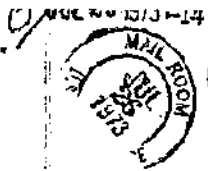


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TITLE: SMOKING ARTICLE

INVENTORS: NORMAN B. RAINER and
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Jarlina Day
9/24/83

SMOKING ARTICLE

Abstract of the Disclosure

Selected heavy metal compounds, particularly copper or nickel in the form of their salts, may be complexed with selected aliphatic or aromatic amines and deposited on a solid support or substrate to provide a material for the detection and/or removal of HCN from a mixture of gases; removal from tobacco smoke being particularly desirable. Certain novel compositions are also provided.

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1 another Keith patent, U.S. Patent No. 3,460,543, the use of
various metal oxides, namely oxides of cobalt, copper, zinc
or iron, on a carrier for removal of hydrogen cyanide is dis-
closed. In a more recent patent, Horseywell et al, U.S.
5 Patent No. 3,550,600, zinc acetate in admixture with an
organic or inorganic base on a smoke filter paper or
cellulose acetate filter support is described as being
effective in the removal of various gaseous components,
including hydrogen cyanide, from tobacco smoke. In the
10 Horseywell et al patent, the examples given indicate a
reduction of from about 57% to as high as 85% of the
original hydrogen cyanide concentration in the tobacco smoke.

An object of the present invention is to provide a
method and means for the colorimetric detection of cyanides.

15 Another object of the present invention is to provide
a method and means for selectively removing cyanides, and
particularly hydrogen cyanide, from gases.

20 A further object of the present invention is to
provide a method and means for removing a major amount of any
hydrogen cyanide which may be present in tobacco smoke.

25 A still further object of the present invention is
to provide novel compositions of matter having utility as
selective filtrants for cyanides from other gases.

1 These and still other objects will be discussed more fully in the description of the invention which follows.

Description of the Invention

5 This invention relates to the treatment of gaseous substances containing hydrogen cyanide. More particularly the present invention is concerned with a method and means for the detection and/or selective removal of hydrogen cyanide from gases such as tobacco smoke.

10 It has been discovered that certain heavy metal salt-amine complexes deposited on suitable bases are highly effective in absorbing or removing substantial amounts of hydrogen cyanide contained in various gas mixtures, in-

15 cluding any hydrogen cyanide which may occur in the smoke of tobacco or a tobacco substitute. It has also been dis-

covered that the removal of the cyanide component from

tobacco smoke by special metal-amine complexes may con-

20 currently release a portion of the amine constituting part

of the complex into the smoke stream. Moreover, incident

to exposure to cyanides, the present metal salt-amine com-

plexes undergo a readily observable color change which serves

as an indicator of the presence of such poisonous substances.

1 The compositions employed in accordance with
the present invention are prepared by reacting a salt
of a transition metal with an organic amine to produce a
metal-amine complex. The complex may be formed in situ
5 on a suitable filter base or may be formed and then
added thereto.

10 The transition metals which may be employed
in the present invention are preferably selected from
the members of the third period elements, and of these,
copper, nickel, iron, cobalt and manganese appear most
desirable.

15 It is not necessary that the foregoing metals
be employed in any particular cationic form. It has
been discovered, however, that divalent nickel salts
and either monovalent or divalent copper salts are
particularly active and, consequently, salts comprising
these cations represent a most preferred embodiment of
the present invention.

20 It has been determined that the anionic portion
of the present metal salts has essentially no effect on
the utility of the present complexes. It is desirable
that the salts be soluble in water or aqueous ammonia,
25 however, and of these, the chlorides are particularly preferred.

1 Other salts - containing sulfate, nitrate, phosphate, and
hydroxyl anions - are also effective. Similarly, metallic
salts formed from organic acids having 1 to about 12 carbon
atoms may also be used in forming the metal salt-amine com-
plexes, and of these the formate and acetate ions are most
efficacious.

There are essentially no limits as to the amines
which may be employed in forming the present metal-salt-amine
complexes. A particularly desirable class of amines,
however, includes those amines having a vapor pressure below
about 0.01 mm. Hg. at 20°C. Examples of such substantially
non-volatile amines are triethylenetetramine, iminobispropyl-
amine, tetraethylenepentamine, pentaethylenhexamine,
diethanolamine, triethanolamine, N-aminoethyl ethanolamine,
N methyl diethanolamine, tri-isopropanolamine, N-(3-amino-
propyl) morpholine, N-(2-hydroxyethyl) piperazine, hexamethyl-
enetetramine, polymers of ethylenimine or polyvinyl amine having
molecular weights of from about 450 to about 60,000 and amino
acids such as glycine, alanine, phenylalanine, proline, lysine,
histidine and the like. Where amines of this non-volatile
class are employed in accordance with the present invention,
little or no amine has been found in the smoke stream and it
has therefore been assumed that it has been retained on the
carrier. Such a result has the advantage that the only ap-
parent effect on the filtered smoke itself is the removal of
detrimental cyanide components. A preferred class of amines
comprises those amines soluble in water to the extent of at
least 10 weight percent.

1 The reaction of the metal salt with the complexing
amine is carried out with a molar excess of the amine,
preferably at a molar ratio, amine to metal salt, of at least
3 to 1 and more preferably at a ratio of at least 4 to 1.

5 The reaction is preferably carried out in a solvent for both
the reactants and the complex product. The reaction is a
straight forward addition of the complexing amine to the
salt of the heavy metal. Where the complex is soluble in the
solvent medium used, any precipitate that is formed may be
10 separated by the usual procedures - for example, by filtration
or decantation - and the complex obtained from the remaining
solution by evaporation or distillation of the solvent.

 The solvent may be any liquid medium in which the
reactants are soluble, such as water, aqueous ammonia, lower
15 alkanols or even the liquid amine itself. Preferably, the
complex formed is also soluble in the reaction medium as im-
purities in the form of precipitates may then be removed
easily and the complex obtained by such usual solvent
removal procedures as evaporation. In the event that the
20 complex formed is insoluble in the reaction solvent
medium, or crystallizes out, it may be separated from the
supernatant - for example, by filtration - washed and,
if desired, purified further.

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1 Temperature conditions for effecting the reaction
are mild. The reaction will proceed satisfactorily at room
or ambient temperatures or at any temperature of from about
0° to about 90°C.

5 If the metal salt-amine complex or addition product
is prepared in a liquid reaction medium, it may be concen-
trated and then absorbed onto a substrate or carrier capable
of acting as a support for the dry metal salt-amine complex.
After deposition of the complex, the product is then dried
10 by various known procedures.

 The preparation of the desired metal salt-amine
complex may also be carried out in situ on the surface of the
carrier or where it is to be used. In such a case, one may
apply a solution of one of the reactants, for example of the
15 metal salt, to the carrier, dry at a temperature of up to
about 100°C and then introduce the second reactant, for
example the amine, either undiluted or in solution, a period
of about a few minutes to about one hour being allowed to
permit the complex to form before drying the composition.
20 The solvents for the separate solutions may be any of those
mentioned for carrying out the reaction. The temperature
conditions required for forming a metal-amine complex by in
situ deposition and reaction will range from about 0°C to about
90°C, but should not exceed the decomposition temperature of
25 any component or product.

1 Where the complex is applied to a support or
substrate from solution, it is obvious that the solvent
should be relatively volatile so that it may be easily
evaporated and removed from the solid substrata. Water,
5 acetone, or a lower alkanol of from 1 to about 4 carbon
atoms are particularly suitable for this purpose.

 The complexes formed in accordance with the
foregoing processes generally exhibit a metal to co-
ordinated amine group mole ratio of about 1:1 to 1:4.
10 This ratio does not, however, reflect the presence of
additional amine groups which may be present in the amine
ligand, but which, for steric or other reasons, are not
co-ordinated with the metal. Thus, for example, where
polymers such as those of ethylenimine are employed,
15 there will ordinarily be an excess of amine groups beyond
those required to fully complex the metal salt.

 Where the complex on the supporting substrate is
to be utilized in a cigarette filter to remove or sequester
20 the cyanide component in the main stream tobacco smoke,
one may employ a cellulosic cigarette filter paper as the
substrate. Such paper is generally sufficiently absorbent
to take up the desired amount of the solubilized complex.

1 Alternatively, one may use a typical cigarette filter
material such as cellulose acetate filaments of 1.5 to 5
denier as the substrate. These filaments are capable of
retaining the solid complex in sufficient quantity to permit
5 adequate contact of the complex with the main stream smoke
so as to remove any cyanide component from the gaseous
fractions. In general, the preferred substrates are of the
porous variety, particularly those having a surface area
greater than 0.4 square meter per gram, most preferably
10 greater than 1.0 square meter per gram.

Other supporting materials that may be used are
activated carbon, charcoal or a molecular sieve such as
that produced by the Linde Division of Union Carbide Corp.
and identified as Linde Type 5A. Additionally, a micro-
15 porous polymeric product of vinyl chloride, preferably
those types described in a Johnson et al patent, namely
U.S. Patent No. 3,526,433, has also proven extremely ef-
fective.

20 Another and particularly useful substrate for the
complex is granular activated alumina having a "BET"
surface area of about $200 \text{ m}^2/\text{g}$ such as that sold by the
Reynolds Chemicals Division of Reynolds Metals Co.,
Richmond, Va., and which is identified as a type RA-1
25 activated alumina.

1 The deposited metal salt-amine complex may be
present in the supporting material in an amount of about 0.1%
to about 40%, preferably 1 to 10%. The complexes generally
have a green, blue or purple color and, as cyanide is absorbed,
5 become colorless. This provides a visual indication of the
extent of utilization of the complexes. The color change is
most apparent when the complex is carried on a white substrate.

 This color change in the metal salt-amine complex
additionally provides a useful means for detecting the
10 presence of cyanides in gaseous or liquid medium. Thus the
complex - supported by a carrier or not - may be utilized as
a detector to warn of the necessity of employing a filtering
device such as the gas mask more fully described below.
Although mere visual inspection of complex is adequate for
15 detection of cyanides in a fluid, this invention also en-
compasses the use of complementary apparatus - for example,
a conventional colorimetric device which would register any
decrease in the absorbence of the complex at its character-
istic wavelength - so as to automate the detector or to
20 convert it into a quantitative measuring device.

 It has additionally been discovered that where the
substrates - for example granular microporous polyvinyl-
chloride - of the present complexes normally exhibit poor
bulk flow characteristics due to interparticle electrostatic
25 attraction, incorporation of such complexes unexpectedly
improves these characteristics. Thus, one advantage inherent
in the present complexes resides in their propensity to reduce
the usual handling difficulties common to any particulate

1 material capable of retaining an electrostatic charge and the specific flow problems attendant to forming cigarette filters with members of the present class of substrates.

5 Cigarette filters may be improved considerably by

incorporating therein the instant metal salt-amine complex described above because, as has already been pointed out, the complexes of this invention are particularly effective in removing practically all of the cyanide ion, whether in the form of hydrogen cyanide or as organic cyanides, found in the gas phase of tobacco smoke. As much as 90% to 100% of the hydrogen cyanide in the tobacco smoke may be removed with the compositions of the invention. Moreover, the concurrent color change may be made readily observable - for example at the filter end or through a transparent peripheral panel - so as to assure the smoker of increased protection against harmful smoke components.

15 The metal salt-amine complexes of this invention - whether supported by a carrier or not - are also valuable in other embodiments such as filtering means for gas masks.

20 Thus where hydrogen cyanide may be present, for example when such compound is used in a chemical reaction or is released as a by-product of a chemical reaction, such masks would provide important protection against harmful exposure.

25 Finally, the polyelectrolytic complexes of the present metal salts have utility beyond their use in cigarette and other gas filtering embodiments. They are film formers

and provide coatings which are electrostatic-inhibiting or electrically conducting. Thus resin powders treated with from about 1 to 20% by weight, preferably about 5 to 10% of such complexes may show improved flow, due to alteration in electrostatic interaction.

The following examples are illustrative:

Example 1

Cuprous chloride (0.99 g, 0.01 mole) and triethanol-amine (5.19 g, 0.035 mole), the latter being intentionally in excess, were dissolved in 100 ml. of methanol. The mixture was shaken well, filtered, and allowed to stand for three days. Small green crystals were deposited. Analysis of these by atomic absorption spectroscopy showed 28.0% Cu; calculated for 1:1 complex, 25.60%. Elemental analysis was as follows:

<u>Element</u>	<u>Found</u>	<u>Calculated</u>
C	28.98	29.04
H	5.95	6.09
N	5.60	5.64
Cl	14.47	14.29

A sample (160 mg) of the green crystals was dissolved in 25 ml of water giving a blue solution. The addition of 22.35 ml of 0.1134 M KCN (2.534 millimoles) discharged the blue color. This gives an equivalent weight for the sample of 63.13 (calculated 62.05), when one assumes a trivalent cuprocyanide ion formed such as $\text{Cu}(\text{CN})_4^{3-}$.

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1 It will be noted that the cuprous, cupric and
 nickelous cations were the most effective.

Example 5

5 Activated alumina and microporous PVC carriers
 impregnated with cuprous - PEI complex prepared as
 described in Example 2 were loaded into the 8 mm long
 space between two short cellulose acetate filter plugs
 (a "plug-space-plug" filter) and the filters were attached
10 to standard 65 mm commercial cigarette rods. These
 cigarettes were smoked and the gas phase was subjected
 to infrared analysis.

 The reduction of certain gas phase components
15 vs. the reduction of cyanide is tabulated below to show
 the relative selectivity for HCN:

<u>Carrier</u>	<u>Complex mg/cigt.</u>	<u>% Reduction</u>		
		<u>HCN</u>	<u>Acetaldehyde</u>	<u>Isoprene</u>
Microporous PVC	25	88	36	8
20 Activated Alumina	10	92	21	(-5)

Example 6

Nickel chloride hexahydrate (57.5 g, 0.20 mole) was dissolved in 200 ml of water. A solution of poly-ethylenimine 18 (PEI-18, 34.8 g, 0.8 nitrogen equivalents) in 100 ml of water was added quickly with vigorous stirring. The light-green nickel solution turned deep blue. The solution was transferred to an evaporating dish and allowed to evaporate to dryness. The glassy solid thus obtained was crushed and further dried under vacuum to yield 80.6 g of blue material.

Nickel analysis: 15.50%, expected 19.3%.

One gram of NiCl_2 /PEI-18 complex was dissolved in 30 ml of water. This solution was used to impregnate a 5.000 g sample of 40/80 mesh alumina (Type RA-1). The alumina was filtered, freed of excess liquid, and dried under vacuum over P_2O_5 . The alumina adsorbed 2.5% (added weight) of the complex. A CuCl /PEI-18 complex was similarly adsorbed onto alumina (3.7% added weight).

Each of the two samples was loaded into a plug-space-plug filter and mounted on a standard cigarette rod. The assembled cigarettes were smoked and analyzed for HCN removal by comparison with the standard.

1	<u>Composition</u>	<u>Loading</u>	<u>RTD</u>	<u>HCN Removal</u>
	Standard cigarette	- - -	5"	- - -
	CuCl/PEI-18	150 mg.	5"	87.5%
	NiCl ₂ /PEI-18	200 mg.	4.9"	87.5%

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Example 7

A granular microporous polyvinylchloride cigarette filter material prepared in accordance with Example 1 of U.S. Patent No. 3,528,433 was divided into two equal portions.

10 One sample - designated A - was maintained as a control, and the second - designated B - was spray-treated with an ethanol solution of the cuprous chloride-polyethylenimine complex of Example 2. After incorporation of 7% by weight of the complex, sample B was dried in a vacuum oven at 30°C

15 to remove the ethanol.

The two samples were then measured in accordance with ASTM specification D 1895-67T, Method A, to determine their relative bulk flow characteristics. In carrying out

20 the test, a stainless steel funnel having a 0.95 cm diameter opening at the bottom was stoppered and then filled to overflowing with a sample. The top of the funnel was then scraped off level with a straight edge.

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1 The bulk flow measurement could then be taken by
recording the time required - after opening of the
funnel's stoppered bottom - for emptying the funnel.

5 For sample A, this emptying time was 35 sec.;
for sample B, 22 sec. Accordingly, the shortened measure
for the treated filter material established the effective-
ness of the complex for improving the bulk flow properties
of particulate materials normally capable of retaining
10 an electrostatic charge.

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WHAT IS CLAIMED IS:

1. A smoking article comprising a tobacco or tobacco-substitute portion and a smoke filtering portion therefor, said smoke filtering portion containing a filtering element and a metal salt-amine complex, said complex being incorporated in said smoke filtering portion in an amount from about 0.1% to 40% by weight thereof, the cation of said metal salt being selected from the group consisting of copper, nickel, iron, cobalt, manganese, and mixtures thereof.

2. The article of Claim 1, wherein the metal salt-amine complex exhibits a mole ratio of metal cation to co-ordinated amine radical of about 1:1 to about 1:4.

3. The article of Claim 2, wherein the amine of the complex is a non-volatile amine having a vapor pressure below 0.01 mm. Hg. at 20°C.

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4. The article of Claim 1, wherein the metal salt of the complex has a cation selected from the group consisting of divalent ion of copper, of nickel, monovalent ion of copper, and mixtures thereof.

5. The article of Claim 3, wherein the metal salt of the complex has a cation selected from the group consisting of divalent ion of copper, of nickel, monovalent ion of copper, and mixtures thereof.

6. The article of Claim 3, wherein the filtering portion comprises a filter base carrier having a surface area greater than 0.4 square meter per gram.

7. The article of Claim 2, wherein the anionic portion of the metal salt is selected from the group consisting of chloride, sulfate, nitrate, phosphate, and hydroxyl ions, organic acid ions having from 1 to about 12 carbon atoms, and mixtures thereof.

8. The article of Claim 7, wherein the metal salt of the complex is selected from the group consisting of cuprous chloride, cupric chloride and nickelous chloride and the amine is a polyalkylenimine having a molecular weight of from about 450 to about 60,000.

9. The composition comprising a metal salt-amine complex, wherein the cation of said metal salt is selected from the group consisting of ions of copper, nickel, iron, cobalt, manganese and mixtures thereof and wherein said amine is selected from the group consisting of polyalkylenimine and polyvinyl amine having a molecular weight of from about 450 to about 60,000.

10. The composition of Claim 9, wherein the metal salt-amine complex exhibits a mole ratio of metal cation to co-ordinated amine radical of about 1:1 to about 1:4.

11. The composition of Claim 10, wherein the metal salt of the complex has a cation selected from the group consisting of divalent ion of copper, of nickel, monovalent ion of copper, and mixtures thereof.

12. The composition of Claim 11, wherein the amine of the complex is a polysalkylenimine having a monovalent weight of from about 450 to about 60,000.

13. A method for detecting the presence of cyanides in a fluid comprising contacting said fluid with a metal salt-amine complex, the metal cation of said complex being selected from the group consisting of copper, nickel, iron, cobalt, manganese, and mixtures thereof and monitoring said complex for change in color thereof.

14. The method of Claim 13, wherein the metal salt-complex is supported on an essentially inert carrier in an amount of from about 0.1% to 40% by weight thereof and the fluid is a gas.

15. The method of Claim 14, wherein the metal cation of the complex is selected from the group consisting of divalent ion of copper, of nickel, monovalent ion of copper, and mixtures thereof.

16. The method of Claim 15, wherein the gaseous fluid is tobacco smoke and the complex is located in a cigarette filter element.

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DECLARATION, POWER OF ATTORNEY AND PETITION

1. ²⁰¹ Norman B. Rainer (Full Name)
2. ²⁰² Charles B. Hoelzel (Full Name)
3. (Full Name)
4. (Full Name)

declare that we are respectively

1. a citizen of the United States of America
residing at Henrico County, City of Richmond, State of Virginia
(City and State or Country)
2. a citizen of the United States of America
residing at Chesterfield County, City of Richmond, State of Virginia
(City and State or Country)
3. a citizen of _____
residing at _____
(City and State or Country)
4. a citizen of _____
residing at _____
(City and State or Country)

that we verily believe we are the original, first, and joint inventors of the invention or discovery in

SMOKING ARTICLE

described and claimed in the attached specification; that we do not know and do not believe that this invention or discovery was ever known or used in the United States before our invention or discovery thereof, or patented or described in any printed publication in any country before our invention or discovery thereof, or more than one year prior to this application, or in public use or on sale in the United States more than one year prior to this application; that this invention or discovery has not been patented in any country foreign to the United States on an application filed by us or our legal representatives or assigns more than twelve months before this application; and that no application for patent on this invention or discovery has been filed by us or our representatives or assigns in any country foreign to the United States, except as follows:

(None)

^{4/5/12}
We hereby appoint Elmer R. Hellerich—Registration No. 12,316, Norman N. Schuttler—Registration No. 13,262, John T. Kelton—Registration No. 16,337, William F. Vogt III—Registration No. 19,439, Herbert Blocker—Registration No. 20,368, Howard K. Kothe—Registration No. 18,403, Thomas V. Heyman—Registration No. 20,313, Robert E. Kosinski—Registration No. 24,837, Stevaff J. Bosses—Registration No. 22,291, George J. Brandt, Jr.—Registration No. 22,021, James J. Daley—Registration No. 24,158, James W. Badie—Registration No. 20,968, Robert J. Eichelburg—Registration No. 23,057, and Robert M. Freeman—Registration No. 16,629 my attorneys, with full power of substitution and appointment of associate attorneys, to prosecute this application and to transact all business in the Patent Office connected therewith.

And send all correspondence to—

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We, the undersigned petitioners, declare further that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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