

## Cigarette Smoke: Formation of Components and Modification of Composition by the Use of Additives

**Fumée de la Cigarette: Formation des Composants et Modification de la Composition  
au Moyen d'Additifs**

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### SUMMARY

The origin of various cigarette smoke components, including phenols, pyridine bases, polynuclear and other aromatic hydrocarbons, indoles, alkenes and smoke gases, is discussed. Special attention is given to studies in which specific tobacco leaf constituents, related compounds and tobacco leaf extracts were pyrolyzed to determine which leaf constituents serve as precursors for the various substances found in smoke. Thus, phenols were shown to arise from carbohydrates, pigment, lignin and others; pyridine bases essentially from nicotine; indole and related compounds from tryptophan, other amino acids and proteinaceous materials; alkenes from long chain paraffins and similar substances; and smoke gases from a variety of sources.

In addition, the report describes the modification of cigarette smoke by the use of additives. Additives discussed include those whose effects were measured by noting resulting changes in

- 1) the burn temperature of cigarettes
- 2) the smoke composition, in the particulate or vapor phase, and
- 3) the pH of smoke.

Data presented compare the burn temperature of cigarettes containing certain additives with the burn temperature of reference cigarettes. Levels of certain significant components of the vapor and particulate phases are tabulated for both additive-treated cigarettes and reference cigarettes. The mechanism by which certain additives exert their effects is also discussed.

### RÉSUMÉ

Discussion sur l'origine de divers composants de la fumée de cigarette, comprenant les phénols, bases pyridiniques, hydrocarbures polynucléaires et autres aromatiques, indoles, alkènes et gaz de la fumée. On accorde une attention spéciale aux études dans lesquelles des constituants spécifiques du tabac, des corps apparentés et des extraits de tabac sont pyrolysés pour déterminer parmi les constituants du tabac en feuilles quels sont les précurseurs des substances trouvées dans la fumée. Ainsi on a constaté que les phénols proviennent des hydrates de carbone, pigments, lignine et autres; les bases pyridiniques proviennent essentiellement de la nicotine; l'indole et composés apparentés, du tryptophane, et d'autres acides aminés et matières protéiques; les alkènes, des paraffines à longue chaîne et de substances similaires; les gaz de la fumée ont des origines variées.

En outre, le rapport décrit la modification de la fumée de cigarette par l'emploi d'additifs. Les additifs considérés comprennent ceux dont les effets ont été mesurés en notant les changements qu'ils ont provoqué dans:

- 1) la température de combustion des cigarettes;
- 2) la composition de la phase particulaire ou de la phase vapeur de la fumée;
- 3) le pH de la fumée.

On présente une comparaison des températures de combustion des cigarettes contenant certains additifs et des cigarettes de référence. Les taux de certains composants des phases vapeur et particulaire des cigarettes contenant des additifs et des cigarettes de référence sont consignés dans un tableau. On discute également du mécanisme par lequel certains additifs exercent leurs effets.

## PART 1 FORMATION OF COMPONENTS

At the outset, we sought in our studies in pyrolysis to determine possible leaf precursors for certain smoke constituents: phenols, pyridine and related bases, polynuclear aromatic hydrocarbons, indoles and others.

### *Phenols*

As early as 1939, WENUSCH (1) had suggested that the phenols in smoke, essentially phenol and the isomeric cresols, originate from carbohydrate, lignin and polyphenolic material present in leaf. Subsequently, in 1966, SPEARS and coworkers (2) demonstrated that carbohydrates comprising as much as 55% of the leaf contribute about 41% of the phenol in smoke. However, we noted, that compared to other leaf constituents, carbohydrates, on pyrolysis, give relatively low yields of phenols, and the contribution of carbohydrates to smoke phenols is made significant only because they comprise so large a portion of the leaf (3, 4). On the other hand, relatively high phenol yields (3) were obtained from pyrolysis of leaf pigment and lignin (both of which have phenolic moieties in their internal structure). Lignin and pigment, however, together comprise only about 8% of leaf weight. Moreover, phenols were generated pyrolytically from other leaf constituents and related materials such as malic acid, sodium lactate and caffeic acid (5, 6). In the case of caffeic acid, catechol was the principal phenol produced (6). Proteins, on pyrolysis, give rise to phenols; the amino acid, tyrosine, appears to be a possible precursor for p-cresol (7, 8). Sodium acetate, surprisingly, generated 3,5-xyleneol, among others, on pyrolysis (9). Furthermore, the pyrolysate from the cigarette additive, menthol, was found to contain the simple phenols characteristic of cigarette smoke (10). In simple experiments, benzene in the presence of air, and at high temperatures, was converted to phenol (11).

In studies (4) in which fractions were sequentially extracted from tobacco with increasingly polar solvents, and subsequently pyrolyzed, we noted that phenols were predominantly in the pyrolysates from the ethanol extract, and from the residue remaining after complete solvent extraction. This is consistent with the foregoing data in that ethanol extracts of to-

bacco contain, inter alia, polyphenols, brown pigments and low molecular weight sugars. The final leaf residue would, most likely, consist largely of cellulose and other high molecular weight carbohydrates, and some pigment and lignin. All of these substances, as postulated by WENUSCH (1), give rise to phenols when pyrolyzed.

### *Pyridine and Related Bases*

It seems fairly obvious that the simple pyridines found in cigarette smoke are thermal degradation products of leaf nicotine, in as much as the greatest portion of them are 3-substituted pyridines. Studies in which nicotine was exposed to high temperatures verified this contention, as expected. Thus in 1944, WOODWARD, EISNER and HAINES (12) identified the following products in nicotine pyrolysates: pyridine, 3-methylpyridine, 3-ethylpyridine, 3-vinylpyridine, 3,2'-nicotyrine and myosmine. JARBOE and ROSENE (13) confirmed the formation of 3-substituted pyridines from pyrolysis of nicotine, and added to the list of compounds identified the following: nicotinonitrile (3-cyanopyridine), 2-cyanopyridine, quinoline, isoquinoline, benzonitrile and naphthalene, among others. In our work (14), we generally confirmed the results of JARBOE and ROSENE, and WOODWARD and coworkers, and added still other compounds to those already identified in nicotine pyrolysates: benzene, pyrrole, toluene, styrene, indene, acenaphthene, anthracene, indole, and skatole among the neutral products, and 2-methylpyridine among the bases. We observed, as well, that leaf constituents other than nicotine (and other alkaloids) can give rise to pyridine bases on pyrolysis. Thus tobacco leaf pigment, on pyrolysis, generated volatile bases characteristic of cigarette smoke and nicotine pyrolysates (14); this was due ostensibly to the reported binding of nicotine to pigment (15). We noted, in addition, that proteins and amino acids on pyrolysis produced similar volatile bases (8), although protein has yet to be isolated from cured tobacco leaf in appreciable quantities.

Not all the nicotine initially present in leaf is degraded in a burning cigarette. From 20 to 30% is distilled intact into the mainstream smoke. This is so because within the temperature gradient characteristic of a burning cigarette, nicotine is subjected to either of two processes (14), distillation or pyrolysis, depending on its position within

the hot zone. This observation is reflected in pyrolysis studies in which nicotine is subjected to increasing temperatures. As the pyrolytic temperature is increased, less nicotine is found in the pyrolysate. Above 600° C, all the nicotine may very well be destroyed, or converted to its characteristic degradation products (14).

#### *Aromatic Hydrocarbons*

There is an extensive literature (18) on the pyrolytic formation of aromatic hydrocarbons, including the polynuclears, from organic materials, especially by BADGER and associates, and there is perhaps little to add to what is already known. In the area of tobacco and its pyrolytic products, however, it is clear to us, at any rate, that the hexane soluble fraction of leaf plays an important role in the pyrogenesis of aromatic hydrocarbons, especially of the polynuclear aromatic hydrocarbons, present in cigarette smoke. Consisting largely of long chain and cyclic paraffins, solanesol, phytosterols, fatty acids and esters and unidentified resins, the hexane soluble fraction comprises approximately 6% of dry leaf weight. Nevertheless, it contributes in a highly disproportionate manner to the levels of aromatic hydrocarbons found in tobacco pyrolysates, 21% of the total volatile (gas chromatographable) aromatics ranging from benzene to pyrene, and up to 60% of the benzo(a)pyrene (16). In addition, representative constituents of the hexane soluble fraction of tobacco, when pyrolyzed individually, produced significant quantities of aromatic hydrocarbons and benzo(a)pyrene (17), although no correlation between quantities of the latter two was evident. The high yields of benzo(a)pyrene obtained from phytol and  $\beta$ -sitosterol might be related to the structural characteristics of these two materials, branching and unsaturation in phytol, and the internal phenanthrene nucleus in  $\beta$ -sitosterol.

Many, if not all, classes of organic compounds, containing carbon bonded to hydrogen, are expected to give rise to aromatic hydrocarbons, including condensed ring systems, on pyrolysis. We obtained aromatic hydrocarbons from pyrolysis of tobacco, of course, and from all fractions extracted from tobacco, from carbohydrates, proteins, amino acids and fatty materials, from tobacco leaf pigment, sodium acetate, menthol and nicotine, from organic acids, ben-

zene, toluene, and styrene and its derivatives. Significantly, we found no detectable amounts of benzo(a)pyrene in pyrolysates from nicotine or protein, although N-containing analogs of benzo(a)pyrene may have been present (8). Sodium formate, unlike sodium acetate, yielded no condensable products, at all (9).

A number of mechanisms have been proposed for the pyrolytic formation of aromatic hydrocarbons. BADGER's (18) is the most often referred to. In our own view, the situation is still exceedingly complex, and our experience indicates that a number of different pathways involving a number of different intermediates are probable during pyrolysis. Intermediates involved may include the classical free radical, benzyne, a phenylcarbene, a four-membered ring, and a distyryl, among others.

#### *Indoles*

In view of its structural skeleton, tryptophan would seem to be a likely precursor of indole, skatole and related compounds, and experimental evidence indicates that this may be so. We, and others, however, have obtained indoles from substances other than tryptophan, and, in addition, it seems unlikely that the latter can be considered a significant constituent of the leaf. PATTERSON and coworkers (7) reported indole, but no skatole, from pyrolysis of tryptophan. The major product, however, turned out to be quinoline, the formation of which is easily rationalized by a ring enlargement mechanism involving the tryptophan side chain. We have confirmed these results (14), obtaining quinoline as the major product in addition to smaller amounts of indole, skatole, a dimethyl (or ethyl) indole and naphthalene. HOFFMANN and RATHKAMP (19) obtained indole and skatole in fairly equivalent amounts from tryptophan, but surprisingly did not report finding quinoline in the pyrolysate. Other products arising from tryptophan pyrolysis include benzonitrile, o-tolunitrile, phenanthrene/anthracene and others.

We also observed indoles (8) in pyrolysates obtained from the nontobacco proteins, collagen and casein, and from the amino acids, proline and glycine. Indoles from casein could be rationalized on the basis of the tryptophan residues in the protein; however, collagen contains no tryptophan, and generation of indoles from it and the

amino acids pyrolyzed would require another pathway not involving tryptophan. PATTERSON and coworkers (20) have shown that pyrolysis of pyrrole results in the formation of indole. They have also obtained indole from the amino acids, lysine and leucine (7).

#### *Alkenes and Smoke Gases*

Additional smoke components, among many others, the formation of which is significant in view of the properties they may impart to the smoke are alkenes and gases. In initial studies, we noted that the long chain alkane, dotriacontane, on pyrolysis at 800° C, generated a product mixture characterized by the presence of aromatic hydrocarbons predominantly if not entirely (17). On the other hand, pyrolysis of the C<sub>32</sub> hydrocarbon at 700° C resulted in the formation of a homologous series of lower hydrocarbons (from C<sub>31</sub> down) as indicated initially by the gas chromatographic pattern produced by the pyrolysate (21). Further characterization of the pyrolysate by combined gas chromatography-mass spectrometry indicated that the homologous series consisted of monoenes, and that simple aromatics, i. e. benzene, toluene, styrene, were also present in the product mixture. At 300° C, dotriacontane merely distilled into the traps. Substances such as stearic acid, 1-dodecene and octadecane displayed pyrolytic properties similar to those of dotriacontane; aromatic hydrocarbons at extreme temperatures, homologous series of alkenes at intermediate temperatures, and starting material (via distillation) at lower temperatures.

Numerous gases have been found in cigarette smoke but not much work has been done to identify leaf constituents from which they originate. Pyrolysis of dotriacontane (22) has resulted in the formation of volatile hydrocarbons including methane, ethylene, propylene and acetylene. Amino acids on pyrolysis, have generated methane, acetylene, carbon dioxide, carbon monoxide, hydrogen cyanide, and ethylene (7). Nicotine yielded ammonia, methylamine and hydrogen cyanide (12). We noted that addition of nitrates (NaNO<sub>3</sub>) to cigarettes resulted in the generation of nitrous oxide, in addition to increasing levels of other nitrogen oxides (23) in the smoke.

## PART 2 — MODIFICATION OF SMOKE

In our attempts to modify the chemical composition of cigarette smoke, we concentrated on the use of tobacco additives. In our initial studies we sought to modify, to a significant extent, the burn temperature of cigarettes, and consequently smoke composition, through the use of "coal-temperature modifiers". Subsequently, we looked for additives that would modify smoke composition either in the particulate or vapor phase without regard to burn temperature. Overall, we wished to effect the removal of undesirable components from cigarette smoke.

#### *Additives that Modify the Burn Temperature of Cigarettes*

That a relationship exists between temperature and pyrolytic generation of polynuclear aromatic hydrocarbons from tobacco, and from organic compounds in general, has been amply demonstrated. GRIMMER (24) has shown that levels of benzo(a)pyrene from pyrolysis of tobacco increase with increasing temperature. Similar results have been obtained by ROBB et al. (25) in a study of cellulose pyrolysis. BADGER and associates (26) have noted a temperature optimum for pyrosynthesis of phenanthrene from n-butylbenzene. We have observed significant differences in pyrolysates of the hexane-soluble fraction of tobacco, and of certain paraffinic material, at 600° C and 800° C (16, 17, 21). At the latter temperature, the pyrolysates are predominantly, if not entirely, aromatic, i. e. composed essentially of polynuclear aromatic hydrocarbons. With these data in mind, it seemed that a feasible approach to altering levels of benzo(a)pyrene (and other substances) in cigarette smoke would be by modifying the combustion temperature of cigarettes (27).

Thus, a large number of possible cigarette additives were tested for their effect on combustion temperature, including free radical initiators and inhibitors, salts of organic acids, inorganic salts, lead-borate glasses, oxidizing agents and others. Most of the additives showed no dramatic increase or decrease of temperature even at high concentrations; some indications of small alterations were obtained in a few cases. The most significant results of the study are summarized in Table 2a. Of all the additives tested, only benzothiazyl disulfide and benzyl disulfide gave some indication of pos-

TABLE 2a  
Effect of additives on combustion temperature of cigarettes (27)

Name	Additive	Conc. (%)	Temperature range (°C)	
			Test cigarette	Control cigarette
Benzothiazyl disulfide		7	932 ± 97	828 ± 52
Benzyl disulfide		5	918 ± 69	853 ± 75
Azobenzene		25	775 ± 26	847 ± 17
Sulfur		5	899 ± 79	837 ± 26
Nickel oxalate		50	697 ± 50	833 ± 10
Basic magnesium carbonate		20	762 ± 23	825 ± 14
Stannous oxalate		50	739 ± 37	853 ± 47
CaCO <sub>3</sub>		40	762 ± 20	841 ± 12
Na <sub>2</sub> CO <sub>3</sub>		30	737 ± 17	841 ± 12
NaCl		40	752 ± 40	854 ± 7
Butox-2*		35	682 ± 42	849 ± 18
V <sub>2</sub> O <sub>5</sub>		20	773 ± 34	835 ± 6
KNO <sub>3</sub>		20	767 ± 31	846 ± 18

\* Commercial oxidative catalyst

sible temperature elevation; however, in the case of both additives, the significance of the difference between test and control cigarettes may be difficult to establish. None of the other free radical initiators and inhibitors markedly altered the combustion temperature. Salts of organic acids did not produce any noticeable effects unless present in cigarettes at concentration levels of 40–50 %; nickel oxalate and stannous oxalate had a small depressive effect. A number of inorganic salts (and other inorganic compounds) produced variable degrees of depression, but nothing significant at 20–40 % concentration levels. In addition, the claimed depression of alkali metal bicarbonates and β-alumina dihydrate (35) could not be confirmed with certainty. Lead borate glasses, added to cigarettes, produced some depression, but no large alteration in burn temperature was observed. The foregoing data, then, typify the data obtained with additives meant to alter cigarette burn temperatures. In general, temperature measurements were difficult to obtain with precision, and led to difficulties in interpreting the data, and attributing significance to the temperature spreads observed. Moreover, in those cases where significant alterations in burn temperature were indicated, the concentration of additive in the cigarette may have been too high for practical use.

*Additives Shown to Alter Smoke Composition*

More feasible than the preceding approach, perhaps, is the search for additives that

can be shown to alter smoke composition „directly“. Thus WYNDER and HOFFMANN (28) added copper nitrate (and independently, nickel acetate) to tobacco, and showed that the resulting cigarette smoke contained significantly reduced levels of particulate matter, nicotine, benzo(a)pyrene and phenol, and in addition was less tumorigenic to mouse skin than smoke from standard cigarettes. The action of these additives is rationalized by their ability to contribute oxygen to the thermal processes operative in a burning cigarette and thus facilitate more nearly complete combustion. Furthermore, it is assumed that in their thermal degradation, these salts form „scavengers“, e. g. NO from Cu(NO<sub>3</sub>)<sub>2</sub>, that inhibit free radical reactions and the consequent pyrosynthesis of polynuclear aromatic hydrocarbons, including benzo(a)pyrene. From the practical point of view, however, Cu or Ni salts are unsatisfactory as additives because of the toxicity of cigarette smoke containing Cu or Ni vapors.

Therefore, it was felt that sodium nitrate (in 8.3 % concentration) would be a better additive, producing similar compositional changes in cigarette smoke, without presumably imparting toxic properties to the smoke (28). Analyses showed that 8.3 % sodium nitrate added to cigarettes reduced dry particulate matter 32 %, nicotine 52 %, phenol 37 % and benzo(a)pyrene 67 % — per cigarette. Moreover, there was an 85 % reduction in the number of mice bearing tumors following application of smoke condensate from treated cigarettes (vs. standard cigarettes). In our own studies (23)

with sodium nitrate and its effect specifically on the composition of the vapor phase of cigarette smoke, we noted that it raised concentration levels of a number of smoke gases including oxides of nitrogen, acrolein and others, as will be discussed (*vide infra*). The latter effect would, to some extent, offset the desirable qualities of this additive.

In relation to, and in contrast with, the use of sodium nitrate as a tobacco additive, it was shown that two tobaccos, especially cultivated so that one was high in nitrate content and the other low, produced, in their corresponding smoke, benzo(a)pyrene levels that were not significantly different (29).

Other additives besides sodium and copper nitrate and nickel acetate have been shown to reduce levels of benzo(a)pyrene, phenol, TPM and nicotine in smoke — including  $\text{NaNO}_2$  and  $\text{KClO}_3$  in one group of additives investigated by BURDICK and coworkers (30). On the other hand, sodium vanadate and ammonium vanadate and a sodium borate-boric acid mixture in another group of additives effected an increase in levels of smoke phenols and benzo(a)pyrene, in spite of a decrease in nicotine and TPM. The differences in compositional effects attributable to the two groups of additives have been related to differences in weight loss (measured by TGA) in the tobacco at different temperatures, resulting from additive-tobacco interaction of some kind (30).

#### *Additives that Change Smoke Composition by Altering Smoke pH*

STEDMAN and coworkers have induced pH changes in cigarette smoke by the use of various acids and bases (31–33). In general, they found that volatility of the

TABLE 2b  
Effect of acidic and basic additives on pH of cigarette tobacco and smoke (31)

Additive	pK <sub>1</sub>	Level (mg/cig.)	pH	
			Tobacco	Smoke
None	—	—	5.5	5.6
Formic acid	3.75	33	4.6	4.1
Sulfuric acid	—	40	3.9	4.3
Phosphoric acid	3.12	50	4.0	4.9
Citric acid	3.08	120	4.3	5.0
Ammonia	4.75	11	8.5	7.8
Diethylamine	2.90	140	7.4	8.1
Dipropylamine	3.09	100	7.5	8.2

additive rather than acid or base strength (as indicated by pK value) was more important in influencing smoke pH (Table 2b).

The additives studied influenced smoke composition in addition to, and perhaps as a result of, effecting changes in smoke pH (Table 2c). For example, cigarettes with formic acid and dipropylamine showed increases in TPM compared to standard (unfiltered) cigarettes. The addition of formic acid, moreover, effected a significant reduction in pyridine in spite of an increase in the nicotine level (Table 2c).

TABLE 2c  
Effect of pH changes on unfiltered smoke (31)

	Additive		
	None	HCOOH	Di(Pr)NH
pH-smoke	5.6	4.1	8.2
TPM (mg/cig.)	24.2	32.0	30.8
Pyridine (μg/cig.)	27.5	9.7	26.5
Nicotine (mg/cig.)	1.73	2.34	2.01

In addition to promoting changes in the composition of the smoke emerging from unfiltered cigarettes, changes in the pH of smoke were shown to influence the selectivity of cigarette filters. Thus, added formic acid had the effect of reducing the selectivity of a multiple filter (cellulose acetate-carbon) for pyridine (Table 2d). Dipropylamine, on the other hand, appeared to increase the selectivity of the multiple filter for nicotine.

STEDMAN and coworkers, moreover, have shown similar effects for other smoke constituents, i. e. phenol, volatile acids, and vapor phase components, as a result of alteration of smoke pH. Lactic acid, for example, added to cigarettes, lowered the smoke pH to 4.2 (from 5.6) and, in addition, effectively reduced levels of formic and acetic acids in smoke (Table 2e). Dipropylamine, however, had the reverse effect — increasing levels of formic and acetic acids (Table 2e). As for their effect on smoke phenols, added formic acid raised the phenol level 50%, while dipropylamine lowered it 10%.

The influence of pH variations (in the smoke) on the selectivity of filters for formic acid, acetic acid and phenol was also determined. Most dramatic was the enhancement of the selectivity of the combined cellulose acetate and carbon filter for acetic acid at lowered smoke pH (4.2 from 5.8–6.1).

TABLE 2d  
Effect of smoke pH variation on cellulose acetate and carbon filter (31)

Additive	Rel. Amts.*			S**	
	TPM	Pyr.	Nic.	Pyr.	Nic.
None	0.63	0.17	0.67	3.62	0.97
Formic acid	0.56	0.38	0.52	1.47	1.09
Di(Pr)NH	0.79	0.38	0.63	2.13	1.29

\* Unfiltered smoke of same pH = 1.0  
\*\* Selectivity = > 1.0

Determination of selectivity:

$$S = \text{selectivity} = \frac{\frac{W_u(X)}{W_u(P)}}{\frac{W_f(X)}{W_f(P)}}$$

in which  
W = weight, u = unfiltered smoke, f = filtered smoke, P = particulate matter in smoke, X = pyridine (or any component in smoke)

In addition, increased selectivity for phenol was noted in the case of filters made of cellulose acetate and of cellulose acetate and carbon when smoke pH was lowered to 4.4–4.9.

The effect of modifiers of smoke pH on the composition of the vapor phase of smoke will be discussed in the next section (vide infra).

One is tempted to rationalize the foregoing data on the basis of simple dissociation of smoke acids and bases under the influence of induced pH changes. Thus at appropriate pH, a smoke acid would be in the form of the free acid (or base as the free base); in this form, the acid (or base) would tend to be found in the vapor phase of the smoke (vs. the particulate phase), and more susceptible to (or available for) filtration. Superficially, it would appear that for

TABLE 2e  
Effect of pH variation on unfiltered smoke (33)

Additive	Smoke pH		
	5.6	4.2	8.2
TPM (mg/cig.)	—	Lactic acid	Dipropylamine
Formic acid*	24.7	29.9	38.4
Acetic acid*	1.0	0.65	3.0
	1.0	0.60	3.0

\* Relative amounts. Levels in pH 5.6 smoke (µg/cig.):  
C<sub>1</sub> = 116, C<sub>2</sub> = 412

more selective filtration of a smoke component, it would merely be necessary to „force“ it into the vapor phase. However, even in the case of smoke acids or bases, such manipulation, through pH alteration, is not always successful. Another factor of possible importance may be the influence of pH change on certain acidic or basic leaf precursors of smoke components, and the resultant modification of pyrolytic patterns in the burning cigarette. Other undetermined factors may, of course, also be involved.

#### Additives that Have Been Shown to Modify Smoke Gases (Vapor Phase Constituents)

Finally, I will discuss our study (23, 34) of a number of additives, the effects of which we looked for in the vapor phase of cigarette smoke. At the time, our objective was to reduce, if not remove entirely, concentration levels of a number of smoke gases that may impart undesirable characteristics to the smoke. The vapor phase constituents of interest to us included hydrogen sulfide, hydrogen cyanide, formaldehyde, acetaldehyde, oxides of nitrogen, oxides of carbon, sulfur dioxide, methane, ethane, ethylene, acetone, acrolein, acetonitrile, oxygen, hydrogen and others.

Concentration levels of these gases were determined by various colorimetric and gas chromatographic techniques. In addition, a suitable smoking apparatus was constructed for the purpose of delivering a standard puff of smoke (or the vapor phase of such smoke) from a cigarette into appropriate collection traps, or sampling valves. Additives that were added to cigarettes, in concentrations usually of 8–10%, and evaluated in this way included some that were examined previously as possible burn-temperature modifiers, a free-radical initiator, and others that have been of interest elsewhere. The complete list of additives screened includes:

- 1) Sodium nitrate
- 2) Basic magnesium carbonate
- 3) Petroleum reforming catalyst (Houdry Process and Chemical Co.)
- 4) Lead borate glass
- 5) Nickel oxalate
- 6) Benzothiazyl disulfide
- 7) "HZ-1" catalyst (Houdry Process and Chemical Co.)
- 8) "Vazo" (Azo-bis-isobutyronitrile)
- 9) Ferric oxide — sugar mixture.

TABLE 2f  
Burn temperatures of modified vs. unmodified cigarettes (34)

	Avg. Burn Temperature***	Temp. change relative to:	
		Control*	Reference**
Control*	849° C		
Reference**	821	- 28° C	
8.3 % Sodium nitrate	788	- 61	- 33° C
10 % Basic magnesium carbonate	804	- 45	- 17
10 % Reforming catalyst (MoO <sub>3</sub> )	829	- 20	+ 8
10 % Lead borate glass	802	- 47	- 19
10 % Nickel oxalate	771	- 78	- 50
8 % Benzothiazyl disulfide	849	0	+ 28
10 % Catalyst HZ-1	824	- 25	+ 3
10 % VAZO	828	- 21	+ 7

\* Commercial 85 mm, non-filter  
\*\* Laboratory 85 mm, non-filter  
\*\*\* Average of 100 or more determinations

While a number of these additives produced some effect on the burn temperature of cigarettes (Table 2f) in the present study, and on the burn rate (Table 2g), no correlation could be established between a change in burn temperature, and a change in the composition of the vapor phase of smoke. However, some significant changes

TABLE 2g  
Burn rates for control and modified cigarettes (to 30 mm butt length)

	Total minutes*	Total puffs
Commercial (control)	8.22	8 +
Lab fabricated cigarette (reference)	11.04	11
8.3 % Sodium nitrate	10.34	10 +
10 % Magnesium carbonate	9.43	9 +
10 % Reforming catalyst (MoO <sub>3</sub> )	10.39	10 +
10 % Nickel oxalate	9.31	9 +
10 % Lead borate glass	9.37	9 +
8 % Benzothiazyl disulfide	18.03	18
10 % Cracking catalyst (HZ-1)	9.43	9 +
10 % VAZO (Azo-bis-isobutyronitrile)	10.49	10 +
11 % Fe <sub>2</sub> O <sub>3</sub> + 9 % sugar	9.90	10
USDA Control	8.34	8 +

\* Average of 2 or more determinations

in the composition of the smoke gases were observed, and must be attributed to the presence of additives in the tobacco. Most marked were the changes induced by sodium nitrate, nickel oxalate, basic magnesium carbonate and a mixture of ferric oxide and sugar. These changes will be discussed.

1) *Sodium nitrate*: The reported effects of sodium nitrate (i. e. reduced tumorigenicity, lower levels of benzo(a)pyrene, phenol, nicotine, TPM in smoke) led us to investigate the effects of this additive on the vapor phase of smoke, as well. Our data from the nitrate-treated cigarettes (containing 8.3 % additive), compared to that from similarly prepared unmodified cigarettes, indicated that sodium nitrate had the effect of increasing concentration levels of a number of vapor phase constituents (i. e. nitrogen oxides, acetaldehyde, acrolein) that might be better reduced in, if not removed entirely from, cigarette smoke.

TABLE 2h  
Effects of NaNO<sub>3</sub> (8.3 %) on vapor phase components (34)

Component	No additive mcg/35 ml puff	NaNO <sub>3</sub>
NO, NO <sub>2</sub>	15.2	48.7
N <sub>2</sub> O	< 1.0	11.0
HCN	13.2	23.3
CH <sub>3</sub> CHO	46.9	146.3
CH <sub>3</sub> CN	12.8	29.0
CH <sub>2</sub> = CH-CHO	5.7	18.4

The level of NO/NO<sub>2</sub> was increased three-fold (Table 2h). Where nitrous oxide (N<sub>2</sub>O) was virtually absent in the reference cigarette smoke, it was present in the smoke of sodium nitrate-treated cigarettes to the extent of 11.0 µg per puff. The level of HCN was doubled, acetaldehyde and acrolein tripled, and acetonitrile more than doubled (the data evaluated represent averages of ten more values obtained on the fifth puff).

Other effects of added NaNO<sub>3</sub> include  
a) two-fold increase in levels of H<sub>2</sub>, CO, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> and CH<sub>3</sub>COCH<sub>3</sub>,  
b) five-fold decrease in H<sub>2</sub>S,  
c) 33° reduction in burn temperature (°C).

2) *Basic magnesium carbonate*: Cigarettes containing 10 % (by weight) of basic magnesium carbonate burned in an erratic manner. Compared to the reference cigarette,

concentration levels (Table 2i) of most of the vapor phase constituents increased significantly — especially that of HCN, aldehydes and hydrocarbons. In addition, H<sub>2</sub>, CO, H<sub>2</sub>S and SO<sub>2</sub> were present in somewhat higher concentrations, and compared to acrolein and acetaldehyde, formaldehyde was lower. Burn temperature was also depressed (−17°C).

TABLE 2i  
Effects of basic MgCO<sub>3</sub> (10%)

Vapor phase component	No additive mcg/35 ml puff	MgCO <sub>3</sub>
HCN . . . . .	13.2	22.4
CH <sub>3</sub> CHO . . . . .	46.9	68.5
CH <sub>2</sub> =CH-CHO . . . . .	5.7	9.6
CH <sub>3</sub> COCH <sub>3</sub> . . . . .	27.0	33.7
NO, NO <sub>2</sub> . . . . .	15.2	23.8
CH <sub>4</sub> . . . . .	69.9	119.9
C <sub>2</sub> H <sub>6</sub> . . . . .	22.9	36.5

3) *Nickel oxalate*: Cigarettes fabricated with 10%, by weight, of nickel oxalate gave a measurable depression (−50°C) in the burn temperature. A considerably greater level of combustion products was observed in the smoke gas, with a corresponding decrease in the quantity of oxygen (Table 2j). The level of most of the vapor phase constituents was increased by a factor of 2. Even though the burn temperature was lower than that of the reference cigarette, the degree of combustion was apparently greater.

4) *Ferric oxide - sugar*: In an isolated experiment, a mixture of 11% ferric oxide —

TABLE 2j  
Effects of nickel oxalate (10%)

Component	No additive mcg/35 ml puff	NiC <sub>2</sub> O <sub>4</sub>
NO, NO <sub>2</sub> . . . . .	15.2	24.7
HCN . . . . .	13.2	23.4
H <sub>2</sub> S . . . . .	1.5	2.6
SO <sub>2</sub> . . . . .	1.9	3.1
CH <sub>3</sub> CHO . . . . .	46.9	66.4
CH <sub>2</sub> =CH-CHO . . . . .	5.7	10.7
	Mol %	
H <sub>2</sub> . . . . .	0.82	2.19
O <sub>2</sub> . . . . .	14.01	10.21
CO . . . . .	1.78	4.13
CO <sub>2</sub> . . . . .	5.46	8.84

9% sugar was tested as a possible cigarette additive. Cigarettes so treated yielded a smoke gas in which the CO content was reduced by 50%, with no corresponding decrease in CO<sub>2</sub> — indicating an alteration in the combustion process. In addition, levels of compounds containing nitrogen (NO/NO<sub>2</sub>, HCN, CH<sub>3</sub>CN) were reduced considerably. In fact, with the exception of formaldehyde and carbon dioxide, the levels of all of the constituents examined were reduced.

5) *Acidic and basic additives*: When the pH of smoke from U. S. commercial cigarettes was varied from 4.2 to 8.2 by the use of acidic and basic cigarette additives, significant alterations in the composition of the vapor phase of smoke were noted especially for H<sub>2</sub>S and HCN. Reductions of 79—91% of H<sub>2</sub>S and more than 90% of HCN in the vapor phase were obtained by changing the pH from 5.6 to 8.2 in non-filter cigarettes (32).

## CONCLUSION

We have tried to cover the important aspects of two areas of tobacco research:

- 1) formation of smoke components and
- 2) modification of smoke composition by the use of additives.

Of necessity, much of the material was not discussed in all the detail it deserved. Notably, we omitted discussion of the influence of physical design of the cigarette on the composition of the vapor phase of smoke. In our studies, at any rate, we learned that modification of such design (length, paper porosity, etc.) could have greater impact on vapor phase composition than many of the additives tested.

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#### *Acknowledgement*

*The author acknowledges the helpful discussions with R. L. Stedman during the preparation of the manuscript.*

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