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Wool Cigarette Filters

Part III: Selective Removal of Volatile Components with Polyethylenimine-Quaternary Ammonium Mixtures*

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INTRODUCTION

Wool cigarette filters prepared from an adhesive-bonded random web treated with polyethylenimine (PEI) selectively remove significant proportions of biologically active volatile aldehydes and weak acids from cigarette smoke (1). Moisture present in the PEI layer on the fibre surface strongly influences the adsorption of these components from the mainstream smoke. Once absorbed, the volatile components are chemically bound to the amino groups of PEI.

An assessment of wool filters treated with PEI in admixture with quaternary ammonium compounds (QUATs) is reported here. These filters retain the volatile aldehydes and weak acids more effectively than those treated with PEI alone. The QUAT acts synergistically; alone it fails to contribute significantly to the removal of the compounds mentioned.

EXPERIMENTAL

Materials

An adhesive-bonded random web (60 g/m²) prepared from carbonized peroxide-bleached Merino wool (60-64s/22.0 μ) was employed as the filter material. Polyethylenimines used as additives were PEI 1000, Montrek 18 [Dow Chemical]; Polymin P and Polymin SN [BASF]. Quaternary ammonium compounds investigated were Vantoc CL, Vantoc N [ICI]; Crodaquat [Croda Chemicals]; Hyamine 1622 [Rohm and Haas]; Ammonyx 2200, P100 [Onyx Chemicals]; Arquad 2HT/75 [Armak] and cetylpyridinium chloride [BDH]. Standard machine-made tobacco columns conditioned at 21° C and 60 % relative humidity for 48 h prior to smoking were used to evaluate filter performance.

Sliver and Filter Preparation

Slivers of the filter material were impregnated with aqueous solutions (200 ml) containing PEI and/or a QUAT placed in the nip of a Peter pad-mangle. The quantity of additive applied to the sliver was controlled by adjusting the initial concentration of the solutions or varying the weight of the pad-liquors picked up. The weight of liquor picked up was determined by weighing the sliver before and after impregnation. The treated sliver was dried in a forced-draught oven (10 min) at 90° C and equilibrated at 21° C and 65 % relative humidity for 24 h prior to preparation of the filters. Methods for fabricating and equilibrating the filters, determining pressure drops and attaching filters to cigarettes have been described (1).

Analytical Procedures

Procedures for the *Paramecia* bioassay and for determining the deliveries of hydrogen cyanide, acetaldehyde, formaldehyde, acrolein, steam-volatile phenols, and acids have been described (1). Hydrogen sulphide analyses were performed on the gas phase of smoke using a sulphide-ion-specific electrode according to the method of *Morie* (2). Total volatile aldehydes in the vapour phase (VP) were determined spectrophotometrically as acetaldehyde with 3-methyl-2-benzothiazolonehydrazone hydrochloride (3). To determine nicotine, particulate matter (PM) collected on a Cambridge filter pad from four cigarettes was extracted with hot methanol and the nicotine content determined by gas-liquid chromatography using m-nitroaniline as an internal standard. Filtration efficiencies were measured as described previously (4).

Smoking Conditions

Standard smoking conditions (1) were employed for chemical and *Paramecia* assays. Two-puff analyses were performed with a 4-channel smoking machine (Filtrona CSM 100) with the appropriate collection apparatus connected to each port. A cigarette was smoked on the first port under standard conditions and, after two puffs, was shifted to the second port, a clearing puff being taken on the first port. Repeating this procedure on the second, third and fourth ports, consecutively, enabled 8 puffs to be taken on the cigarette. Three more cigarettes were smoked in turn by this procedure. Analyses for hydrogen cyanide, total volatile aldehydes and steam-volatile phenols were then carried out on the components collected at the individual smoking ports.

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Table 1. The removal of hydrogen cyanide, acetaldehyde and cytotoxic vapour phase components by wool filters treated with PEI/QUAT mixtures (1:1)*.

Treatment PEI/QUAT	Removal of smoke components (%)**		Increase in *Paramecia* survival time** (number of puffs)
	Acetaldehyde	Hydrogen cyanide	
PEI 1000/Vantoc CL	32	79	+10.5
PEI 1000/Crodaquat	27	84	+13
PEI 1000/Vantoc N	32	84	+10.5
PEI 1000/ cetylpyridinium chloride	24	72	+ 7.5
PEI 1000/ Hyamine 1622	25	70	+ 5.5
PEI 1000/ Ammonyx 2200, P100	15	52	+ 4
PEI 1000/ Arquad 2HT/75	17	48	+ 4
Montrek 18/ Crodaquat	33	85	+ 9.5
Montrek 18/ Vantoc CL	29	85	+11.5
Montrek 18/ Hyamine 1622	29	71	+ 6
Polymin P/ Crodaquat	25	81	+10.5
Polymin P/ Vantoc CL	26	69	+ 9.5
Polymin P/cetyl- pyridinium chloride	31	68	+ 7.5
Polymin SN/ Vantoc N	22	65	+ 6.5
Polymin SN/ Vantoc CL	31	73	+12.5
Polymin SN/ Crodaquat	33	67	+10

* Filters contained 5 % (w/w) of each additive and were equilibrated at 65 % relative humidity for 48 h prior to testing.
** With respect to an untreated wool filter.

Table 2. The retention of hydrogen cyanide, acetaldehyde and cytotoxic vapour phase components by PEI-treated wool filters*.

PEI	Removal of smoke components (%)**		Increase in *Paramecia* survival time** (number of puffs)
	Acetal-dehyde	Hydrogen cyanide	
PEI 1000	18	45	+4
PEI 600	19	46	+4
Montrek 18	19	46	+4
Polymin SN	16	32	+4
Polymin P	19	23	+3

* Filters contained 4—5 % (w/w) of PEI and were equilibrated at 65 % relative humidity for 48 h prior to testing.
** With respect to an untreated wool filter.

Table 3. The retention of hydrogen cyanide, acetaldehyde and cytotoxic vapour phase components by QUAT-treated wool filters*.

QUAT	Removal of smoke components (%)**		Increase in *Paramecia* survival time** (number of puffs)
	Acetal-dehyde	Hydrogen cyanide	
Vantoc CL	2	14	+1
Vantoc N	0	10	+0.5
Crodaquat	0	16	+1
Hyamine 1622	0	3	0
Cetylpyridinium chloride	2	9	0

* Filters contained 5 % (w/w) of QUAT and were equilibrated at 65 % relative humidity for 48 h prior to testing.
** With respect to an untreated wool filter.

Table 4. A comparison of the effectiveness of PEI-1000- and PEI-1000/Vantoc-CL-treated wool filters in removing a variety of undesirable smoke components.

Smoke component	Average concentration in each puff (µg/puff)			
	Unfiltered	Untreated wool	PEI 1000	PEI 1000/ Vantoc CL
Hydrogen cyanide	27.7	24.0	13.2 (45)*	5.0 (79)*
Formaldehyde	4.9	4.1	2.0 (51)	0.7 (83)
Acetaldehyde	90	92	75 (18)	67 (27)
Acrolein	7.2	7.4	6.3 (15)	6.0 (19)
Total phenols (s. v.)**	18.3	7.4	5.7 (23)	3.4 (54)
Total acids (s. v.)**	100	62	49 (21)	39 (37)
Hydrogen sulphide	5.6	5.6	–	4.1 (27)
Nicotine+	–	1.16	1.35	1.28
Total particulate matter (TPM)++	–	56	54	54

* Figures in parenthesis give removal (%) with respect to untreated wool filters.
** Steam-volatile.
\+ Delivery in mg/cig.
++ Filtration efficiency (%).

Table 5. The effect on filter performance of varying the PEI/QUAT ratio.

PEI/QUAT ratio+		Removal of smoke components (%)*			Increase in *Paramecia* survival time* (number of puffs)
PEI (% w/w)	QUAT (% w/w)	Hydrogen cyanide	Acetal-dehyde	Phenols (steam-volatile)	
7.0	–	43	16	4	+ 4
7.0	2.6	50	20	40	+ 4.5
7.0	4.9	57	23	45	+ 7
7.0	5.6	70	23	44	+ 7
7.0	7.0	82	26	42	+ 8
7.0	7.9	81	33	55	+ 9
7.0	9.0	84	29	60	+10.5
7.0	12.2	78	32	57	+10

* With respect to untreated wool filters. + PEI 1000 and Vantoc CL.

pH Measurement

Two methods were employed to determine the pH of the mainstream smoke. In one, the pH of smoke condensate collected on a Cambridge filter pad from four cigarettes was determined by the method of *Artho* and *Grob* (5). A second determination was performed on whole smoke utilizing a combined electrode. The method and apparatus were similar to those described by *Sensabaugh* and *Cundiff* (6). The electrode was immersed in a buffer solution (0.02 M phosphate / pH 6.85 or 0.02 M acetate / pH 4.70) containing 0.1 % of the surfactant Antarox CO 630 [GAF] and then withdrawn to form a thin film of buffer over the glass membrane, extending to the porous plug at the side of the electrode. It was positioned in a chamber connected to a smoking machine (CSM 100) such that smoke passed over the electrode tip during each puff. The pH was monitored by a recorder during the smoking of four cigarettes by which time an equilibrium value was reached. Determinations were performed with each buffer and the mean of the equilibrium values was taken as the smoke pH.

RESULTS AND DISCUSSION

The effectiveness of wool filters treated with PEI/QUAT mixtures in removing acetaldehyde and hydrogen cyanide from the mainstream smoke is shown in Table 1. Increases in the *Paramecia* survival times, with respect to untreated filters, reflect decreases in the cytotoxicity of the vapour phase due to removal of some C_1–C_8 aldehydes. Similar assays applied to filters treated with the PEI or QUAT, separately, are given in Tables 2 and 3. Filters that contained only a QUAT did not remove acetaldehyde and retained only a small quantity of hydrogen cyanide. The PEI-treated filters, as expected, removed significant amounts of these components and reduced the cytotoxicity of the vapour phase. However, treatment of the filters with a mixture containing equal proportions of a PEI and QUAT substantially improved filter performance. This improvement is clearly larger than that expected from the performance of the filters containing either of the additives separately and indicates that the QUAT acts synergistically. Possibly, electrostatic interactions between the cationic PEI and QUAT cause unfolding of the intra-molecularly hydrogen-bonded PEI chains and expose additional reactive sites (amino groups) to the smoke stream.

Earlier work (1) showed that the performance of PEI-wool filters is essentially independent of the type and molecular weight of the PEI. In the treatments reported here the structure of the QUAT was of considerable importance. For example, only water-soluble and surface-active QUATs containing one hydrocarbon chain of more than ten carbon atoms attached to nitrogen exhibited the synergistic effect in the combined treatments. Except for Ammonyx 2200, P100 and Arquad 2HT/75 the QUATs shown in Table 1 fall within this classification. These two exceptions are surface-active QUATs with a low solubility in water and contain two long hydrocarbon chains attached to nitrogen. Their combination with PEI on wool filters did not improve filter performance. Best results were obtained with commercial formulations containing mixtures of C_{12}-C_{18} alkyldimethylbenzyl ammonium chlorides.

Table 4 illustrates the variety of biologically active volatile and semivolatile components that are selectively removed by the treated filters. Clearly, the PEI/QUAT combination is superior to PEI in every case. Both treated filters increased the delivery of nicotine due to their basicity (pH ~ 8.3). Their filtration efficiencies, however, remained essentially unchanged from that of an untreated wool filter.

The effect on filter performance of varying the PEI/QUAT ratio is shown in Table 5. Optimum retention of hydrogen cyanide, acetaldehyde and phenols occurred when the ratio was in the range 0.8 to 1.0. *Paramecia* survival times indicate that cytotoxic VP constituents were most effectively removed with a PEI/QUAT ratio of 0.8. A substantial improvement in the retention of phenols is evident when only a small quantity of QUAT is incorporated with PEI. Application to the filter material of 5–10 % by weight of each additive provided optimum efficiency.

A considerable loss in the performance of PEI-treated filters occurs on reducing their moisture content by equilibration in an atmosphere below 60 % relative humidity (1). The performance of PEI/QUAT filters, however, was affected to a much smaller extent by changes in relative humidity below 60 %. Apparently, the greater reactivity of the PEI/QUAT combination compensates for the loss in solvent adsorption that occurs on decreasing the moisture content of the filter. As expected, equilibration at 70–90 % relative humidity significantly improved filter performance due to the increased contribution of solvent adsorption in removing the VP constituents.

To examine for possible impairment of the filter performance as the burning zone approaches the filter, chemical assays were performed on the smoke collected at two-puff intervals. Table 6 shows that the delivery of some VP components, particularly hydrogen cyanide and phenols, increases significantly on progressing from the first to the last puff of a cigarette. Re-volatilization and pyrolysis of components retained in the tobacco column probably cause this effect. However, the effectiveness of PEI/QUAT filters in retaining these components remains remarkably constant from the first two puffs to the last two puffs. Thus, PM collected on the fibres does not impair the functioning of the additives on the fibre surface. Furthermore, it demonstrates that volatile constituents retained by the treated filters are not released as the heat zone approaches the filter.

Table 7 shows that PEI and PEI/QUAT filters significantly increase the pH of the mainstream smoke as evaluated by the pH measurement of whole smoke and smoke condensate. In contrast, the pH of smoke delivered by charcoal-filtered cigarettes remained essentially unchanged from that of cigarettes having untreated

Table 6. The effectiveness of PEI/QUAT filters at stages along the tobacco column as indicated by 2-puff analyses.

Filter type	Puff no.	Hydrogen cyanide (µg)	Total volatile aldehydes (µg)	Steam-volatile phenols (µg)
Untreated wool	1, 2	36.7	315	5.6
	3, 4	56.0	334	7.2
	5, 6	59.0	360	10.0
	7, 8	72.5	390	13.1
Total	8 puffs	224	1399	36
PEI-1000 (6 %)/ Vantoc-CL (6 %) - treated wool	1, 2	13.1 (64)*	237 (25)*	3.1 (45)*
	3, 4	17.9 (68)	245 (27)	4.4 (39)
	5, 6	26.4 (55)	263 (27)	5.9 (41)
	7, 8	25.6 (65)	306 (22)	8.4 (36)
Total	8 puffs	83	1051	22

* Figures in parenthesis show the removal (%) with respect to the untreated filter.

wool or cellulose acetate filters. Evidently, the basic polymers provide a more effective medium than charcoal for the removal of acidic smoke components. The pH of cigarette smoke has received considerable attention in recent years (7–10). It has been suggested, for example, that a possible factor in the lower incidence of lung cancer in cigar and pipe smokers is due to the diminished acidity of pipe and cigar smoke (8). Smoke of a higher pH is less readily inhaled and contains a greater proportion of unprotonated nicotine (7, 11). Nicotine, as the free base, is more readily absorbed through the oral mucosa than the protonated forms (7). Assuming that part of the satisfaction of smoking is due to the pharmacological effects of nicotine, it follows that reduced inhalation of a more alkaline smoke is required for a given intake of nicotine. Besides reducing the tendency of smokers to inhale, higher pH smoke has been shown to be less harmful on exposure to animals (8, 9).

The advantages of PEI/QUAT wool filters appear to be in their high selectivity for components that chemically interact with amino or quaternized amino groups and their efficient removal of acidic smoke components. Filters containing solid absorbents such as charcoal tend to retain a broad range of volatile components and are not particularly effective in removing acidic compounds. The treated wool filters can be readily incorporated adjacent to the tobacco column in multi-component filters. Segments at least 15 mm in length remove a significant proportion of the biologically active VP components.

Table 7. The effect of filters on the pH of cigarette smoke.

Filter	Smoke pH	
	Whole smoke	Smoke condensate
Unfiltered	5.15	–
Untreated wool*	5.55	5.6
Cellulose acetate*	5.40	5.6
Cellulose acetate-charcoal*	5.50	5.7
PEI 1000 on wool	6.50	6.9
PEI 1000/Vantoc CL on wool	6.55	7.0

* Commercial 20 mm filters.

SUMMARY

Chemical and biological assays showed that wool filters containing mixtures of commercially available polyethylenimines (PEI) and quaternary ammonium compounds (QUAT) selectively removed proportions of the biologically active volatile constituents of cigarette smoke. The action of the QUAT was synergistic in that it enhanced the performance of PEI filters but, alone, was ineffective in retaining volatile components. Only water-soluble QUATs with one long hydrocarbon chain (> 10 C-atoms) attached to nitrogen were effective. The best removal efficiencies were obtained with a PEI/QUAT ratio in the range 0.8–1.0 and 5–10 % by weight of each additive on the filter material. Analyses of puffs at stages along the tobacco column indicated that the treated filters retained their effectiveness from the first to the last puffs. The treated filters significantly increased the pH of the mainstream smoke.

ZUSAMMENFASSUNG

Chemische und biologische Untersuchungen zeigten, daß Wollfilter, die Mischungen von handelsüblichen Polyäthyleniminen (PEI) und quartären Ammoniumverbindungen (QUAT) enthielten, Teile der biologisch aktiven, flüchtigen Inhaltsstoffe des Cigarettenrauches selektiv entfernen. Die quartären Ammoniumverbindungen wirkten synergistisch insofern, als sie die Leistung von Polyäthylenimin-Filtern steigerten, allein aber keine flüchtigen Rauchbestandteile zurückhielten. Eine Wirksamkeit konnte lediglich bei wasserlöslichen quartären Ammoniumverbindungen mit einer langen, an Stickstoff gebundenen Kohlenwasserstoffkette (> 10 C-Atome) beobachtet werden. Die beste Retentionswirkung wurde erhalten, wenn PEI und QUAT im Filtermaterial im Verhältnis 0,8–1,0 und in 5–10 Gewichtsprozenten jedes Zusatzes vorlagen. Die Untersuchung einzelner Züge an verschiedenen Abschnitten des Tabakstranges zeigte, daß die behandelten Filter vom ersten bis zum letzten Zug wirksam waren. Die behandelten Filter erhöhten den pH-Wert des Hauptstromrauches signifikant.

RESUME

Des expériences chimiques et biologiques ont démontré que les filtres en laine, contenant des mélanges de PEIs (polyéthylènimines) et QUATs (composés d'ammonium

quaternaire) disponibles sur le marché, suppriment sélectivement certains composés volatiles de la fumée de cigarettes, composés qui sont biologiquement actifs. L'action du QUAT est synergétique dans ce sens qu'elle renforce l'efficacité des filtres PEI, par contre le QUAT seul ne peut retenir les composés volatiles. Parmi les QUATs solubles dans l'eau seuls sont efficaces ceux contenant une longue chaîne d'hydrocarbures (>10 atomes C) attachée au nitrogène. Les suppressions les plus efficientes ont été obtenues pour une concentration de PEI/QUAT comprise entre 0,8–1,0 et 5–10% par poids de chaque additif dans la matière du filtre. On a pu observer par analyses de bouffées à différents stades du cylindre de tabac que les filtres traités gardent leur efficacité des premières aux dernières bouffées. Les filtres traités apportent une augmentation significative du pH du flux principal de fumée.

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