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3,319,635

**PROCESS FOR THE PURIFICATION OF
TOBACCO SMOKE**Eldor E. Stahly, Ellicott City, Md., assignor to
Oliver W. Burke, Jr., Fort Lauderdale, Fla.No Drawing. Original application Dec. 14, 1962, Ser.
No. 244,573, now Patent No. 3,246,654, dated Apr. 19,
1966. Divided and this application Apr. 18, 1966, Ser.
No. 543,051

10 Claims. (Cl. 131—262)

This invention relates to the improvement of tobacco smoke by the reduction or removal of metal compounds, e.g., carbonyls therein. Strictly speaking, a metal carbonyl is a compound of metal and carbon monoxide, but in a broader sense the term metal carbonyl also includes the analogous metal nitrosyl carbonyls and the metal hydrocarbonyls, which are similar compounds in which one of the carbonyl groups has been replaced by a nitrosyl or a hydrocarbonyl group, and except where the context indicates to the contrary, the term is employed in said broader sense herein.

Objects of the invention, severally and interdependently, are to provide a process for the purification of tobacco smoke by removing metal carbonyls therefrom by converting the same to non-volatile materials; to provide an improved cigarette smoke from which metal carbonyls are substantially eliminated; to provide an improved method in which volatile metal carbonyls present in tobacco smoke in small amounts are converted to non-volatile materials in a manner which effectively prevents their remaining in the tobacco smoke; and to provide an improved method in which a ligand material is reacted with volatile metal compounds in the tobacco smoke and converts them into non-volatile compounds.

Other objects and advantages of the invention, and of preferred embodiments thereof, will be apparent from the following description and from the illustrative examples appended thereto.

The invention resides in the new and useful methods and products herein disclosed, and is more particularly defined in the appended claims.

GENERAL DESCRIPTION

Conventional tobacco smoke from smoking articles, more particularly conventional cigarette, cigar and pipe tobacco smoke, contains substantial traces of metal carbonyls, and especially of nickel, cobalt and iron carbonyls, and such materials are reported to be toxic and carcinogenic to animals.

Thus, it has been reported in a paper by the Drs. F. W. Sunderman (Sr. and Jr.), based on tests of six different brands of cigarettes, that nickel carbonyl containing from 0.4 to 0.6 micrograms nickel per cigarette (corresponding to about 20% of the total nickel of the tobacco) passes through the butt and filter of conventional plain or filter cigarettes, reaching the smoker (Medical Science, page 617, May 25, 1961; American Journal of Clinical Pathology, 35, 203 (1961)). In studies with rats, small amounts of nickel carbonyl were found by the Drs. Sunderman to be carcinogenic. The nickel delivered in the smoke drawn from the butt ends of the cigarettes amounted to up to 8 micrograms nickel per pack of 20, or 23.5 micrograms nickel carbonyl per pack of 20 of unfiltered cigarettes; and up to 12 micrograms nickel or 35 micrograms of nickel carbonyl per pack of filtered cigarettes. On the basis of their studies, cumulative exposure to these quantities of nickel was suggested by the Drs. Sunderman to be a possible cause of the so-called smokers pulmonary cancer.

Based on the reported figures, a person who smokes a

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pack of cigarettes per day over a period of a year subjects himself to about one and one-half times the amount of nickel required to induce pulmonary cancer in rats, which are considered to be notably resistant to pulmonary cancer.

Aside from the nickel carbonyl reported, I have found that traces of volatile cobalt and iron compounds are also present, apparently as carbonyls, in cigarette smoke. The cobalt is present in somewhat smaller amounts than the nickel, about 1.3 micrograms of cobalt passing the filters per pack of filter cigarettes; and the iron is present in about twice the amount of nickel in the smoke of some brands of cigarettes.

Aside from the carcinogenic aspects of metal carbonyls reported by the Drs. Sunderman, it has long been known that such compounds are highly toxic and dangerous materials even in trace amounts. Thus Sax, Handbook of Dangerous Materials, published in 1951 by Reinhold Publishing Company, New York, prescribed a maximum allowable concentration of cobalt in the air as 0.4 parts per million, and the Twenty-Second American Conference of Government Hygienists in April 1960 placed the maximal atmospheric concentration of nickel carbonyl for a working day at 1 part per billion (A.M.A. Arch. Environmental Health 1, 140-144, year 1960). Iron carbonyl is also considered to be toxic, although less toxic than nickel and cobalt carbonyls. Accordingly, the cumulative toxicity effects of these three metal carbonyls in tobacco smoke can be expected to be greater than that reported for nickel carbonyl alone. Hence it is evident that the quantities of metal carbonyls present in the smoke from conventional plain and filter cigarettes exceed the quantities deemed objectionable by the above authorities.

By the present invention such content of metal carbonyls may be reduced in, or practically eliminated from, the tobacco smoke, and this invention thus can serve as a safeguard to smokers against excessive exposure to metal carbonyls.

My new process for the treatment of tobacco smoke is based on the removal of metal carbonyls from the tobacco smoke by the formation of non-volatile complexes by combination of the metal carbonyls with a ligand, which for the purposes of this invention, is an organic complexing agent which forms complexes of low volatility with transition metal carbonyl compounds in the presence of other constituents of tobacco smoke, more particularly in the presence of moist carbon dioxide. Generally the complexes of the metal carbonyl with ligand organo-phosphorus compounds are materials of low volatility. Furthermore, these ligand organo-phosphorus compounds form relatively stable complexes with the transition metals in the presence of moist carbon dioxide. The practice of my invention does not depend on the formation of exact empirical complexes since mixtures of such complexes may be formed with equal benefit for my process.

Thus volatile metal compounds in the cigarette smoke by the present invention are converted to non-volatile complexes by contacting the smoke with one or more ligand and organo-phosphorus compounds. Such ligands may be hydrocarbon or hydrocarbonxy substituted compounds of phosphorus, e.g., alkyl, alkenyl, alkynyl, cycloalkyl, terphenyl, aryl, alkaryl and aralkyl phosphines, hypophosphites, phosphites, diphosphines, phosphine oxides, phosphates, phosphonates, and polyphosphite compounds of polyols and carbohydrates. Further the substituent groups on the phosphorus can be nitrogen-containing radicals as hereinafter set forth. The complexes are formed by passing the smoke containing the metal carbonyls into contact with one or more of said ligands or over or through a filter material acting as a carrier body for the ligand material, and preferably comprising fibrous material, for example, cellulose acetate tow, prepared with the ligand

therein or wholly or partly coated with the ligand or with material carrying the same.

In the practice of my invention for example in making tobacco smoke filters one or more of the ligands or complex-forming compounds or components with or without a solvent or plasticizer are preferably dispersed on adsorbents; for example, the liquid or solid complex-forming components may be vaporized onto said adsorbent material, or a solution of such ligands may be applied to said adsorbent material such as carbon (especially activated carbon), silica, pumice, vermiculite, clay, asbestos, polyesters, polystyrene, and cellulosic materials, e.g., cotton, cellulose, cellulose acetate, cellulose acetate-butyrate, cellulose propionate, tobacco and other absorbing materials having a high surface area per unit weight or per unit volume and combinations of these adsorbents.

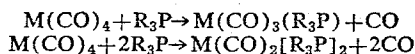
The smoke-permeable bases or carriers may embody various adhesive, adsorbent and surface area augmenting materials, and may be of any known or suitable form. The ligands employed in the present invention may be incorporated in filter bodies of fibrous material during the preparation of such bodies as otherwise disclosed, for example, in U.S. Patents as follows:

2,215,620, Sept. 24, 1940; 2,228,383, Jan. 14, 1941; 2,770,241, Nov. 13, 1956; 2,917,054, Dec. 15, 1959; 2,928,399, Mar. 16 1960; 2,928,400, Mar. 15, 1960; 2,940,456, June 14, 1960; 2,948,282, Aug. 9, 1960.

Types of ligands useful in my present invention and typical complexes believed to be formed thereby from transition metal carbonyls are exemplified by the following wherein R represents alkyl, alkenyl, alkynyl, cycloalkyl, terphenyl, aryl, alkaryl, alkoxyaryl, haloaryl, aralkyl, pyridyl, alkylpyridyl, quinolyl, morpholinyl, piperazinyl, pyrrolidinyl, and the like, and $x=1$ or 2.

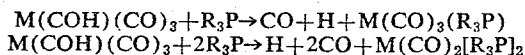
Ligand	Typical Complex
R_3P -----	$Ni(CO)_4[R_3P]_x$ $Co(CO)_3[R_3P]_x$ $Co(NO)(CO)_2[R_3P]_x$ $Fe(CO)_5[R_3P]_x$
$(RO)_3P$ -----	$Ni(CO)_4[(RO)_3P]_x$ $Co(CO)_3[(RO)_3P]_x$ $Co(NO)(CO)_2[(RO)_3P]_x$ $Fe(CO)_5[(RO)_3P]_x$ $Fe(NO)_2(CO)_2[(RO)_3P]_x$
$(RO)_3PO$ -----	$Ni(CO)_4[(RO)_3PO]_x$ $Co(CO)_3[(RO)_3PO]_x$ $Fe(CO)_5[(RO)_3PO]_x$

The complex formation probably occurs by a reaction of the ligand with metal carbonyl similar to the following:



wherein the valence of the metal atom M, i.e., iron, nickel or cobalt, is considered to be zero.

With a transition metal hydrocarbonyl the reaction with the ligand is similar, viz:



wherein the metal M is again in the zero valent state. Likewise, the ligands employed herein form non-volatile complexes with other metal carbonyls, such as:

$Ni(CO)_4$	$Co(NO)(CO)_3$
$Ni(NO)(CO)_3$	$Fe(CO)_5$
$Co(COH)(CO)_3$	$Fe_2(CO)_9$
$Co(CO)_4$	$Fe_3(CO)_{12}$
$Co_2(CO)_8$	$Fe(COH)_2(CO)_2$
$Co_3(CO)_{12}$	$Fe(NO)_2(CO)_2$

While carbonyls such as $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ are not volatile at room temperature they decompose giving volatile $Fe(CO)_5$ at temperatures of 100° C. and higher. Heating above 100° C. aids in the formation of the non-

volatile complexes, particularly with iron carbonyls. The heat of the tobacco smoke which contributes to the formation of the volatile iron carbonyl thus also aids in the rate of formation of the complexes in the cigarette filters of the present invention.

Vapor pressures observed for representative metal carbonyls and indicative of the volatility thereof, are:

	Mm. Hg, ° C.
$Ni(CO)_4$ -----	134 at 0; 238 at 15
$Co(CO)_3COH$ -----	760 ca. 10
$Co(NO)(CO)_3$ -----	91 at 20
$Co_2(CO)_8$ -----	0.72 at 16
$Fe(COH)_2(CO)_2$ -----	11 at -10
$Fe(CO)_5$ -----	26 at 16
$Fe(CO)_2(NO)_2$ -----	760 at 110

The alkyl groups preferred as R substituents in the organo-phosphorus ligand are the alkyls containing not more than 18 carbon atoms (i.e., methyl to stearyl). Both primary and secondary alkyls, straight chain and branched chain alkyl groups may serve as R in the ligand. Thus tri-n-nonyl phosphite, tri-(2,4,5-trimethylhexyl) phosphite, and tri-(2-nonyl) phosphite were found effective as ligands or complexing agents for the metal carbonyls concerned.

Alkenyl groups preferred as R in the ligands are vinyl, alkyl, butenyl, etc., up to alkenyl groups containing not more than 18 carbon atoms.

Alkynyl R groups of the alkynyl ligands are exemplified by propargyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, etc., up to those containing preferably not more than 18 carbon atoms.

Cycloalkyl R groups of the cycloalkyl ligands are exemplified by cyclo-C₅, -C₆, -C₇, -C₈, cyclododecyl and the like cycloalkyls, ac-tetrahydro-naphthyl, decahydronaphthyl, and mono polyalkyl cycloalkyls, and contain preferably not more than 18 carbon atoms.

When R in the ligand is terphenyl it can be menthyl, carvomenthyl, alpha, beta, and gamma terphenyl, and the like available ten-carbon radicals, including hydrocarbon-substituted terphenyl radicals containing preferably not more than 18 carbon atoms.

When R in the ligand is an aryl group it preferably contains not more than 18 carbon atoms and may be phenyl, naphthyl, ar-tetra-hydronaphthyl, alkoxy or alkyl phenyl, alkoxy or alkyl naphthyl, or alkoxy or alkyl substituted ar-tetra-hydronaphthyl. Thus ortho and para-methoxy phenyl and ortho and para-methyl phenyl as R in $(RO)_3P$ are effective ligands in forming stable complexes with metal carbonyls. Again, mono and poly-substituted aryls are useful as R in the ligand or complexing agent. Tri(nonylphenyl) phosphites were found to be very effective as a ligand or complexing agents for the metal carbonyls. The tri-(p-nonylphenyl) phosphite, the mixture of this with tri-(o-nonylphenyl) phosphite and a minor amount of tri-(m-nonylphenyl) phosphite, and a mixed compound such as di-(p-nonylphenyl)-(o-nonylphenyl) phosphite all served as ligand or complexing agents. Finally, R may be an arylene compound, as in the triphenylene diphosphite ligand.

The aralkyl substituents R in the ligand which are useful in the present invention may be unsubstituted or hydrocarbon substituted and range from phenylmethyl to phenyldecyl, and from mono and dimethyl-benzyl to mono and dioctylbenzyl. Aralkyl and arylene groups containing not more than 18 carbon atoms are preferred.

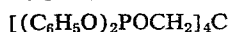
The nitrogen-containing R groups useful in the ligand include the morpholinyl, pyridyl, pyrrolidinyl, piperazinyl, isoquinolyl and quinolyl groups, both unsubstituted and mono and dialkyl substituted to have a total carbon content preferably not more than 18 carbon atoms. For example, trimorpholyl phosphorus, tri-(phenylmorpholinyl) phosphorus, tri-(pyridyl) phosphorus, and tri-(dimethyl-quinolyl) phosphorus are active ligands useful in the present invention.

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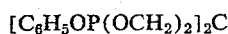
Further it has been found that organo-phosphorus compound ligands represented by $RR'R''P$; $R'R''PO$; $(R''O)(RO)(R'O)P$; $ROPO_2$ and $(RO)(R'O)(R''O)PO$; $RR'(R''O)PO$; $R(R'O)(R''O)P$ and $R'P-R''R'''$ are effective in the present invention wherein R has the same significance as hereinbefore defined, and R', R'' and R''' may be the same or different groups selected from the group of radicals listed hereinbefore for R. Thus didecyl phenyl phosphite, diphenyl decyl phosphite, decyl phenyl cresyl phosphite, triphenyl phosphite and tridecyl phosphite all serve as the ligand or complexing agents. Thus the three radicals R, R', and R'' may be the same or different for the ligands defined as P or PO compounds. Likewise RO, R'O and R''O may be the same or different.

Of particular advantage in the present invention are the ligand tetra-R-substituted diphosphines, and also solid polyphosphite ligands as exemplified by tetra-diphenylphosphitopentaerythritol and diphenylpentaerythritoldiphosphite (commercially available as resin stabilizers under the trademarks "Pentite" and "Dipentite," respectively). Because of polyfunctional grouping these polyphosphorus ligands do not conform to the general formula of the hereinbefore listed phosphine, phosphite and phosphate type ligand compounds or complexing agents for metal carbonyls. The formulae for these ligands are:

(1) Tetra-diphenylphosphitopentaerythritol ("Pentite")



(2) Diphenylpentaerythritoldiphosphite ("Dipentite")



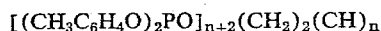
Analogous polyphosphites of value in the present invention are the phosphite ligand derivatives of ethylene glycol, diethylene glycol, triethylene glycol, higher polyethylene glycols, glycerol, erythritol, xylitol, mannitol, and the like; for example:

(3) Bis(diphenylphosphito) polyethylene glycols



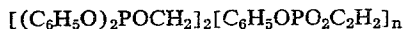
where n is preferably 1 to 6.

(4) Poly(ditolylphosphito) polyols



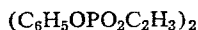
where n is preferably 1 to 6;

(5) Bis(diphenylphosphito) poly(phenylphosphito) polyols

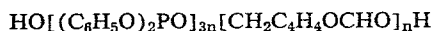


where n is preferably 1 to 3.

(6) Bis(phenylphosphito) erythritol

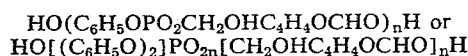


(7) Poly(diphenylphosphito) cellulose, sugars or starches



where n is from 1 to 1000.

(8) Poly(phenylphosphito) cellulose, sugars, or starches



where n is from 1 to 1000.

These ligands (1)-(8) conform to the polyfunctional formulae $D[O_{2-x}P(OR)_x]_s$ where D is a polyvalent organic polyol moiety, R is a hydrocarbon radical as hereinbefore defined, $s=2$ to 1000, or more, $x=1$ or 2. In general, the ligand materials preferred are low in melting point or are softenable with a solvent or plasticizer. Any radical of the R group above can serve in place of the phenyl of the above diagrammed formulae. Examples of complexes which are formed from metal carbonyls by these polyfunctional ligands include mono, di, tri and tetra nickel compounds for the "Pentite," mono and di-nickel compounds with the "Dipentite" and one nickel per phosphorus atom of the carbohydrate derivative; for example:

(Pentite) $[Ni(CO)_4]_4$; (Dipentite) $[Ni(CO)_4]_2$; and $HO(C_6H_5O)_5=POC_6H_5)_nH[Ni(CO)_4]_n$.

Further I have discovered that ligands may be prepared in which thio atoms are substituted for oxygen atoms of the phosphites, phosphates, phosphine oxides, phosphonates, etc. to form other ligands.

It has also been found that polar-substituted derivatives of the foregoing radicals are useful as R, R', R'' and R''' of the above formulae for the ligand or complexing agents for the practice of my invention. Such polar groups are exemplified as follows:

Halogen, e.g., in tri(o-, m-, and p-halophenyl)phosphate

Hydroxyl, e.g., tri(hydroxyphenyl)phosphite (o, m, and p)

Carboxyl, e.g., (carboxyphenyl)-diphenyl phosphite

Carbethoxyl, e.g., tri(o-carbethoxyphenyl)phosphite

Amine, e.g., tri(dimethylaminophenyl)phosphite

Cyano, e.g., in tri(2-cyanoethyl)phosphine

Cyanato, e.g., in tri(m-cyanato-phenyl) phosphine

Thiocyano, e.g., in tri(o-thiocyanophenyl)phosphate

Nitro, e.g., in (m-NO₂-C₆H₄)₃PO₃

Nitroso, e.g., in (p-NO-C₆H₄)₃P

Sulfonate, e.g., in (m-SO₃H-C₆H₄)₃PO

Sulfenate, e.g., in (SOH-C₆H₄)₃PO₃

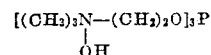
Sulfinate, e.g., in (SO₂H-C₆H₄)₃P

Alkoxy, e.g., in tri(o-, m-, and p-methoxyphenyl) phosphite

Acyl, e.g., in (acetophenyl)diphenyl phosphite

Mercapto, e.g., in (mercaptophenyl) diphenylphosphite

In addition to the foregoing, other types of organo-nitrogen-phosphorus materials have been found to be active ligands of my invention, such as amino-alcohol esters of acids of phosphorous, e.g., tri-cholanyl phosphite,

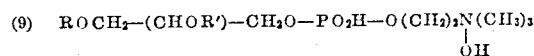


and tris(aminoethyl) phosphate, $[NH_2(CH_2)_2O]_3PO$.

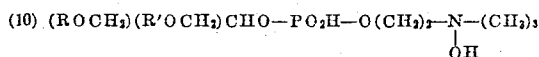
Of especial interest and advantage as organo-nitrogen-phosphorus ligands in my invention are the phosphorus-containing lipids derived from plant or animal sources.

The terms "phospholipid" or "phosphatide" as used herein designate the natural and synthetic phospholipids and phosphatides, derivatives thereof, and mixtures of the foregoing, including the hydrogenated and partially hydrogenated products thereof, which yield on hydrolysis phosphoric acid, an alcohol, fatty acid compounds, and a nitrogenous base. Thus the terms phospholipid and phosphatide as used herein exclude the combinations of these materials with animal proteins, such as occur in animal tissues, unless essentially freed of the proteinaceous components so as to be stable against bacterial spoilage. Thus I have found that phosphatides serve as effective ligands for removal of iron, cobalt and nickel carbonyls from tobacco smoke, e.g. the lecithins, cephalins and sphingomyelins, as well as hydrogenation products thereof. Hydrogenation products of these phosphatides are more stable and have a reduced tendency to darken as a result of saturation of olefinic bonds present in the phosphatides. Crude soybean oil contains from 1.8 to 3.2% of these natural phosphatides, and commercial phosphatides are presently obtained by recovery therefrom and from other animal and vegetable materials.

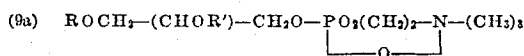
The lecithins are alcohol-soluble and are further defined by the Formulae 9 and 10 wherein glycerin is di-esterified with saturated and unsaturated acids, R and R' representing fatty acid, i.e. acyl groups, and monoesterified with phosphoric acid which in turn is esterified with choline. In other words the lecithins are choline esters of di-fatty acid esters of glycerophosphoric acid.



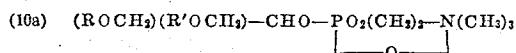
alpha-phosphatidylcholine



beta-phosphatidylcholine



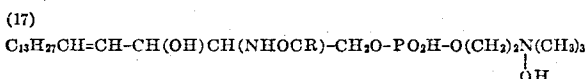
alpha-endo-lecithin



beta-endo-lecithin

The alcohol-insoluble phosphatides, e.g., from soya beans, are termed cephalins, which prove to be a more complex fraction from which several components have been separated and characterized, as defined by Formulae 11 to 17 wherein R and R' and fatty acid groups ranging from C₁₄ to C₂₄ acids, including mono, di, tri and tetra olefinic acids, and G is the galactosidyl group:

- (11) $ROCH_2(CHOR')-CH_2OPO_2H-O(CH_2)_2NH_2$
Alpha-cephalin (α -phosphatidylethanolamine)
- (12) $(ROCH_2)(R'OCH_2)CHOPO_2H-O(CH_2)_2NH_2$
Beta-cephalin (β -phosphatidylethanolamine)
- (13) $ROCH_2(CHOR')CH_2OPO_2H$
Alpha-phosphatidylserine
 $-OCH_2CH(NH_2)COOH$
- (14) $(ROCH_2)(R'OCH_2)CHOPO_2H$
Beta-phosphatidylserine
 $-OCH_2CH(NH_2)COOH$
- (15) $RR'G(C_6H_7O_6)(PO_3H_2)$
Monophosphoinositide (soybean lipositol)
 $-CH(COOH)CH(OH)COO(CH_2)_2NH_2$
- (16) $RR'G(C_6H_6O_6)(PO_3H_2)_2$
Diphosphoinositide
 $-CH(COOH)CH(OH)COO(CH_2)_2NH_2$



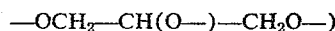
Sphingomyelin

Hydrogenated and partially hydrogenated products obtained from phospholipids likewise are effective ligands for removal of metal carbonyls from tobacco smoke.

The ligand types exemplified by 9 to 14 may be represented by the following formula:

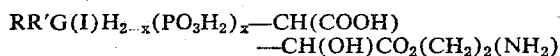


wherein gl=glyceryl (i.e.,



R and R' are the same or different acyl radicals selected from group of C₁₄ to C₂₄ saturated and mono, di, tri and tetra unsaturated acyl radicals, and Y is an amino-derivative radical containing from 2 to 5 carbon atoms, preferably selected from the group consisting of tri-methyl-hydroxy-ammonium-ethyl, aminoethyl, and amino-carboxy-ethyl groups.

The ligand types represented by 15 and 16 conform to the simplified formula:



where G=galactose, R and R' are as above defined, I=hexavalent inositol radical (C₆H₆O₆), and x is 1 or 2.

The sphingomyelin Formula 17 is a 2-amino-propanediol-1,3 derivative wherein carbon 1 is substituted with C₁₅H₂₉ radical (i.e., C₁₃H₂₇CH=CH-), the amino group has C₂₃H₄₇CO acyl substituent and the hydroxyl on carbon 3 is esterified with cholinylphosphoric acid.

Each of the ligand types exemplified by 9 to 17 inclusive and the hydrogenated and partially hydrogenated products thereof may be broadly defined as an alkanolamine ester of a phosphoric acid ester of a polyhydroxy alkane or cyclo-alkane derivative. In 9 to 14 the poly-

hydroxy compound is glycerin, in 15 to 16 it is inositol and in 17 it is 2-amino-propanediol-1,3. The lecithins and cephalins have fatty acyl substituents replacing two of the hydroxyls of glycerin, the inositides have a galactosidyl substituent and 2 acyl substituents for three of the inositol hydrogens, a tartaryl substituent for a fourth hydrogen, the tartaryl group being esterified with serine or ethanolamine, and the remaining 2 hydroxyls of inositol being esterified with one or two phosphoric acid groups.

10 Synthetic compounds of the phosphatide type having ligand properties, can be prepared for use in accordance with the present invention.

EXAMPLES

15 The invention as above disclosed will be more fully understood by reference to the following examples which are to be taken as illustrative and not restrictive of the invention, and which are conducted in three series, namely:

20 Series A, in which a synthetic gas mixture of volatile metal carbonyl and carbon monoxide was prepared containing small quantities upward of 100 parts per million of the metal carbonyl (at least equal to the maximum proportion thereof in tobacco smoke), and in which the ability of typical organo-phosphorus ligand materials to extract such traces from the diluent gas was established.

Series B, in which the same synthetic metal carbonyl gas mixtures were employed to test the efficacy of typical organo phosphorus ligands of this invention in single pass cigarette filters.

Series C, in which the synthetic metal carbonyl gas mixtures were replaced by tobacco smoke and the advantage of the invention in reducing the metal carbonyl content of such smoke was demonstrated.

For the series A and series B examples, metal carbonyls were prepared, or obtained commercially, and put into a gas stream from which they were subsequently removed by the ligand materials employed in the present invention. These tests were followed by the Series C actual cigarette smoking tests wherein ligands were employed as filter components.

Series A

45 Example 1.—(Control).—Nickel tetracarbonyl was generated by passing carbon monoxide of 98% purity from a cylinder over 3.75 grams Raney nickel (2.625 g. Ni on a carrier) which had been pre-dried by heating to above 200° C. in an atmosphere of carbon monoxide. (Girdler G-49A Raney nickel was used.) The gas containing the nickel tetracarbonyl was passed through a fritted glass scrubbing equipment. The outlet tube from the scrubber was run to the base of a Meeker burner wherein unabsorbed nickel carbonyl was mixed with the burner gases and was combusted along therewith.

50 In Example 1 the nickel carbonyl was passed through the empty fritted-glass scrubber, i.e., containing no scrubbing solution. Two simple tests were used to demonstrate the presence of the nickel tetracarbonyl in the gas: (1) the flame of the burner displayed a grey luminosity when the nickel carbonyl was present in an amount as low as 1 p.p.m. and (2) pin-point heating of the glass outlet from the generator deposited a "spot" nickel deposit or mirror on the wall of the glass tube. As little as 10⁻⁶ mole of nickel tetracarbonyl gave an observable metallic nickel deposit in this test, and thus was used as a sensitive test. Also, the weight of a mirror formed in a small glass tube served to establish the metal carbonyl content of a measured quantity of gas.

70 When the gas at 200 cc./minute was shown to contain at least 100 p.p.m. of nickel tetracarbonyl (by mirror test) Example 2 was carried out. The flame of the burner showed a strong grey color in this range of concentration of nickel tetracarbonyl. This test demonstrated that the scrubbing apparatus itself did not decompose

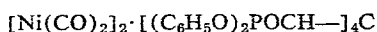
the nickel carbonyl, and did not remove the nickel carbonyl from the gas.

Example 2 (Control).—100 ml. of benzene was placed in the scrubber of Example 1 and the gas rate from the nickel tetracarbonyl generator was held at 200 cc./minute. Appreciable removal of nickel tetracarbonyl was not observed either by mirror test or change in intensity of the grey color after about 10 minutes of passing the gas through the scrubber. This example demonstrated that a solvent alone in the absence of a ligand does not remove the nickel carbonyls from the gas stream to an effective degree because of the appreciable partial pressure of the nickel carbonyl in the solution.

Example 3.—The benzene of Example 2 was replaced with 100 ml. of a 50 vol. percent solution of triphenyl phosphite in benzene. After charging this solution to the gas scrubber the grey nickel color completely disappeared from the flame, and the mirror test was negative for nickel. Upon prolonged standing, white crystals (the stable $\text{Ni}(\text{CO})_3 \cdot (\text{C}_6\text{H}_5\text{O})_3\text{P}$ complex) gradually deposited on the glass wall at the liquid level. This example in comparison with Example 2 demonstrates the efficiency of nickel carbonyl removal from gas by contacting with an aromatic solution of the triphenylphosphite ligand.

Example 4.—An adsorbent was prepared by dissolving 1.263 g. of "Pentite" $[(\text{C}_6\text{H}_5)_3\text{PO}-\text{CH}_2-]_4\text{C}$ in a mixture of 50 ml. pentane and 10 ml. benzene, shaking with 21 g. decolorizing carbon (No. 1551 from General Chemical Division of Allied Chemical Corp.) and warming to 100°C . to evaporate the solvent.

The resultant ligand in a gas permeable carbon body was placed in a 50 ml. Erlenmeyer flask which was installed in the line succeeding the nickel tetracarbonyl generator of Example 1 so that the gas passed from the bottom through the carbon-Pentite adsorbate. After an hour during which time about 6 liters of gaseous carbon monoxide containing about 1% $\text{Ni}(\text{CO})_4$ vapors (10,000 p.p.m.) had been passed through the carbon, the carbon was sampled and analyzed for nickel by arc spectrophotometry. The sample showed 0.69 wt. percent nickel in comparison to nil (less than 0.001% not detected) for a carbon-Pentite sample prior to use in the test. The amount of $\text{Ni}(\text{CO})_4$ adsorbed was calculated to be approximately 2 moles per mole of Pentite on the carbon, corresponding to formation of



indicating that the ligand was utilized to 50% of its theoretical capacity in this test.

Example 5.—The fritted glass scrubber was charged with a homogeneous mixture of 100 ml. of triphenyl phosphite and 90 g. of cyclododecatriene (prepared by cyclopolymerization of butadiene) containing about 90% of the trans, trans, trans-1,5,9-cyclododecatriene and 10% cis, trans, trans isomer. Passage of the nickel tetracarbonyl-containing gas through the resultant scrubbing solution at the rate of about 100 ml./minute for 10 minutes resulted in complete removal of the nickel carbonyl as evidenced by the negative flame and mirror tests.

Example 6.—A mixture of cobalt tetracarbonyl hydride and cobalt tetracarbonyl was generated according to the procedure of Gilmont and Blanchard (Inorganic Syntheses, vol. II, pp. 238-243, McGraw-Hill Book Company, Inc., 1946). The hydride in the glass trap was volatilized at about 30°C . by passing a stream of carbon monoxide into the trap, the outlet of which was attached to the fritted glass scrubber of Example 1 containing a 50 volume percent solution of triphenyl phosphite in benzene. The exit gas from the scrubber contained nil cobalt compounds by the mirror test and the flame test.

Example 7.—Example 6 was repeated substituting cyclododecatriene for the benzene solution in the scrubber. The exit gases showed substantially complete removal of volatile cobalt carbonyl compounds.

Example 8.—Example 6 was repeated except that the scrubber was replaced with an absorber tube containing about 5% "Pentite" on finely divided decolorizing carbon (No. 1551 from General Chemical Division of Allied Chemical Corporation). At a gas rate of 50 ml./minute, substantially all of the cobalt compounds were removed from the gas.

Example 9.—Iron tetracarbonyl dihydride was prepared from iron pentacarbonyl (Antara Chemical Co.) by the method of Blanchard and Coleman (Inorganic Syntheses, vol. II, pp. 243-4, McGraw-Hill Book Co., Inc., 1946). The trap containing the iron tetracarbonyldihydride (1 gram) was allowed to warm (by removal of the Dry Ice trap) while passing a stream of carbon monoxide therethrough. The carbon monoxide gas containing the small amounts of iron carbonyl and carbonyl hydride was passed through the tube containing 20 grams of Philbach "O" (a carbon black produced by Phillips Petroleum Company) having 5% Dipentite deposited thereon. At a rate of 250 ml. gas/minute, the iron compounds were substantially completely removed from the gas, the carbon black absorbate after 40 minutes showing an iron content of about 0.70% (0.146 g. iron) or about one iron atom per mole of Dipentite.

Example 10.—Example 5 was repeated wherein the phosphite scrubbing solution was replaced with a 10% solution of triphenylphosphine in cyclooctene. Results were similar to those of Example 4, the nickel carbonyl removal being substantially complete.

Example 11.—Carbon black coated with Pentite (about 5%) from benzene solution was placed in a 1" length of $\frac{5}{16}$ inch (inside diameter) glass tubing. The coated carbon black weighed 0.40 grams. This filter tube was inserted in the nickel carbonyl gas line from the generator of Example 1 and the gas was passed therethrough at a rate of about 15 ml./minute for 10 minutes. The analysis showed 0.12% nickel content for the carbon.

This example was repeated but using the decolorizing carbon without the liquid, i.e., without Pentite. The carbon showed only 0.002% nickel content thus demonstrating the effectiveness of the ligand on the gas permeable carbon body.

Modification of this example demonstrated the removal of iron, nickel and cobalt metal carbonyls from gases when said gases were contacted with ligands deposited in gas pervious carrier bodies. In these modified examples the ligands were dissolved in aromatic solvents, e.g., toluene, xylene, mixed C_9 aromatic hydrocarbons, mixed C_{10} aromatic hydrocarbons and the like, and said solutions were adsorbed in smoke permeable finely divided, expanded, or fibrous carriers of polystyrene, carbon, silica, cellulose, cellulose acetate-butyrate, cellulose propionate, regenerated cellulose, vermiculite, pumice, polyvinylpyridine, polyesters, polyacrylates, polyurethanes and the like. These examples confirmed the removal of the metal carbonyls by the ligand materials in smoke permeable carrier bodies.

Series B

Example 12.—Cellulose acetate filters were cut from cigarettes (Brand B) and soaked in 100 g. of a benzene solution containing 5 g. Pentite. Ten of these filters were dried and found to contain about 6% Pentite. They were placed end to end compactly in a glass tube into which they fit snugly (ca. $\frac{5}{16}$ inch I.D.). This filter tube was substituted for the carbon-Pentite Erlenmeyer flask of Example 4. When the generated gas contained 400 p.p.m. of nickel carbonyl, at a gas rate of 15 ml./minute the nickel tetracarbonyl could not be detected in the exit gas from the tube. The test was ended after 10 minutes. Analysis by a spectrochemical method showed that the filters had gained 0.01% nickel, i.e. 148 micrograms of nickel.

Example 13.—Example 12 was repeated employing 3 cellulose acetate cigarette filter sections from Brand A.

These filters were dipped three times into a dilute benzene solution containing about 1% Dipentite, drying after each dipping. The coated filters weighed a total of 0.444 grams (0.018 g. Dipentite). The filter tube holding said three filter sections were placed in a line through which a nickel carbonyl-containing gas from the generator described in Example 1 was passed at a rate of about 40 ml./minute for 10 minutes. The filters, analyzed by a spectrochemical method showed a gain in nickel content of 0.007% or an absorption of about 90 micrograms nickel carbonyl. In a similar test without Dipentite the cellulose acetate absorbed only about 10 micrograms of nickel carbonyl.

Example 14.—0.236 parts by weight of Pentite were dissolved in 11 parts by weight benzene; cellulose acetate filters (0.661 parts by weight), removed from cigarettes, were immersed in the solution for 4 hours. The filters were drained of liquid and dried at about 80° C. for 1.5 hours. Their weight was then 0.701 part by weight (0.04 part gain due to Pentite absorption). A sixty percent portion of these coated filters was placed in a glass tube into which they fitted snugly. Carbon monoxide containing traces of nickel carbonyl was generated as in Example 1 using 5 g. fresh Girdler G-49A Raney nickel catalyst. The gas was passed through the glass tube containing the Pentite coated cigarette filters. The gas rate was measured at 15 ml./minute and the time of passage was ten minutes. Analysis by a spectrochemical method showed the filters to have gained 0.03% nickel. This example again demonstrates the removal of nickel carbonyl from the gas by the Pentite.

Example 15 (Control).—The cigarette filter control with 3 cigarette filters in a tube was tested without addition of any ligand. The conditions were as in Example 14. The analysis showed less than 10 p.p.m., i.e., less than 4 micrograms of nickel was absorbed.

Example 16.—A solution of 0.414 g. of tri-(nonylphenyl)-phosphite (commercially available as an antioxidant for rubber under the trademark "Polygard") in 12 ml. of benzene was prepared and 5 cigarette filters made of an acetone-soluble cellulose acetate were immersed therein for about a minute. After removal and drying at an average of 80° C. for 1 hour, the filters showed 11.5% increase in weight. Three of these filters (0.43 gram in total weight) were placed in a snug-fitting glass tube situated in the carbon monoxide stream containing nickel carbonyl and following the nickel carbonyl generator of Example 1. In ten minutes about 150 ml. of gas was passed therethrough. The filter showed by spectrochemical analysis a nickel content of 0.086% or 0.370 mg. total nickel as compared to less than 0.004 mg. in Example 15 in the absence of ligand on the filter.

Example 17.—Tributyl phosphate (0.263 gram) was dissolved in benzene and 5 cigarette filters of cellulose acetate were immersed therein for 10 minutes. The filters were removed, dried at about, 80° C. for 2 hours and 3 of the filters in a glass tube were placed in the stream of carbon monoxide containing nickel tetracarbonyl from the generator of Example 1 for 10 minutes. The gas rate was about 15 ml./minute. Spectrochemical analysis showed a nickel content of 0.176 mg. (as compared to less than 0.004 mg. in Example 15) demonstrating the ability of the tributyl phosphate ligand to remove the nickel carbonyl from the gas stream.

Examples 18-20.—Example 17 was repeated using 3 cigarette filters coated with 10% trimorpholyl phosphorus, the coating technique being the same as in Example 17. The nickel content after 10 minutes in the gas stream showed 30 micrograms of nickel (compared to less than 4 for the uncoated filters in Example 15).

Similar tests showed effectiveness of tripyridyl and triquinolyl phosphorus ligands in removal of nickel, cobalt and iron carbonyl from gases.

Example 21.—Example 17 was repeated using cigarette filters coated with about 25% triphenyl phosphorus. The

gain in nickel content of the filters at the end of the test was found to be 57 micrograms.

Series C

Examples 22-23.—A 3% solution of Pentite in benzene was prepared. Nine unused filter sections of cellulose acetate were removed from Brand A cigarettes and were immersed in the Pentite solution for 2 to 4 minutes. After drying to constant weight it was determined that the cellulose acetate had adsorbed an average of about 5% Pentite. Each of these filter sections was placed in a glass tube ($\frac{3}{16}$ " inside diameter) in which they fit snugly, and 2 Brand A cigarettes from which the manufacturer's filters had been removed, were smoked with each of these Pentite-cellulose acetate sections, the glass tube serving as a cigarette holder. Analysis showed that the nine filters had absorbed a total of 23.9 micrograms of nickel or 1.27 micrograms per cigarette smoked. Likewise 1.6 micrograms of iron was absorbed and 0.1 microgram cobalt per cigarette.

A specific control test (Example 23) was made with 18 cigarettes of Brand A using the filters as supplied with the cigarettes. Analysis showed that the filters had absorbed only 0.8 microgram nickel per cigarette, 0.05 microgram cobalt and 1.3 micrograms of iron/cigarette. The difference, in the amount of the nickel absorbed with Pentite and without Pentite was 0.47 microgram of nickel. Based on the determinations of the Drs. Sunderman, this would represent a reduction of about 80% of the 20 percent of nickel content usually passing the filter, or a smoke containing less than 10%, e.g., only about 4%, of the initial nickel content of the tobacco.

Example 24.—Example 24 was similar to Example 22. Ten cellulose acetate filters from Brand A cigarettes were impregnated with 20% tri(p-nonylphenyl) phosphite, and each filter was employed as a filter for smoking 2 Brand A cigarettes from which the manufacturer's filters had been removed. The ten filters absorbed a total of 26.8 micrograms of nickel or 1.34 micrograms per cigarette; also 1.7 micrograms of iron per cigarette smoked was found. In comparison with the untreated filters of Example 23, the ligand tri-(nonylphenyl) phosphite, removed 0.54 microgram more nickel than the filter supplied by the manufacturer of the Brand A cigarette. Based on the determination of the Drs. Sunderman this would represent a reduction of about 70% of the 20% of nickel content usually passing the filter, or a smoke containing less than 5%, e.g., only about 2%, of the initial nickel content of the tobacco.

Example 25.—Example 24 was repeated except that five cellulose acetate filters impregnated with tri-o-nonylphenyl phosphite were employed as filters for smoking Brand B cigarettes, without removal of the filters from Brand B. Thus the impregnated filters served as a second or "back-up" filter. The impregnated filters were used in smoking 2 each of Brand B cigarettes. After smoking, the filters supplied with Brand B were removed from the butts and were analyzed for comparison with the "back-up" or impregnated filters.

The cellulose acetate filters supplied by the manufacturer on the Brand B cigarettes picked up approximately the following amounts of the metals: 0.8 microgram nickel per cigarette, 1.3 micrograms iron and 0.06 microgram of cobalt. The "back-up" filters containing the impregnating phosphite showed absorption of 1 microgram of nickel, 1.6 micrograms iron and 0.07 microgram of cobalt which had passed through the Brand B filters, per cigarette smoked.

Examples 26 and 27.—Examples analogous to Example 25 demonstrated that trimethylphosphite and triauryl trithiophosphite were effective for removal of nickel, iron and cobalt carbonyls from tobacco smoke.

Example 28.—An alcohol-insoluble phosphatide, substantially mono and diphosphoinositide, was employed in this example. Cellulose acetate tow (about 40% acetyl

content, 5 denier fibers) was immersed for one minute in a benzene solution containing 10% of the phosphatide; after draining and drying the coated tow was found to have 23% of the phosphatide. Twenty portions of this coated tow, each weighing 0.20 ± 0.005 g. were individually press-fitted into a $\frac{1}{16}$ " I.D. glass tube to serve as a filter for Brand C cigarettes. Each of the 20 filters was used to smoke 2 Brand C cigarettes from which the filters had been removed. The used filters were dried at room temperatures and analyzed. The relative efficiency of the treated filter for removal of nickel carbonyl from the smoke, in comparison with the manufacturer's filter of Brand C cigarettes, is apparent since 0.5 microgram of nickel was absorbed per cigarette smoked with the treated filter, while the manufacturer's filter, after smoking of the cigarette, contained only 0.08 microgram of nickel.

Example 29.—In Example 29 alcohol-soluble lecithin was used in place of the alcohol-insoluble phosphatide of Example 28 as coating material for the cellulose acetate tow. Tow (3 grams) from the same batch of cellulose acetate was coated by immersing in a solution consisting of 3 g. lecithin, 27 grams isopropanol and 30 g. benzene. After one minute the tow was squeezed to drain off excess solution, and was dried in an 80° C. stream of air. The coated tow contained 9.5% lecithin. Twenty portions of the tow (0.16 ± 0.005 g. each) were snug-fitted into twenty 2-inch lengths of $\frac{1}{16}$ " I.D. glass tubes and each tube was employed as a filter for smoking two Brand C cigarettes from which the manufacturer's filters had been removed. Analyses of the used filters showed that the filters had absorbed the following amounts of metal as carbonyls (values are in micrograms of metals per cigarette smoked); iron 6.5; nickel 0.67; cobalt 0.11. As in the case of Example 29, the removal of the 0.67 micrograms of nickel per cigarette, contrasts markedly with the failure of the manufacturer's Brand C filter to remove any significant amount of nickel (see Example 28).

Example 30.—Example 29 was repeated using cephalin as ligand material for coating cellulose acetate tow. The coated tow contained about 16.5% cephalin. Each of 20 portions (0.180 ± 0.005 g.) of this filter material was used as filter for smoking 2 Brand C cigarettes. Analysis showed absorption of the following amounts of metals by the treated filters in micrograms per cigarette smoked: nickel 0.91; cobalt 0.01; iron 8.56. Again the nickel removed contrasted with the failure of the manufacturer's filter to remove any significant amount of nickel from the smoke.

Example 31.—As ligand material for coating the cellulose acetate tow, the lecithin and cephalin fractions from soya bean were employed in combination, i.e., without preliminary separation. The coated tow contained 12% of combined phosphatides, and 0.285 ± 0.005 g. of the coated tow were used as "back-up" filter material for smoking 2 Brand C cigarettes per plug. The plugs were made by press fitting the weighed portions of coated tow into a $\frac{1}{16}$ " I.D. glass tube which served as a cigarette holder and filter. Brand C cigarettes were employed without removal of manufacturer's filter. Analyses after smoking showed the following absorptions of metal (in micrograms) per cigarette smoked: nickel 0.8; cobalt 1.5; iron 10.2. Thus the treated filters were efficacious for removing from the smoke the volatile metal compounds.

Example 32.—Total lecithin and cephalin fractions similar to those used in Example 31 were hydrogenated to substantially reduce unsaturation as in Example 34 following. Cellulose acetate tow (about 40% acetyl content, 5 denier fibers) were impregnated with the hydrogenated phosphatide product to give a filter containing about 10% of the hydrogenated phosphatides. This coated tow was used in smoking Brand C cigarettes as in Example 31, with substantially similar results.

Example 33.—Cephalin of the type employed in Example 30 was hydrogenated according to the method of

U.S. Patent 3,026,341 issued Mar. 20, 1962, to substantially reduce unsaturation, and the hydrogenated product was used to impregnate cellulose acetate tow to give a filter material containing about 15% of hydrocephalin.

Twenty portions of this filter (0.170 ± 0.005 g.) were used to repeat the smoking procedure of Example 31. Analyses of the filters before and after use, by difference showed absorption from the cigarette smoke of approximately 10 micrograms of iron, 0.8 micrograms of nickel and 0.2 micrograms of cobalt per cigarette smoked.

With respect to Examples 28–33 it was noted that the filter supplied by the manufacturer contained only 0.08 microgram of nickel after smoking of the cigarette, and it was also noted that the filter of the present invention absorbed larger amounts of nickel when used as back-up filters following the filters of the Brand C cigarettes, than when they were substituted for such filters. Analyses of Brand C filters before and after smoking were accordingly made which showed that the unused Brand C filters contained nickel in a larger amount than the used Brand C filters, and thus had actually contributed volatile nickel compounds to the smoke, in contrast to the Brand A filters, which absorbed some nickel from the smoke as shown by Example 23.

While there have been described herein what are at present considered 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. It is therefore to be understood that the exemplary embodiments are illustrative and not restrictive to the invention, the scope of which is defined in the appended claims, and that all modifications that come within the meaning and range of equivalency of the claims are intended to be included therein.

I claim:

1. A process for the purification of tobacco smoke from the burning, in a smoking article, of conventional tobacco which produces a smoke that may contain trace quantities of transition metal compounds, which method comprises passing said smoke through a filter into the mouth of the user downstream therefrom, said filter containing a base material carrying a non-toxic organo-phosphorous compound having a metal chelating ligand grouping, said compound being other than tri(nonylphenyl)-phosphite and being essentially free of animal protein so as to be stable against bacterial spoilage, and being selected from the class consisting of the following groups:

- (a) the phosphines, phosphites and phosphates having three substituent radicals selected from the radicals of group I, said group I consisting of the following radicals: the alkyl, alkenyl, alkynyl, cycloalkyl, terpenyl, aryl, alkaryl, alkoxyaryl, haloaryl, aralkyl, arylene, morpholinyl, pyridyl, alkylpyridyl, pyrrolydyl, piperazinyl, quinolyl and isoquinolyl radicals which contain not more than 18 carbon atoms;
- (b) the diphosphines having four substituent radicals selected from said group I;
- (c) the solid polyphosphite compounds having the formula $D[O_{3-x}P(OR)_x]_3$ wherein D is a polyvalent polyol moiety, x is 1 or 2, s is an integer from 2 to 1000, and the R of each OR group is selected from said group I;
- (d) the amino-alcohol esters of acids of phosphorous; and
- (e) the phosphatides.

2. A process according to claim 1, in which the filter through which the smoke is passed as aforesaid contains an organo-phosphorous compound selected from group (a) therein.

3. A process according to claim 2, in which the organo-phosphorous compound from group (a) is tri-phenyl phosphite.

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4. A process according to claim 1, in which the filter through which the smoke is passed as aforesaid contains an organo-phosphorous compound selected from group (b) therein.

5. A process according to claim 1, in which the filter through which the smoke is passed as aforesaid contains an organo-phosphorous compound selected from group (c) therein.

6. A process according to claim 4, in which the organo-phosphorous compound from group (c) is tetra-diphenyl-phosphito-pentaerythritol.

7. A process according to claim 1, in which the filter through which the smoke is passed as aforesaid contains an organo-phosphorous compound selected from group (e) therein.

8. A process according to claim 7, in which the organo-phosphorous compound from group (e) is an alcohol insoluble phosphatide.

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9. A process according to claim 7, in which the organo-phosphorous compound from group (e) is an alcohol soluble lecithin.

10. A process according to claim 7, in which the organo-phosphorous compound from group (e) is a hydrogenated organo-phosphorous compound selected from said group.

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