Composition of Cigarette Smoke: Effects of Ammonium Sulfamate in Cigarette Paper*

by Irving Michelson and Gunter Rathkamp

Environmental Health and Safety Research Associates, New Rochelle, New York, USA

and

Tobacco Analysts and Consultants, White Plains, New York, USA

The use of ammonium sulfamate (AS) in cigarettes to produce a substantial reduction in benzo(a)pyrene in cigarette smoke was reported by Alvord and Cardon (1) in 1956. Because benzo(a)pyrene was then considered the most important of the known carcinogens in cigarette smoke, the report stimulated further studies, with conflicting results: some confirmed the reduction (2, 3), some found no reduction (4, 5, 6), and some found increases rather than reductions (6, 7). Thereafter, interest in the use of AS waned. Recent biological tests, however, have demonstrated that AS in cigarette paper reduces the carcinogenic activity of cigarette smoke on mouse skin (8). Chemical tests have also revealed differences in concentrations of several constituents in smoke of AS-treated cigarettes, though not in benzo(a)pyrene. We present here the differences which we have found so far.

MATERIALS AND METHODS

The tests were performed on treated and untreated cigarettes which differed only in that the treated cigarettes had had AS applied to the paper. The AS was first incorporated into a commercial cigarette paper by running part of a 500 lb. roll through a solution of AS in water (about 15% by weight), then through squeeze rolls, and finally over heated drying cylinders. The treated paper contained approximately 0.3 mg AS/cm². The remainder of the roll was used to make the untreated control cigarettes.

King size (85 mm) non-filter cigarettes were made in a commercial cigarette making machine, using conventional American-blend tobacco. The treated cigarettes contained approximately 7 mg AS/cigarette. Smoking was done by the standard method of the U.S. Federal Trade Commission: puff volume 35 ml, puff duration 2 sec., puff frequency 1/min., butt length 23 mm; tar** and nicotine were determined by the procedures specified in this method (9). Comparative tests were performed only between treated and untreated cigarettes made from the same batch of tobacco and the same roll of paper.

The static burning rates of the cigarettes were determined by the method of Hoffmann and Wynder (10), and the pH of the whole smoke by the method of Sensabough and Cundiff (11). The polycyclic hydrocarbons were determined by the methods of Wynder and Hoffmann (7), with some modifications by Guerin (12) and Rathkamp and Hoffmann (13). The nitrosamines were determined by the method of Hoffmann and Vais (14), and the indoles by the method of Hoffmann and Rubin (15).

Gas phase components were determined by the following methods: acetaldehyde and acrolein, by the method of Laurene et al. (16); formaldehyde and NO_x, by the methods of Newsome et al. (17); HCN, by the method of Collins et al. (18); and CO and CO₂, by the method of Newsome and Keith (19). These methods were modified to some extent by Guerin (12).

The comparison of the taste of treated and untreated cigarettes was performed by triangular taste tests, in accordance with the procedures of Roessler et al. (20). The panel members were each presented with three unidentified cigarettes, two of which were alike and one was different (either two treated and one untreated, or two untreated and one treated), and asked to identify which one tasted different from the others.

The quantitative data presented below are either in the form of yield/cigarette when smoked to equal butt length, or in the form of concentration per equal volume or equal weight of effluent. These concentrations per equal volume or equal weight correspond to yields per cigarette when the treated cigarettes are smoked to an equal number of puffs/cigarette, or an equal tar yield/cigarette, as the control cigarettes. In some cases, the data are presented in both forms.

RESULTS AND DISCUSSION

Tar and Nicotine

Since AS is a fire retardant, the treated cigarettes burned at a slower rate than the untreated controls. As a result, more puffs were obtained from the treated cigarettes, when both were smoked to the same standard butt length. The tar and nicotine yields were likewise also increased. The pH of the smoke,

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** The term "tar" is used throughout for convenience. It is acknowledged that it is not chemically accurate in the strictest sense.

Table 1. Smoking characteristics of untreated and treated cigarettes when smoked to 23 mm butt.

	Untreated	Treated	Change
Static burning rate, mg/min.	74	56	- 24 %
Puffs/cigarette	8.7	9.8	+ 12 %
Tar, mg/cigarette	20.7	26.0	+ 26 %
Nicotine, mg/cigarette	0.85	1.10	+ 29 %
pH of smoke, puff $\pm$ 3	6.08	6.06	-
pH of smoke, puff $\pm$ 9	5.85	5.90	-

however, was not affected by the AS treatment. Table 1 presents the average yields of tar and nicotine and puffs found in tests by three laboratories. Since increased yields of tar and nicotine may be objectionable, the yields of treated cigarettes can be reduced to those of untreated cigarettes, e. g., by limiting the number of puffs that can be drawn, by reducing the diameter or length of tobacco rod smoked. Such a limitation is achieved in some commercial cigarettes by replacing part of the tobacco rod by filter tips of more-than-average length. This technique would be particularly suitable for AS-treated cigarettes, in part to prevent the increase of yields of tar and nicotine, and also to take advantage of the possible saving in the tobacco cost, with no reduction in delivery of taste elements to the smoker.

Polycyclic Hydrocarbons

Three polycyclic hydrocarbons considered important for characterizing the chemical nature of cigarette smoke were assayed: the benzo(a)pyrene, benzo(a)-anthracene, and phenanthrene were found to be virtually unchanged in concentration. But the profile analyses (13) of the fractions containing these hydrocarbons revealed changes in concentrations of associated hydrocarbons (Table 2).

The hydrocarbons listed in Table 2 were determined quantitatively by means of internal standards (^{14}C -labelled traces of these hydrocarbons added prior to isolation of the fractions). In addition to those listed, many other smoke components were observed on the gas chromatograms, but were not assayed quantitatively because internal standards for these had not been added. Nevertheless, the chromatograms indicated considerable

Table 2. Concentrations of polycyclic hydrocarbons in the smoke of untreated and treated cigarettes.

Polycyclic hydrocarbon	Untreated	Treated	Change
Benzo(a)pyrene	1.12 ppm	1.05 ppm	- 6 %
Benzo(a)anthracene	1.68	1.57	- 7 %
Phenanthrene	21.0	21.2	+ 1 %
Chrysene*	2.2	1.9	- 14 %
Fluorene**	16.9	12.1	- 28 %

* from benzo(a)anthracene profile

** from phenanthrene profile

changes in the smoke of treated cigarettes, most notably in the benzo(a)pyrene fraction, in which there were extensive changes (Figure 1), in two analyses of each. Two of the benzo(a)pyrene fraction components which appear to have been reduced by over 50% have been tentatively identified by mass spectrometry: benzo-fluoranthenes (80% pure), at 74 min., and perylene, at 92 min.

A series of other as-yet unidentified components in this profile, which appear in the chromatogram of the control cigarette in the interval between 48 and 64 min., and at 38, 43, 79, and 99 min., have also been largely eliminated by the AS treatment. In contrast only a few new peaks, also unidentified, have been introduced.

Nitrogenous Compounds

Two kinds of nitrogenous compounds were determined in the smoke of these cigarettes: nitrosamines and indoles. These components were of interest because nitrosamines exhibit carcinogenic activity, and 3-methylindole (skatole) has been recently reported to cause pathological damage in pulmonary tissues (21), and because the high nitrogen content of AS caused us to suspect that the nitrosamines and indoles might thereby be increased in the smoke of AS-treated cigarettes.

Total delivery of these compounds, when the cigarettes were smoked to equal butt length, showed only small changes. But when compared on a concentration basis, these components were found to have been moderately reduced in the smoke of the treated cigarettes (Table 3).

Table 3. Nitrosamines and indoles from untreated and treated cigarettes.

Component	Yields/cigarette smoked to 23 mm butt			Yields/cigarette smoked to equal tar deliveries		
	Untreated	Treated	Change	Untreated	Treated	Change in Concentration
	(ng/cig.)			(ng/cig.)		
Dimethylnitrosamine	118	108	- 8 %	118	86	- 27 %
Methylethylnitrosamine	47	42	- 11 %	47	33	- 30 %
	($\mu\text{g}/\text{cig.}$)			($\mu\text{g}/\text{cig.}$)		
Indole	11.1	12.3	+ 11 %	11.1	9.8	- 11 %
3-Methylindole	11.8	12.2	+ 3 %	11.8	9.7	- 18 %

Figure 1. Gas chromatograms of the benzo(a)pyrene fractions of ammonium-sulfamate-treated cigarettes and untreated controls.

(50 ft. column, 10% Dexsil on Gaschrome Q, temperature 335° C, carrier gas helium, flow 40 ml/min., flame ionization detector.)

Gas Phase Components

Seven constituents of the gas phase were determined. When smoked to standard butt length, the treated cigarettes generated about 10% less of three components (i. e. acetaldehyde, acrolein, and formaldehyde) despite the 12% increase in puffs per cigarette. When only equal numbers of puffs are drawn from both kinds of cigarettes, the smoke of the treated cigarettes had about 20% lower yields (or concentrations) than that of the controls (Table 4).

On the other hand, three components (i. e. carbon dioxide, hydrogen cyanide, and nitrogen oxides) were found to be virtually unchanged in concentration, and one, carbon monoxide, was increased 29%. The problem of the carbon monoxide is discussed elsewhere (8).

Taste

Since its effect on the taste of the smoke is an important consideration in the practicality of a cigar-

Table 4. Gas phase components from untreated and treated cigarettes.

Component	Yields/cigarette smoked to 23 mm butt			Yields/cigarette smoked to equal number of puffs		
	Untreated	Treated	Change	Untreated	Treated	Change in Concentration
	(mg/cig.)			(mg/cig.)		
Acetaldehyde	1.00	0.94	- 6 %	1.00	0.84	- 16 %
Acrolein	0.098	0.085	- 13 %	0.098	0.076	- 23 %
Formaldehyde	0.030	0.026	- 13 %	0.030	0.023	- 23 %
Hydrogen cyanide	0.203	0.223	+ 10 %	0.203	0.199	- 2 %
Nitrogen oxides	0.380	0.425	+ 12 %	0.380	0.380	-
				(vol.%)		
Carbon dioxide				9.4	9.4	-
Carbon monoxide				4.70	6.08	+ 29 %

Table 5. Triangular taste tests (treated versus untreated cigarettes).

Session #	Type of cigarette	No. of smokers	No. of correct identifications
1	Commercial, filter	17	6
2	Commercial, non-filter	18	3
3	Commercial, non-filter	18	7
4	Custom, non-filter	18	7
5	Custom, non-filter	18	7
Average		18	6
Conclusion: no detectable difference in taste of smoke.			

ette additive, the effect of the AS treatment was explored by triangular taste tests. The taste panels were made up of 17–18 smokers; five smoking sessions were held, using two of the most popular commercial cigarettes (filter and non-filter) at three sessions and custom-made samples at the others. (The AS was applied to the commercial cigarettes manually, by means of a cellulose sponge.)

Approximately six correct identifications of the odd cigarette could be expected at each session by chance alone, if no difference in taste were detectable. A significantly larger number would be possible only if a detectable difference actually existed: with 10 correct identifications, a statistically significant difference is barely reached (20). As shown in Table 5, the panels averaged 6 correct designations, showing that the panels were unable to distinguish the treated cigarettes from the untreated controls (22).

SUMMARY AND CONCLUSIONS

Treatment of cigarette paper with ammonium sulfamate was found to cause changes in the composition of cigarette smoke, in the concentrations of components of both the gas and particulate phases. The concentrations of several polycyclic hydrocarbons were reduced by over 25%, though benzo(a)pyrene was virtually unchanged. The concentrations of two nitrosamines were also reduced more than 25%, while indole and skatole concentrations were reduced about 15%. Among the gas phase components, acetaldehyde, acrolein and formaldehyde were reduced about 20%; only carbon monoxide was moderately increased.

Since these tests explored only small segments of the spectrum of cigarette smoke components, it is not known which of the observed reductions, if any, contributed to the reduction of biological activity of the smoke of treated cigarettes reported by Bock et al. (8). The tests indicate only that the nature of the smoke has been modified in several respects.

The tar and nicotine yield of the treated cigarette was higher than that of the control cigarette, but this can be compensated for by reducing the diameter or length of tobacco rod available to be smoked.

ZUSAMMENFASSUNG UND SCHLUSSFOLGERUNGEN

Es wurde beobachtet, daß die Behandlung von Cigarettenpapier mit Ammoniumsulfamat Veränderungen in der Zusammensetzung des Cigarettenrauches, d. h. in den Konzentrationen von Inhaltsstoffen der Gas- und der Partikelfase, bewirkt. Die Konzentrationen mehrerer polycyclischer Kohlenwasserstoffe wurden um mehr als 25% vermindert, wohingegen der Gehalt an Benz(a)pyren unverändert blieb. Die Konzentrationen zweier Nitrosamine wurden gleichfalls um mehr als 25% reduziert, während Indol und Skatol um etwa 15% verringert wurden. In der Gasphase gingen die Gehalte an Acetaldehyd, Acrolein und Formaldehyd um etwa 20% zurück; nur der Gehalt an Kohlenmonoxid stieg schwach an.

Da die Analysen nur kleine Teile des Spektrums der Zusammensetzung des Cigarettenrauches erfaßten, geben sie keinen Aufschluß darüber, welche der beobachteten Reduzierungen, wenn überhaupt, zu der Verminderung der biologischen Aktivität des Rauches Ammoniumsulfamat-behandelter Cigaretten beigetragen haben könnte, über die Bock et al. berichteten (8). Die Untersuchungen zeigen lediglich, daß die Beschaffenheit des Rauches in mehrfacher Hinsicht verändert wird.

Die Ausbeute an Kondensat und Nikotin war bei Ammoniumsulfamat-behandelten Cigaretten größer als bei den Vergleichscigaretten; dies kann aber dadurch ausgeglichen werden, daß der Durchmesser oder die Länge des zu verrauchenden Tabakstranges vermindert werden.

RESUME ET CONCLUSIONS

On a observé que le traitement du papier de cigarette par du sulfamate d'ammonium provoque un changement de la composition de la fumée, tant dans la phase gazeuse que particulaire. Les concentrations de plusieurs hydrocarbures polycycliques ont été réduites de plus de 25%, malgré que la teneur en benzo(a)pyrène reste inchangée. La concentration de 2 nitrosamines est réduite également de plus de 25%, les concentrations d'indole et de scatole environ de 15%. Dans la phase gazeuse, on observe une diminution d'environ 20% des concentrations en acétaldéhyde, acroléine et formaldéhyde, tandis que seule la teneur en monoxyde de carbone augmente faiblement.

Ces tests ne concernant que de petites parties du spectre des composants de la fumée de cigarette, on ne peut en déduire quelles réductions observées provoquent la diminution de l'activité biologique de la fumée décrite par Bock et al. (8) dans les cigarettes traitées. Les tests démontrent seulement que la nature de la fumée est modifiée.

Le rendement en condensats et nicotine des cigarettes traitées est plus élevé que celui de la cigarette témoin, mais on peut compenser ceci en diminuant le diamètre ou la longueur du boudin de tabac.

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The authors' address:

Environmental Health and Safety Research Associates,
155 Calhoun Avenue, New Rochelle, New York,
10801, USA.