The Identification of Aromatic Polycyclic Hydrocarbons in Carbon Blacks

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In previously reported experiments, the carcinogenic potency for mice of extracts of processed rubber was traced to the presence of 3,4-benzpyrene and related compounds (13). A search for the origin of these hydrocarbons was next undertaken. Samples of crude rubber, both natural and synthetic, did not contain any of these hydrocarbons when they were sought by extraction, chromatography, and ultraviolet spectrophotometry. A study of a typical formula for the processing of rubber suggested carbon black as the most likely source of the hydrocarbons. Samples of 24 carbon blacks were then examined by methods similar to those mentioned above. The absorption spectra of 3,4-benzpyrene and six related aromatic hydrocarbons were detected in a great number of the carbon blacks. The aromatic hydrocarbons found in carbon blacks were the same as those identified in processed rubber except that (a) coronene was found in carbon blacks but not in rubber and (b) chrysene and the phenanthrene derivative, which had been detected in processed rubber, were not found in any carbon black.

Extensive literature exists on the possible relationship of soot, carbon black, and related dusts to human skin and respiratory tract cancer, on the carcinogenicity of soot and dusts in experimental animals, on the carcinogenicity of extracts from such atmospheric contaminants, and on the physicochemical identification of carcinogens in such products. These subjects will be considered in detail in the discussion, because they are closely related to the work here reported and to follow.

Both soot and carbon black are forms of amorphous carbon made by the pyrolysis of organic substances. Soot is the more general term; it includes all carbon blacks. Carbon black is a commercial product made by the controlled combustion of natural gas and related fuels. Its content of acetone-extractable tars is usually below 1 per cent. In some soots this figure may go much higher.

The present paper deals with the identification of polycyclic aromatic hydrocarbons in different types of carbon blacks and with their possible significance. The following paper is concerned with the adsorptive capacity of carbon black for chemical carcinogens. A subsequent paper is planned to deal with the biological significance of these observations to carcinogenesis.

EXPERIMENTAL

Twenty-four samples of carbon blacks were obtained from four different manufacturers. One-pint aliquots of the blacks were placed in large flasks, enough redistilled benzene was added to cover the material, and the suspension was heated on a hot-water bath under a reflex condenser for 30 minutes. When cool, the mixture was filtered, and the residue was re-extracted. The combined filtrates were taken to dryness under a stream of nitrogen and were analyzed for their absorption spectra in a Beckman ultraviolet spectrophotometer with ether as the solvent. To resolve mixtures of hydrocarbons, extraction with sulfuric acid was used to isolate 3,4-benzpyrene (3), and anthanthrene was purified by means of precipitation with iodine (4).

For identification of the compounds by their absorption spectra, what were believed to be the corresponding purified commercial aromatic hydrocarbons were analyzed spectrophotometrically, and the spectra were compared. The absorption spectra of compounds for which commercial prod-
ucts were not available for comparison were identified by comparison with data given by Clar (9, 10).

The 24 samples included 7 commercial brands of channel blacks and 17 brands of furnace blacks. The aromatic hydrocarbons identified in these blacks are given in Table 2. No aromatic hydrocarbons could be eluted from the channel blacks or method of manufacture all samples were stated to be either channel blacks or furnace blacks. All channel blacks were made from natural gas, while the furnace blacks were made from natural gas, gasoline fractions, or petroleum residues. In the channel blacks no aromatic hydrocarbons could be detected. Many of the furnace blacks, however, regardless of the raw material used, contained all from a few of the furnace blacks. In most of the furnace blacks, however, the following seven polycyclic aromatic hydrocarbons were identified: pyrene, fluoranthene, 3,4-benzpyrene, anthanthrene, 1,2-benzpyrene, 1,12-benzperylene, and coronene. The structural formulae of these compounds are given in Chart 1. One absorption spectrum has not been identified as yet. The absorption spectra of the eight compounds are given in Charts 2 to 9, together with spectra of commercial samples of these compounds. The identification was confirmed by melting-point determinations in the cases of pyrene, fluoranthene, 1,12-benzperylene, and coronene. Not enough purified crystals of the remaining three compounds were obtained for confirmatory tests. In a furnace black of a type not investigated in this study pyrene had been previously isolated by Campbell et al. (6), and fluoranthene had been isolated by Rehner (35).

It is of interest to note that all the compounds detected in this study belong to the series of aromatic hydrocarbons with peri-condensed ring systems, i.e., one or more carbon atoms are shared by three rings. This is the class of hydrocarbons which has the smallest proportion of hydrogen to carbon for their molecular weight.

The carbon blacks which were studied were obtained from commercial sources. We did not verify the nature of the materials from which they were manufactured; when it is available, information on the raw material is given in Table 2. According to

### Table 1

#### Chromatogram of a Semi-Reinforcing Furnace Black

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluant: per cent</th>
<th>Physical properties</th>
<th>Chemical nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1—7</td>
<td>Petroleum ether</td>
<td>Colorless crystals</td>
<td>Pyrene</td>
</tr>
<tr>
<td>8—10</td>
<td>Petroleum ether</td>
<td>Yellow crystals</td>
<td>Fluoranthene</td>
</tr>
<tr>
<td>11—12</td>
<td>Petroleum ether</td>
<td>Yellow crystals</td>
<td>Unknown</td>
</tr>
<tr>
<td>13</td>
<td>Petroleum ether</td>
<td>Yellow oil</td>
<td>3,4-Benzpyrene</td>
</tr>
<tr>
<td>14</td>
<td>Petroleum ether</td>
<td>Yellow crystals</td>
<td>1,2-Benzpyrene</td>
</tr>
<tr>
<td>15</td>
<td>Petroleum ether</td>
<td>Orange crystals</td>
<td>Anthanthrene*</td>
</tr>
<tr>
<td>16</td>
<td>Petroleum ether</td>
<td>Orange crystals</td>
<td>1,12-Benzperylene</td>
</tr>
</tbody>
</table>

* Further purification by iodine precipitation.

### Table 2

#### Polycyclic Aromatic Hydrocarbons Identified in Carbon Blacks

<table>
<thead>
<tr>
<th>Classifications of carbon blacks</th>
<th>Starting material</th>
<th>Average particle diameter</th>
<th>Compounds identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel blacks:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. High color</td>
<td>Gas</td>
<td>10</td>
<td>None</td>
</tr>
<tr>
<td>2. Ink</td>
<td>Gas</td>
<td>14</td>
<td>None</td>
</tr>
<tr>
<td>3. High structure</td>
<td>Gas</td>
<td>17</td>
<td>None</td>
</tr>
<tr>
<td>4. Medium processing</td>
<td>Gas</td>
<td>29</td>
<td>None</td>
</tr>
<tr>
<td>5. Eaury processing</td>
<td>Gas</td>
<td>20</td>
<td>None</td>
</tr>
<tr>
<td>6. High abrasion</td>
<td>Gas and gasoline</td>
<td>26</td>
<td>1,2 (9-6)</td>
</tr>
<tr>
<td>7. High modulus</td>
<td>Gas and gasoline</td>
<td>55</td>
<td>1,8 (9-6)</td>
</tr>
<tr>
<td>8. Reinforcing</td>
<td>Gas</td>
<td>38</td>
<td>None</td>
</tr>
<tr>
<td>9. Reinforcing</td>
<td>Gas</td>
<td>39</td>
<td>None</td>
</tr>
<tr>
<td>10. High structure</td>
<td>Oil</td>
<td>50</td>
<td>1,2</td>
</tr>
<tr>
<td>11. High modulus</td>
<td>Oil</td>
<td>41</td>
<td>1,2</td>
</tr>
<tr>
<td>12. Reinforcing non-staining</td>
<td>Oil</td>
<td>43</td>
<td>1-7</td>
</tr>
<tr>
<td>13. Semi-reinforcing</td>
<td>Oil</td>
<td>51</td>
<td>1,8</td>
</tr>
<tr>
<td>14. Reinforcing non-staining</td>
<td>Oil</td>
<td>60</td>
<td>1,8 (9-6)</td>
</tr>
<tr>
<td>15. Semi-reinforcing</td>
<td>Gas</td>
<td>80</td>
<td>1-7</td>
</tr>
<tr>
<td>16. Non-staining</td>
<td>Gas</td>
<td>80</td>
<td>1-7</td>
</tr>
<tr>
<td>17. Semi-reinforcing</td>
<td>Oil</td>
<td>83</td>
<td>1-7</td>
</tr>
<tr>
<td>18. Semi-reinforcing</td>
<td>Gas</td>
<td>85</td>
<td>1-7</td>
</tr>
<tr>
<td>19. Semi-reinforcing</td>
<td>Gas</td>
<td>160</td>
<td>1-7</td>
</tr>
</tbody>
</table>

* 1 = Pyrene; 2 = fluoranthene; 3 = 3,4-benzpyrene; 4 = 3,4-benzpyrene; 5 = 1,12-benzperylene; 6 = anthanthrene; 7 = coronene.
† Traces only.
‡ Larger than average yield.

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seven of the aromatic hydrocarbons; the remain-
der contained few or none (see Table 2). The pos-
sibility exists that the aromatic hydrocarbons
found in many of the furnace blacks might have
been introduced in a preformed state with the
crude starting material. This possibility could be
eliminated as the sole explanation, if it could be
shown that the same aromatic hydrocarbons are
present in carbon black made from gas in the
laboratory, since these aromatic hydrocarbons are
solids and are not volatile at room temperature.

Accordingly, gas of known composition, which
was stated to be a mixture of natural and coke
oven gas, was burned in the laboratory on a Bun-
sen burner with a supply of air insufficient for
complete combustion, and the flame was made to
impinge on an inverted metal tray. The soot so
formed was extracted with benzene. The fluores-
cent extract was chromatographed. Spectrophotometric analysis revealed the presence of the same
seven aromatic hydrocarbons found in many fur-
nace blacks. This observation establishes the fact
that these aromatic hydrocarbons can be formed
from gas in the process of carbon black formation.

A correlation can be made between the physical
properties of the carbon particles of the blacks
with the extraction of aromatic polycyclic hydro-
carbons. In 11 out of 24 samples studied, 3,4-
benzpyrene was identified by its spectrum. In ad-
dition, six other closely related aromatic hydro-
carbons were detected. Whenever 3,4-benzpyrene
was found, most of the others were also present.
These eleven carbon blacks belong to the groups of
"high modulus furnace" and "semi-reinforcing
furnace" blacks which are said to have an average
particle diameter of 48–160 \( \mu \text{m} \). Only two hydro-
carbons could be obtained from a number of fur-
nace blacks (Table 2); they belong to the "high
abrasion furnace" and "reinforcing furnace"
blacks. They have an average particle diameter
of 26–50 \( \mu \text{m} \). The third group, from which aro-
matic hydrocarbons could not be eluted in de-
tectable amounts, is composed of the "channel
blacks" with particle size ranging from 10 to 30 \( \mu \text{m} \).

No quantitative experiments were made, be-
cause, as will be shown in the following paper, the
phenomenon of adsorption makes quantitative re-

CHART 1.—Structural formulae of compounds detected in
furnace blacks.

CHART 2: — Absorption spectrum of purified commercial pyrene.
— Absorption spectrum of pyrene isolated from carbon black.
CHART 3: Absorption spectrum of purified commercial 3,4-benzpyrene.
Absorption spectrum of 3,4-benzpyrene isolated from carbon black.

CHART 5: Absorption spectrum of 1,12-benzperylene isolated from carbon black. (Compare with Clar [9].)

CHART 4: Absorption spectrum of 1,2-benzperylene isolated from carbon black. (Compare with Clar [10].)

CHART 6: Absorption spectrum of coronene isolated from carbon black. (Compare with Clar [9].)
covery of hydrocarbons difficult if not impossible, and comparative extraction is difficult because of variation in particle size.

To evaluate the relative importance of the different types of carbon blacks, it should be realized that total production has increased fourfold in the last 15 years, that manufacture of blacks by furnace processes has risen from less than 10 to 50 per cent of the total production, and that 90 per cent of the furnace blacks belong to the "semi-reinforcing" and "high modulus furnace" blacks (26). The blacks of the types from which we have extracted 3,4-benzpyrene have reached a considerable proportion of the total production during recent years.

Extractable aromatic hydrocarbons were found in carbon blacks of large particle diameter and not in those of small particle size. The particle size of carbon blacks depends on the method and conditions of manufacture. It is possible, because of the adsorption phenomenon to be mentioned, that many, if not all, carbon blacks contain aromatic hydrocarbons and that the differences here reported are due to failure of elution and not due to absence of these substances.

DISCUSSION

Carbon black is practically pure amorphous carbon, the particle size of which ranges in diameter from 10 to 160 m. Soot is also amorphous carbon produced by the combustion of a variety of organic substances. Its particle size ranges up to 5,000 m. The two terms are used at times to designate identical or closely related products, although soot is the broader and more inclusive term. Almost all persons, and especially those in urban populations, are exposed to soot among other atmospheric dusts. In some localities and in some occupations exposure may be particularly heavy. Soot may also contaminate laboratory equipment and materials in experiments on carcinogenesis, among others. The observation that carbon blacks and soot may contain aromatic polycyclic hydrocarbons, one of which—3,4-benzpyrene—in pure form is a strong carcinogen for animals, while another—1,2-benzpyrene—is a weaker carcinogen (2) would therefore be a matter of wide concern if these substances and compounds should be shown to be harmful in man.

Probable origin of these polynuclear aromatic hydrocarbons.—The presence of complex aromatic hydrocarbons, all belonging to one group, in the extracts of carbon blacks, with the exclusion of all other types of hydrocarbons is an interesting phenomenon. Some light can be thrown on the mecha-

CHART 7.—Absorption spectrum of anthanthrene isolated from carbon black. (Compare with Clar [9].)

CHART 8: Absorption spectrum of fluoranthene, obtained through the courtesy of R. N. Jones.
nism of formation of these peri-condensed ring systems from information found in the literature. At 1,100°–1,600° C., the temperature reached in production of carbon blacks, all known hydrocarbons tend to decompose into amorphous carbon and hydrogen gas. A study of the products of pyrolysis of the constituents of natural gas as compiled by Ellis (12) gives, in a very much simplified form, the following picture: Methane, the main hydrocarbon constituent of “dry” natural gas, breaks down at 1,100° C. into a methylene radical and hydrogen. This unstable free radical dimerizes to ethylene, which breaks down further to hydrogen gas and to “nascent acetylene,” a term coined by Groll (14). The “nascent acetylene” partly decomposes to carbon, hydrogen, and methane and partly polymerizes to simple aromatic hydrocarbons. The aromatic hydrocarbons in part lose hydrogen, forming more complex aromatic hydrocarbons, and in part break down to acetylene, carbon, and hydrogen.

The pyrolysis of ethane, propane, butanes, and pentanes, all constituents of “wet” natural gases used at times in carbon black formation, yields the same type of breakdown products as in the case of methane, but larger quantities of “nascent acetylene” and consequently of aromatic hydrocarbons are formed.

This simplification of the processes involved in the decomposition of hydrocarbons gives a plausible explanation of the side reaction products during carbon black formation. This mechanism may also explain the formation of carcinogenic tars by pyrolysis of all organic materials which were tested by Kennaway (19).

In 1925 Kennaway (20) indicated the type of reaction involved in the formation of strongly carcinogenic tars by pyrolysis of isoprene. He found that polycyclic aromatic hydrocarbons were not produced unless the temperature of pyrolysis reached 750°–820° C. At this temperature he detected benzene, naphthalene, anthracene, phenanthrene, chrysene, and their homologs in the tars which were strongly carcinogenic. The existence of a critical temperature, which must be reached before aromatic hydrocarbons with carcinogenic properties are formed, was mentioned also by Dickens and Weil-Malherbe (11). No evidence of carcinogenicity of extracts of wood soot, produced by them at 400°–450° C., was obtained by skin painting of mice over a period of 2 years.

Identification of carcinogens in soot.—There is ample evidence that at least one—and the most important one, namely, 3,4-benzpyrene—of the aromatic hydrocarbons which we have found in carbon blacks is also present in a number of soots.

For example, McDonald and Woodhouse (29) isolated from city dust a fraction in which they identified by its ultraviolet absorption spectrum a compound which they believed to be 3,4-benzpyrene. Hieger (17) exposed pure benzene to city air and observed that it acquired the fluorescence spectrum of 3,4-benzpyrene. By the same physical method 3,4-benzpyrene was detected by Gulden and Tipler (15) in domestic soot in concentrations of 0.03 per cent, and by Waller (44) in the dust of nine British cities in concentrations ranging from 0.02 to 0.5 µg. per cubic meter of air filtered. The quantity of carcinogen in some city air appears therefore to be quite large.

Epidemiological evidence for carcinogenic hazard in soot and atmospheric dusts.—The foregoing evidence of our own on the presence of carcinogenic compounds in carbon blacks together with the evidence summarized from the literature would appear to indicate the possibility of considerable hazard in soot-polluted air. However, a survey of clinical, epidemiological, and statistical evidence in the literature bearing on this problem does not unequivocally indicate a hazard.

If soot and carbon black were to induce human
tumors it would be expected that the resulting tumors would be chiefly located at the points of maximum contact, namely, the skin and respiratory tract, including the lungs. Published statistical studies on the incidence of human cancer in dusty occupations give conflicting results, which may be explained by differences in the composition of the dusts, in the type of contact, and in the method of epidemiological and statistical analysis.

In 1907, Lueke (37) reported a series of cases of epithelioma of the skin in carbon workers. Carbon itself, however, was not definitely established as the cause, because the workers had contact with both ground coke and an oily liquid obtained from tars or pitch. An epidemiological study of cancer mortality and morbidity in a large carbon black manufacturing industry was recently reported by Ingalls (18). He concluded that carbon black workers face no more than the ordinary risks of cancer encountered by other male working populations. It might be pointed out, however, that among the carbon black workers which he studied, only 79 had been employed for 10 years or more, and only 34 for 15 years or longer; furthermore, only 32 were 50 years old or over, and of these only 7 had been employed for 10 years or more: finally, former employees retired for age were not included in the statistics.

A number of statistical reports are available on the incidence of human lung tumors in relation to occupation and environment, but the inhaled atmospheric dusts were only partly soot. The correlation of lung cancer prevalence with occupation seems to incriminate some dusts which are comparatively free of soot, rather than soot itself. For example, Turner and Grace (48) found that steel foundry and furnace workers had the highest incidence of lung cancer, followed by sandblasters. Brockbank (5), in an analysis of 900 lung tumor cases, observed the predominance of unskilled laborers and dusty occupations. Versluys in Holland (49) found a high incidence of pulmonary cancers in many occupations which appear to have little in common and no undue exposure to soot; he also observed a low incidence in farmers and general laborers, the latter contrary to Brockbank in England. Kennaway and Kennaway in Great Britain (21, 22) remarked on the low incidence of cancer of the respiratory tract in agricultural workers (like Versluys) and in coal miners. Mills and Mills-Porter (30) working with the vital statistics of several American cities reported the mortality from respiratory tract cancer to be greater in areas of high soot fall than in clean districts. Additional comment along this line is provided by the recent discussion by McDonald, Drinker, and Gordon (28). It is apparent that the epidemiological studies do not incriminate soot beyond a doubt as an etiological agent in respiratory tract cancer in man.

Experiments were made to demonstrate carcinogens in extracts of anthracotic human cancerous and cancer-free lungs (40). The weak carcinogenic activity which was demonstrated was nearly as great in extracts of fetal lung as from those of adults. It was concluded, therefore, that no exogenous carcinogen had been demonstrated. In recent studies we have attempted to demonstrate the presence of aromatic hydrocarbons in extracts of anthracotic human lungs by spectrophotometry but have failed to find evidence for such compounds.2

The evidence for soot as a carcinogen in human cutaneous tumors, however, is stronger than that for lung cancer. Sir Percivall Pott long ago described cancer of the skin of the scrotum and other sites in chimney sweeps and ascribed them to exposure to soot (38, 54). The subsequent confirmation and the development of knowledge on this subject has recently been reviewed by Henry (16). Ingalls (18) has correctly pointed out the possible great difference in carcinogenic hazard between the chimney soots which have a high content of acetone-extractable matter and the industrial carbon blacks with a low tar content.

The available evidence indicates that, while soot is mildly if at all carcinogenic in the respiratory tract of man, it must be considered responsible for some human skin cancer. This difference, as we shall point out later, may be explained by the lack of appropriate solvent for the carcinogen in the respiratory tract and presence of such solvent in the form of sebaceous secretion on the skin.

Experimental evidence for carcinogenic activity of soot.—The experimental evidence on the carcinogenicity of soot and soot-containing dusts in animals is also equivocal. Leitch in 1928 (23) reported unsuccessful attempts to produce cancer of the scrotum with soot, but his experiments continued for only 1 year, and he used the relatively skin-tumor-resistant rats and rabbits. Seelig and Benignus (37) exposed 100 Buffalo strain mice to coal soot substituted for shavings and observed 8 lung tumors as compared to 1 tumor among 50 controls. However, in a later experiment these authors (38), in repeating the experiment with 100 C57 black mice and a 10 per cent mixture of carcinogenic gas works tar in lamp black, induced no lung tumors in the experimental mice, whereas 2 of their controls had tumors. In neither experiment was any

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2 P. E. Steiner, J. Afterman, and H. L. Falk, unpublished data.
skin tumor reported, although the mice lived on the soot. Campbell (7) exposed 75 mice to a moderate cloud of chimney soot 30 times a week during a whole year and observed a lung tumor yield of 20 per cent. As the lung tumor yield in his controls also was as high as 20 per cent in some groups, it is doubtful whether his soot was carcinogenic for lung tissue. In summarizing his experiments on the production of lung tumors in mice, Campbell (8) pointed out the similarity between human and mouse lung cancer as regards the agents which increase the yield of these tumors, the time and age factors, some aspects of susceptibility, and the morphology of the tumors. He placed emphasis on the inorganic constituents rather than on the tars as the carcinogenic agents. McDonald and Woodhouse (29), repeating the work of Seelig and Benignus but using two types of city dusts instead of soot, observed a yield of lung tumors of 22.8 per cent compared to 14.3 per cent in the control group. Schnurer and Haythorn (36) exposed eight rats and one rabbit to a mixture of coal smoke and air during 80 days. The animals developed fibrous reactions around the carbon deposits and lung changes analogous to those of bituminosis as seen in soft-coal miners, but lung tumors were not observed up to 14 months following exposure. Sulman and Sulman (41) studied the carcinogenicity of wood soot from the chimney of a sausage factory. On subcutaneous injection into rats they observed a 16.6 per cent sarcoma yield, while no tumors were induced on intrascrotal implantation of soot or by feeding of the smoked sausage. In conclusion, there has been reported no unequivocal experimental evidence, to our knowledge, for the presence of functioning carcinogens for the respiratory tract in soot.

**Experimental evidence for carcinogenic activity in extracts of soot.**—Although there is little experimental evidence for carcinogenicity of soots, extracts of soots have consistently shown carcinogenic activity both by skin painting and by subcutaneous injection.

The earliest experiments on this subject were described by Passey (31), who painted an ether extract of household soot from bituminous coal on the skin of mice and observed nine malignant tumors in 18 animals surviving 1 year. In a subsequent paper, Passey and Carter-Braine (32) attempted a fractionation of the soot extract by fractional distillation. The activity was found in the distillate above 190° C. and in the residue. Subcutaneous injection of chimney soot extracts, prepared by Shimkin and Leiter (39), gave a 40 per cent yield of sarcomas in C57H mice. An extract of wood soot was painted on the skin of ten mice in which three neoplasms were observed by Sulman and Sulman after 2 years (41). Extracts of city atmospheric dusts were investigated by Leiter et al. for their carcinogenicity on subcutaneous injection into mice at a 50-mg. dose level. Their tars produced 18 sarcomas in 291 mice (24) and 50 sarcomas in 372 mice (25). The activity of these dust extracts showed considerable variation, depending on the locality of collection. A study was made by McDonald and Woodhouse (29) on the lung tumor incidence after skin painting twice a week for 1 year with a purified extract of city dust. Their 50 mice showed a 25 per cent tumor yield, compared to 15.8 per cent in the control group. Campbell (7) painted 34 mice twice a week for 26 weeks with an extract of chimney soot (of the same type used for his inhalation experiments described above) and found 9 papillomas, 7 of which became malignant. In attempting to explain his positive results with the extracts and the negative results with whole soot, he suggested that the presence of the soot decreased the action of the carcinogen.

In contrast to the low activity of whole soot, these tests with extracts demonstrated clear-cut carcinogenic activity. The extracts were active regardless of type of soots or their content of extractable tarry matter which varied from 0.5 to 11.8 per cent of the original soots. This apparent discrepancy between the carcinogenicity of soot and of its extracts needs to be explained.

**Lipid solvents and adsorption.**—The equivocal evidence for carcinogenic activity in soot by inhalation and dusting experiments in animals and by epidemiological studies on respiratory tract cancer in man, despite demonstrated presence of carcinogens in many soots and of carcinogenic activity in extracts of soots, requires an explanation. Two immediately come to mind. They are (a) that an adequate solvent for extraction of the carcinogen from the carbon may be lacking at some sites of contact and (b) that the carcinogen may be held by adsorption so firmly as to be biologically inactive.

Two points of evidence for the importance of the lipid solvent factor have already been mentioned. First, soots are carcinogenic on the skin of man where sebaceous secretions are present and questionably active in the respiratory tract where such secretions are absent. Second, lipid solvent extracts of soot have consistently produced tumors when tested in animals. It is possible that in the human respiratory tract the carcinogen was present but did not make proper contact with the cells for lack of solvent.

There is also evidence for the adsorption hypothesis. If a carcinogenic hydrocarbon is added to

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*Falk and Steiner—Hydrocarbons in Carbon Blacks*
some carbon blacks under special conditions, it can be recovered incompletely or not at all. This phenomenon is the subject of the paper which follows. Furthermore, this adsorption phenomenon was easily demonstrated in the test tube by another method. When a furnace black from which hydrocarbons could be eluted was mixed with a channel black from which none could be extracted, in a proportion of 3:1, aromatic hydrocarbons were not extractable from the mixture. This phenomenon is not clarified by the experiments of Anderson and Lorenz (1). When they injected a mixture of charcoal and 1,2,5,6-dibenzanthracene, they observed the same yield of sarcomas at the site of subcutaneous injection in the experimental as in the 1,2,5,6-dibenzanthracene controls, but fewer lung tumors in the former. They attributed the latter difference to adsorption of the chemical on the charcoal. Examination of their methods, however, shows that they used a ratio of charcoal to carcinogen of 2:1. This is a much larger amount of carcinogen than could have been adsorbed to the charcoal, so that their explanation is not fully adequate.

There is much chemical but little biological evidence for the importance of the adsorption phenomenon. Extensive biological tests bearing on these points are now under way.

**SUMMARY**

1. Benzene extracts of some carbon blacks were found to contain 3,4-benzpyrene, a strong carcinogen for animals; 1,2-benzpyrene, a weak carcinogen; and five other related aromatic hydrocarbons: pyrene, fluoranthene, 1,12-benzperylene, anthanthrene, and coronene.

2. By these compounds possess peri-condensed ring systems in which carbon atoms are shared by three rings. They contain the smallest possible proportion of hydrogen to carbon for molecules of this type and size. A theory of their formation is presented.

3. Furnace blacks, with an average particle diameter of 80 m, or more, possessed all 7 of the aromatic hydrocarbons; those with particle size below 50 had few or none. A rough correlation existed between yield of extractable aromatic hydrocarbons and average particle diameter of the carbon blacks.

4. These hydrocarbons were not detected in any channel blacks, which have small particle diameter averaging from 10 to 30 m, and are made by a different process.

5. Based on these observations an interpretation of the apparently contradictory reports in the literature on the carcinogenicity of soot is possible.

3,4-Benzpyrene seems to be the principal carcinogenic agent. This hydrocarbon can be extracted from many soots with lipid solvents, and these extracts produce tumors in animals at the site of application. Soot itself appears to be carcinogenic on skin but possibly not on respiratory tract epithelium. It is suggested that this difference in behavior is explained by the presence of lipid solvent (the sebaceous secretions) in the skin and its absence in the respiratory tract.

6. It is further suggested that the differences in extractable aromatic hydrocarbons from carbon blacks can be explained by the phenomenon of adsorption.

**REFERENCES**


The Identification of Aromatic Polycyclic Hydrocarbons in Carbon Blacks

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