material which replaced the butt tobacco, as well as through the wall paper surrounding the tobacco.

While there have been described herein what are at present considered to be preferred embodiments of the invention, it will be obvious to those skilled in the art that modifications and changes may be made without departing from the essence of the invention. Thus any desired means of introducing air into the tobacco smoke, following the combustion zone, and prior to entering the smoker, may be used, it being considered desirable to pass the air-diluted smoke through a filter section of filter material other than tobacco to remove oxides, hydroxides, or other residue of the iron, nickel and cobalt carbonyl reaction products with air. The type of filter material is non-critical and any otherwise acceptable conventionally-used filter material such as cellulose esters, cellulose, alkyl cellulose, polystyrene, activated carbon, silica, silicates, alumina and the like, may be used. It is therefore to be understood that the exemplary embodiments are illustrative and not restrictive of the invention.

What is claimed is:

1. A method of reducing metal carbonyls in cigarette tobacco smoke which comprises adding oxygen to the smoke in part derived from the incorporation of an oxygenating non-toxic peroxy compound in the burnable charge of the cigarette, said compound being selected from the group consisting of perborates, peroxides and percarbonates of alkali forming metals and ammonium, tertiary butyl hydroperoxide and urea peroxides, and in part from air introduced laterally through the cigarette wrapper, the peroxy compound evolving 0.06 to 0.2 volumes of oxygen per volume of tobacco smoke, and the laterally introduced air constituting 0.3–1 volumes per volume of smoke.

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