XXI.—*Note on (I) the Behaviour of the Nitrogen of Coal during Destructive Distillation, and (II) a Comparison of the Amounts of Nitrogen left in Cokes of Various Origin.*

By WATSON SMITH.

MR. WM. FOSTER at the close of his interesting paper read before this Society, and published in this Journal (1833, Trans., 105—110), summarises his results as follows :—

Percentage of nitrogen in the coal	1·730
Percentage of nitrogen of coal evolved as ammonia during destructive distillation.....	0·251
Percentage of nitrogen in coal evolved as cyanogen during destructive distillation.....	0·027
Amount of nitrogen remaining in coke furnished by 100 parts of coal	0·842
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	1·120
Nitrogen from 100 parts of coal unaccounted for, the larger portion of which is presumably present as free nitrogen in the coal-gas. Some is no doubt in the tar	0·610

If we further reduce these figures to percentages on 100 parts of nitrogen, their relation to each other becomes more intelligible:—

Nitrogen of coal evolved as ammonia	14·50
Nitrogen of coal evolved as cyanogen	1·56
Nitrogen of coal present in the coal-gas in the elementary condition.....	35·26
Nitrogen of coal remaining behind in the coke	48·68
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	100·00

“ I have not made any experiments on the amount of nitrogen in the tar, nor am I in possession of any information on the subject, but I have assumed that the quantity is relatively small.”

Mr. Foster's last remark referring to the amount of nitrogen in the tar interested me on first reading it, and for the following reason:—As far back as the year 1868, when making distillations either of coal-tar or crude coal-tar oils, I observed, whenever the distillations were carried so far that pitch remained in the retort, and these residues of pitch were further heated until partial coking took place, that on leaving the whole to cool partially, and then removing the stopper of the retort, a smell of ammonia was always perceptible, reddened litmus-paper was turned blue, and a stopper moistened with hydrochloric acid fumed strongly. I have also been informed more recently by tar distillers that after coking pitch, when the man-hole lids of the stills have been removed, the odour of ammonia is very powerful. The experiment is so easily performed with a little hard pitch broken up small and placed in a retort and heated to coking, that it would form a very good lecture experiment, to illustrate the fact that nitrogen compounds of considerable stability exist in hard pitch, and in partially coked pitch, and that at temperatures near the softening point of glass, these compounds are so decomposed, that on

partial cooling and in contact with moist air, ammonia is evolved. It is a remarkable fact that not the slightest smell of ammonia could be perceived, if the retort-stopper were removed whilst the retort is still very hot. The most favourable time for obtaining the evidence of the presence of ammonia is when the retort has cooled so far that its bulb may be held in the hand.

My supposition all along has been that the nitrogen in the partially coked pitch has been brought into so unstable a form of combination; and that, on cooling down and a back-suction of moist air into the retort taking place, such unstable nitrogen compounds in the highly porous mass in presence of moisture, are decomposed or altered so as to yield ammonia.

It was determined to attempt to estimate the amount of nitrogen in ordinary coal-tar and in the oils obtained at different stages from that tar, as well as in the pitch left as a residue. The numbers given are the means of at least two experiments for each sample.

The tar analysed was thoroughly well settled from ammoniacal water, but beyond this no attempt was made to remove suspended solution of ammoniacal salts.

The crude benzene contained ammonia in solution, which communicated to it a pungent odour. The "light oil" likewise smelt slightly of ammonia, but the "creosote oil" was quite free from ammoniacal odour.

Nitrogen in the Tar.—The mean of two experiments gave — 1·667 per cent.

<i>Crude benzene</i> , obtained from the above tar (mean of two experiments)	= 2·327
" <i>Light oil</i> ," obtained from the above tar (mean of two experiments)	= 2·186
" <i>Creosote oil</i> ," obtained from the above tar (mean of two experiments)	= 2·005
<i>Red oil, or Oils</i> from which the crude anthracene has been separated by filtration (mean of two experiments)	= 2·194
<i>Pitch</i> , obtained from the above tar (mean of two experiments).....	= 1·595

It would thus appear that nitrogen compounds of high boiling points occur in the oils drained from the crude anthracene to a considerable extent, and that though there is a falling off in the pitch (in the above case a hard pitch), yet still in this product certain very stable nitrogen compounds occur; further, that the amount of nitrogen contained in ordinary coal-tar oils (from Lancashire coaltars) may be stated as 2 per cent. on the average.

Of course the lighter naphthas will contain the pyridine bases, the intermediate naphthas and oils, more especially the quinoline bases, whilst the anthracene oils and pitch will contain the carbazols and acridine, and possibly other nitrogenous bodies of high boiling and melting points not yet examined.

II. *Comparison of the Amounts of Nitrogen left in Cokes of Various Origin.*—Three varieties of coke were now analysed, with the object of determining the nitrogen in them, viz. :—

- (1.) Ordinary gas-retort coke.
- (2.) Beehive metallurgical coke.
- (3.) The hard compact metallurgical coke from the Simon-Carvès coke-ovens.

The results are as follows :—

Kind of coke examined.	Percentage of nitrogen found.
(a.) Ordinary gas-retort (mean of two experiments)	1·375
(b.) Beehive metallurgical coke (mean of two experiments)	0·511
(c.) Metallurgical coke from the Simon-Carvès coke-ovens (mean of three experiments)...	0·384

From the above results it may, I think, be concluded that in (a) the effect of a sharp heat of short duration is shown under the usual circumstances of gas-retort work, not to be so efficacious in decomposing certain very stable nitrogen compounds so as to drive the nitrogen out of the coke, as a long-continued high temperature such as is found in (c). In (a) a charge of from 2—3 cwts. of coal is heated for 6 hours, whereas in (c) a charge of 4 tons is heated for about 40 hours. The temperatures employed are not much unlike in (a) and (c), though on the whole the heat of the Simon-Carvès oven will be the stronger.

No note was taken or inquiry made as to the *part* of the interior of the ovens from which the cokes under examination were taken. In the case of gas-retort and Simon-Carvès oven cokes no such note or inquiry is necessary, since in both cases external heat is uniformly applied to the mass of fuel disposed in a thin layer, which in the former case is arranged horizontally, in the latter vertically. With the Beehive coke, certain differences of temperature might occur in different parts of the mass; *e.g.*, the portions of coke lying nearer the surface of the mass in the ordinary Beehive, and nearer the small air-inlet, but not necessarily nearer the walls (not externally heated, but rather cooled) might be expected to have been more strongly heated than those lying next the floor of the oven. In the Jameson oven the temperature throughout the coking and coked mass will be much more

uniform than in the ordinary Beehive. In the above-mentioned experiments, simply a well-burnt sample of Beehive coke was taken for examination, exhibiting an average appearance and texture.

The analyses recorded in this note were made by Mr. R. J. Gow in the Chemical Laboratory of the Owens College, and to him I beg to express my best thanks.

The apparatus used for collecting and measuring the nitrogen was that of Staedel, which possesses the considerable advantage over the usual apparatus, that the hands of the operator are spared, there being no necessity to bring them into contact with the caustic alkaline solution.

For the removal of air from the materials and interior of the combustion tube, a Swan's modification of the water air-pump was used, the washing action of the carbonic acid from the heated magnesite being aided by the exhaustion.