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Cigarette filter.

A cigarette filter comprises a base made of acetate, cellulose or acetate-cellulose fibers and impregnated with an adsorbing agent which is a N,N'-bis(3-triethoxysilylpropyl)thiocarbamide organo-silicon monomer (C₂H₅O)₃Si(CH₂)₃NH - C(S) - NH(CH₂)₃Si-(OC₂H₅)₃.

EP 0 493 026 A2

Field of the invention

The present invention relates to techniques for purifying tobacco smoke of cancerogenic and toxic substances and in particular to a cigarette filter. The filter can be used in the tobacco industry in manufacturing filter cigarettes.

Background of the Invention

Known in the art are filters comprising a base charcoal of acetate-cellulose fibers in combination with charcoal. The charcoal is contained in the base, as mechanical inclusions, and forming a coat of the base or simply contacting it. These filters are deficient in that they do not completely eliminate a harmful effect of a number of the cancerogenic and toxic components of tobacco smoke.

In this connection effective filtration means are needed which remove, if possible, the great amounts of tobacco smoke harmful components, but permit preserving its organoleptic characteristics.

Also known is another cigarette filter made from hydroxyapatite in combination with acetate fibers or activated coal. Said hydroxyapatite may be represented by the formula $3[\text{Ca}_3(\text{PO}_4)_2] \cdot \text{M}(\text{OH})_2$. It is substantially a material having a particle size of from 2 to $5\mu\text{m}$ and used in the filter in an amount of from 0, 1 to 20% of the tobacco weight in the cigarette. This filter can be made in the form of a tablet, sleeve, mouthpiece and etc. The filter contributes to an improved absorption of harmful substances from the tobacco smoke, such as nicotine, tar, carbon monoxide. It does not promote, however, to absorbing cancerogenic and toxic substances, from tobacco smoke such as polycyclic aromatic hydrocarbons benz(a) pyrene, benz(g,h,i) perylene, dibenz(a,h) anthracene, dihenz(a,c) anthracene and volatile nitrosoamines (N'-nitrosodiethylamine, N'-nitrosopyrrolidine).

There are known various cigarette filters which decrease a toxic effect of tobacco smoke and consist of a base made of acetate, cellulose or acetate-cellulose fibers with substances applied onto the base which having absorption properties or impregnated with these substances.

The adsorbing agents used are represented by activated charcoal, the inorganic and organic salts of mercaptoalkanesulfonic acids (cysteine, acetylcysteine and phthalocyanins).

These filters are deficient in that the range of substances absorbed by them is restricted in all cases, while the very filters can degrade on heating with the formation of toxic compounds. For instance, employment of phthalocyanine as a sorbent may result in forming the following products of decomposition: organic cyanides, ammonia, benzene derivatives etc.

Closest to the claimed filter is one (ref. publication No. 0351252, dated January 17, 1990, of European Patent Application No. 89307209.0) containing a base made of acetate, cellulose or acetate-cellulose fibers, and impregnated with an absorbent agent which is a complex compound of ferrous iron with a ligand being in reality a thiol-containing low molecular compound in which a ratio of iron ions to the number of ligand molecules not more than 1:2 and a proportion of the absorbing agent is between 3 and 13% of the total weight of the filter.

In the filter as described the sources of obtaining ferrous iron usually were the salts of iron, for example, FeSO_4 , FeCl_2 , $\text{Fe}(\text{NO}_3)_2$, and as the thiol-containing low-molecular compounds were used monothiol-containing compounds (thiol-sulphate of sodium, cysteine, reduced glutathione etc) and dithiol-containing organic compounds (diethyldithiocarbamate, dimethyldithiocarbamate, ethyl-xanthate of sodium etc).

The filter as described enables one to efficiently clean tobacco smoke from nitrogen oxide, but it does not raise, just as all the filters described earlier, the content in the tobacco smoke such cancerogenic and toxic substances as polycyclic aromatic hydrocarbons (benz(a) pyrene, benz(g, h,i) perylene, dibenz(a,h) anthracene, dibenz(a,c) anthracene), volatile nitrosoamines (N'-nitrosodiethylamine, N'-nitrosopyrrolidine) as well as metals, such as magnesium, calcium, strontium, copper, lead, arsenic, vanadium, chromium, manganese, iron, cobalt and nickel.

Summary of the Invention

An object of the present invention is to raise the degree of purification of tobacco smoke of cancerogenic and toxic substances.

Said object is achieved by a cigarette filter comprising a base of acetate, cellulose or acetate-cellulose fibers impregnated with an adsorbing agent. According to the invention, the adsorbing agent used is represented by an N,N'-bis(3-thiethoxysilylpropyl)thiocarbamide organo-silicon monomer $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}-\text{C}(\text{S})-\text{NH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$.

The filter as claimed provides for the 100% removal of polycyclic aromatic hydrocarbons, of about 60% of volatile nitrosoamines and up to 90% of metals owing to the employment of the adsorbing agent as proposed.

The content of adsorbing agent should preferably be from 6 to 15,3% of the weight of the base fibers, a factor that assures the maximal efficiency of purification of tobacco smoke from cancerogenic and toxic agents.

Detailed Description of the Invention

5

The invention is further explained by a description of its specific embodiments.

A cigarette filter comprises a base of acetate, cellulose or acetate-cellulose fibers, impregnated with an adsorbing agent which is an N,N'-bis(3-thiethoxysilylpropyl)thiocarbamide organo-silicon monomer $(C_2H_5O)_3Si(CH_2)_3NH-C(S)-NH(CH_2)_3Si(OC_2H_5)_3$.

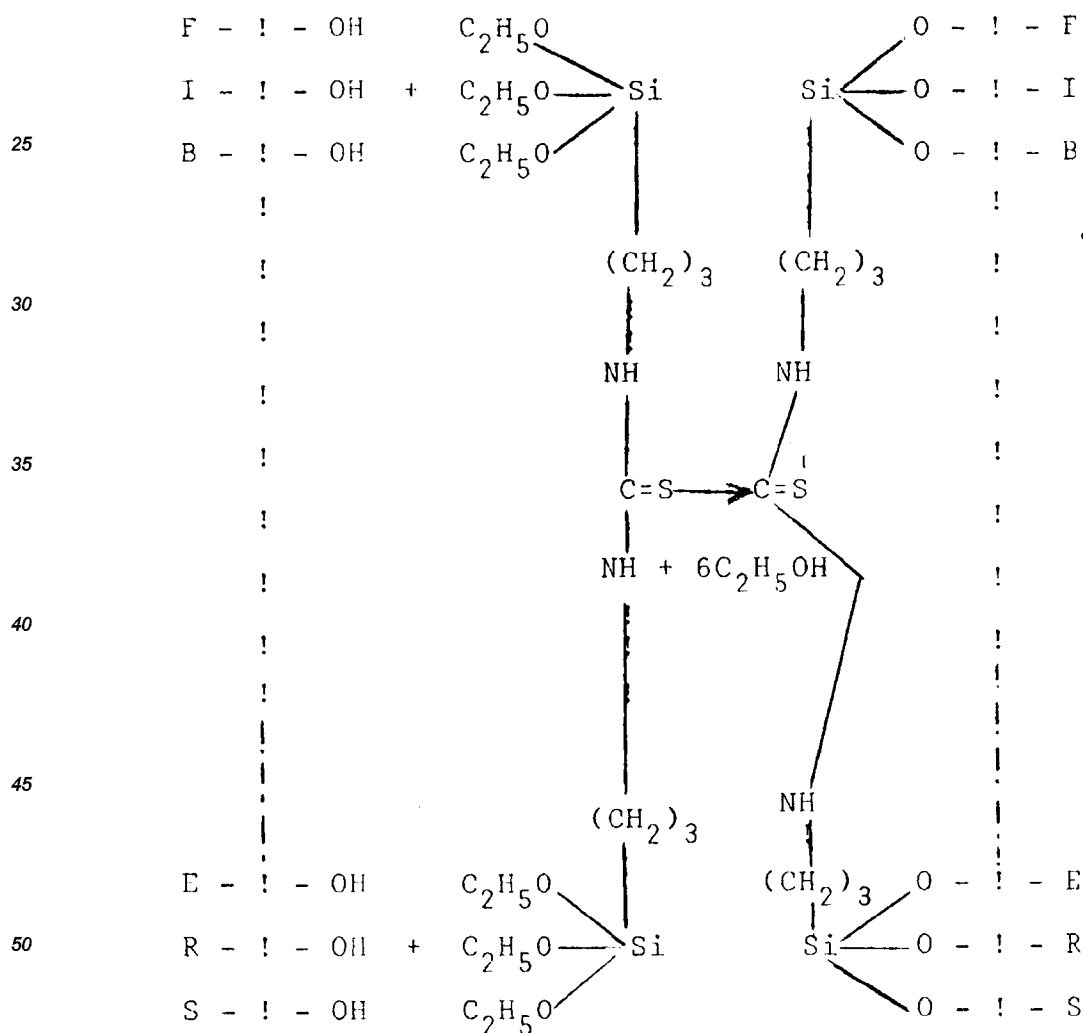
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The content of said monomer in the filter is from 6 to 15,3% of the weight of the base fibers.. With the content of the monomer of less than 6% the base fiber proves to be insufficiently impregnated with this monomer, and its adsorption properties get worse. With the content of the monomer more than 15,3% its quantity proves to be excessive, and a certain amount of the monomer penetrates into the tobacco of a cigarette and deteriorate its quality.

15

A mechanism of binding a monomer with the material of a filter base is based on a chemical modification of acetate, cellulose or acetate-cellulose fibers of the base due to the condensation of reactive surface groups (hydroxylic ones, in particular) of said monomer. Condensation is carried out in a way similar to the known modification of a silica gel of various brands according to the possible scheme as follows:

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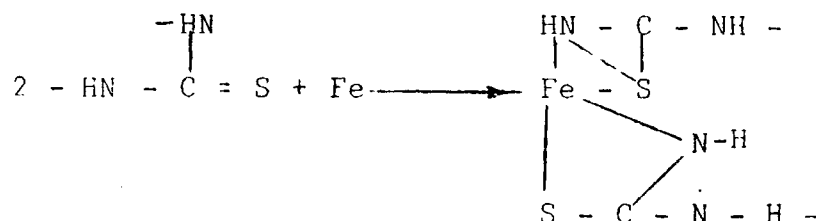
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During this process on the surface of acetate, cellulose or acetate-cellulose base fibers there is formed a layer of a polysiloxane polymer which is chemically bound therewith and has effective adsorption properties.

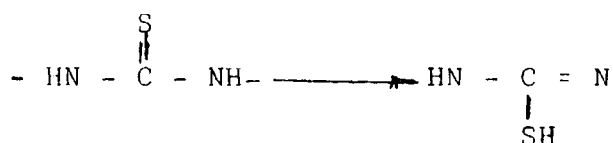
The high sorption activity of the monomer for nitrosocompounds and polycyclic aromatic hydrocarbons is explained by the presence therein of reaction centres, as a siloxane base, thiocarbonyl groups and aminog-

roups, each of them is capable of the chemisorption of the cancerogenic or toxic elements of tobacco smoke.

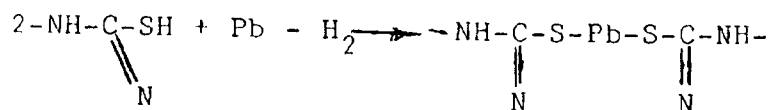
The effective absorption of metals is explained by the complex formation of metals with a pair of active groups of the monomer which contain the atoms of sulfur and nitrogen according to the possible scheme as given below:



In the case of sorption of metals whose nature depends on ion bonds, a process for sorption proceeds according to the following scheme



This process is characteristic, for instance in the sorption of lead and arsenic which, on the example of lead, process according to the following scheme:



The filter as described above is manufactured in the following way.

A base of acetate, cellulose or acetate-cellulose fibers is impregnated with 4 to 10% of a solution of the above-identified organo-silicon monomer in an organic solvent and dried.

Following below are the specific examples illustrating a process of manufacturing the filter claimed.

Example 1

A 4% solution of a monomer is prepared in ethyl alcohol, and the solution obtained in an amount of no less than 13 ml is used to impregnate the base of a filter made of acetate fibers in the form of a cylinder having a diameter of 7,9 mm, a length of 15 mm and a weight of 110 mg. The resulting base is then dried, and along with this, the weight of the monomer is 6% of the weight of acetate fibers. During drying the monomer is polymerized and bonded with said base acetate fibers.

Example 2

A 7% solution of a monomer is prepared in ethylalcohol. The obtained solution 13 ml is used for impregnating the base of a filter which is made from acetate-cellulose fibers in the form of a cylinder having a diameter of 7,9 mm, a length of 18 mm, and weight of 137 mg whereupon the resulting base is dried and polymerization takes place of the monomer during drying and its binding with the acetate-cellulose fibers of the base, and along with this, the weight of the monomer is 10,7% of the weight of the said base acetate-cellulose fibers.

Example 3

A 10% solution of a monomer is prepared in ethyl alcohol. The obtained solution is used in an amount of 13 ml for impregnating the base of the filter which is made from cellulose fibers in the form of a cylinder, having a diameter of 7,9 mm, a length of 18 mm and a weight of 130 mg.

The obtained base is then dried, and during drying the monomer is polymerized and bound with the cel-

lulose fibers of the base. The weight of the monomer is 15% of the cellulose fibers of the base.

Cigarettes with the above-described filters were tested according to the following manner.

Prior to analysis, all the cigarettes were conditioned during 48 hours, at 22°C and with a relative humidity of about 60%. They were smoked on a 20-position rotor smoking machine RM20 / CS (Germany "Borgwaldt"),

according with the methods given in the "International Standards Organization ISO 3308. "Cigarettes - Routine analytical cigarette smoking machine. Definitions and standard conditions", Geneva, 1986, P.6.

The volume of puff was 35 ml, duration—2 seconds, frequency—I puff per minute on I Cambridge filter.

The analysis of the contained polycyclic aromatic hydrocarbons in a tobacco smoke condensate was performed according to the modified methods as described in the publication by A.Ya.Khesin et al. "Vozmozhnost kolichestvennogo opredeleniya politsiklicheskikh aromatcheskikh uglevodorodov v zagryazneniyakh okrouzayushchei cheloveka sredy na osnove kvazilineichatykh spektrov lyuministsentsii i vozbouzhdeniya". The journal of applied spectroscopy, 1983, XXXV111, N 6, pp.922-933. The condensate of tobacco smoke of 10 cigarettes smoked on one Cambridge filter having the diameter . of 92 mm was extracted with benzene on an ultrasound bath, 60 watt, 30 minutes, twice, and evaporated on a rotor evaporator up to 5 ml, at 35°C. Further, 1 ml extract was fractionated with the aid of thin layer chromatography with a non-attached thin layer of aluminium oxide in a hexane benzene system with their ration of 3:1. The composition of polycyclic aromatic hydrocarbons was analyzed by registering a quasiline spectrum of fluorescence with the selective excitation of hydrocarbons on a spectrofluorimeter "HITACHI," Japan at a temperature of liquid nitrogen.

The content of metals in the condensate of tobacco smoke was determined according to the modified method set out in the publication by Westcott D., Sprincer D.

"The cadmium, nickel and lead content of tobacco and cigarette smoke" Beifr. Tabakporsch, 1974, v.7, N 4, pp.217-221, Jenkins R. "Occurrence of selected metals in cigarette tobacco and smoke. Environmental carcinogens selected methods of analysis", Lyon, 1986, IARC Sci. Publ. No.71, v.8, pp.129-138.

More, the atomic-absorption method has been replaced with a plasma emission one. Analysis was performed on a plasma emissive JV-48 spectrometer (Jobin-Ivon, France) with the use of a Cambridge filter having a diameter of 44 mm through which five cigarettes were smoked.

The contained volatile N'-nitrosoamines, N'-nitrosodiethylamine and N'-nitrosopyrrolidine were strictly determined according to the methods as described in the monograph of the International agency of research of cancer IARC. Scientific publications No.45. Environmental carcinogens selected methods of analysis. Vo.6, N-Nitrozo Compounds", Lyon, 1986, pp.69-103.

The results of the above-described investigations are tabulated (Tables 1,2,3). Data contained in these tables are average data for the filters having a base made of acetate, cellulose or acetate cellulose fibers. In these tables a control cigarette is a cigarette with a filter, having a base non-impregnated with the claimed monomer.

From inspection of Tables 1,2,3 the claimed filter permits efficiently catching such cancerogenic and toxic agents from tobacco smoke as polycyclic aromatic hydrocarbons, volatile nitrosoamines and metals. Also, the organosilicon monomer utilized in the given filter as an adsorbing agent is non-toxic, the bases impregnated with this monomer are stable in time and retain their properties on heating up to 240°C.

Table I

5 The efficiency of catching the polycyclic aromatic
 hydrocarbons in the main stream of tobacco smoke by the
 cigarette filter with the base impregnated with
 10 N,N'-bis(3-thriethoxysilylpropyl)thiocarbamide with its
 content of 6%, 10,7% and 15,3% of the weight of the base.

Name of Poly- cyclic aroma- tic hydrocar- bons	Control ciga- rette	15,3%	10,7%	6%	Efficiency,%		
		n g/cigarette			15,3%	10,7%	6%
Benz(a)pyrene	30,5	8,9	9,5	15,4	70,8	68,8	66,9
Benz(g,h,i) perylene	96,2	not revealed		traces	54,0	100	100
25 Diben(z,a,h) anthracene	25	- " -	- " -	19,1	100	100	23,6
30 Diben(z,a,c) anthracene	2,1	- " -	- " -	2,14	100	100	0,0

Table 2

Efficiency of catching metals in the main stream of tobacco smoke by the cigarette filter with the base impregnated with N,N'-bis(3-thiethoxysilylpropyl)thiocarbamide with its content of 6%, 10,7% and 15,3% of the weight of the base

Name of metal	Control cigarette	15,3%	10,7% mg/ml	Efficiency %		
				15,3%	10,7%	6%
Ca	5.15±1.54	0.9±0.23	1.66±0.15	2.41±0.32	82,5	67,9
Ni	0.21±0.08	0.05±0.01	0.038±1E-3	0.026±0.01	76.2	81.9
Cu	0.18±0.025	0.043±6E-3	0.059±1.5E-3	0.075±0.12	76.1	67.2
Zn	1.95±0.3	0.42±0.09	0.49±0.05	0.555±0.23	78.4	75.2
Mg	0.81±0.27	0.15±0.03	0.24±0.07	0.33±0.08	81.5	70.0
Al	1.53±0.15	0.48±0.01	0.42±0.06	0.36±0.06	68.6	72.3
Cr	0.145±0.015	0.039±6E-3	0.042±0.001	0.044±0.01	73.1	72.0
V	0.053±0.021	5.75E-3±1.05E-3	0.019±0	0.018±0	89.2	78.0
Cd	0.044±0.01	5.25E-3±9.5E-4	0.013±1E-3	0.02±2E-3	88.1	71.3
Sr	0.063±0.013	0.014±2E-3	0.012±2E-3	0.029±5E-3	77.8	66.0
Co	0.12±0.06	0.02±2E-3	0.025±1E-3	0.03±7.5E-3	83.3	79.0
Ti	0.45±0.078	0.16±0.033	0.14±0.01	0.12±0.05	64.4	68.9
Pb	0.063±0.012	-	0.05±0.06	0.047±4.5E-3	100	62.7
Mn	0.051±0.012	0.028±3.45E-3	0.03±1E-3	0.029±5E-3	45.1	44.0
Fe	2.2±1.1	0.39±0.095	0.4±0.1	0.41±0.19	82.3	81.9
As	0.48±0.23		0.03±0.001	0.113±0.05	100	88.4

Table 3

The efficiency of catching the volatile nitrosoamines in the main stream of tobacco smoke by the cigarette filter with the base impregnated with N,N'-bis(3-thriethoxysilylpropyl)thiocarbamide with its content of 5%, 10.7% and 15.3% of the weight of the base

Name	Controlled cigarette	15.3% ng/cigarette	10.7%	6%	Efficiency, %		
					15.3%	10.7%	6%
N'-nitroso-diethylamine	2.19±0.07	0.82±0.09	1.06±0.07	1.29±0.035	62.6	52	41.4
N'-nitroso-pyrrolidine	5.53±0.61	4.18±0	3.44±0.08	2.7±0.1	24.4	37.8	51.2

Claims

1. A cigarette filter comprising a base made of acetate, cellulose or acetate-cellulose fibers and impregnated with an adsorbing agent, characterized in that the adsorbing agent used is a N,N'-bis(3-thiethoxysilylpropyl)thiocarbamide organo-silicon monomer $(C_2H_5O)_3Si(CH_2)_3NH-C(S)-NH(CH_2)_3Si(OC_2H_5)_3$.
2. A filter according to Claim 1, characterized in that the content of the adsorbing agent is from 6 to 15,3% of the weight of the base.