BHADRAVATI WOOD-TAR AND ITS UTILIZATION.

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I. COMPOSITION OF THE TAR.

The tar obtained by the distillation of hardwood is known to be a mixture of extraordinary complexity, and detailed investigations of its constituents are few in number. Among the most noteworthy are those of Behal and Choay (*Compt. rend.*, 1893, **116**, 197 ; 1896, **119**, 166) who found phenol, the three cresols, *o*-ethylphenol, 1 : 3 : 4- and 1 : 3 : 5-xylenols, guaiacol, creosol and ethylguaiacol in the tar from beech and oak wood, and of Pieper, Acree and Humphrey (*Ind. Eng. Chem.*, 1917, **9**, 462) who found the dimethyl ethers of pyrogallol, methylpyrogallol and propylpyrogallol in the higher fractions of maple tar. Coerulignol was observed by Pastrovitch (*Monatsh.*, 1883, **4**, 188) in beech tar, homopyrocatechol dimethyl ether was separated by Tiemann and Mendelsohn (*Ber.*, 1875, **8**, 1136) from the same material, while more recently, Williams, Lasselle and Reed (*Ind. Eng. Chem.*, 1925, **17**, 85) have described the detection of pyrogallol monomethyl ether.

The products of the Mysore wood distillation plant at Bhadravati differ from those commonly obtained in commerce in that they are derived from more than 50 species of woods, as opposed to the one or two usually utilized. The tar is thus likely to be even more complex in character than normal tar, but at the same time the possibility of finding unusual constituents seemed to render an examination worth while and consequently the tar has been separated as far as possible into its components.

Most of the experiments were made with a 5-gallon sample of " refined tar " drawn from the bulk supply. This consisted of the tar settled from the pyroligneous acid after heating to expel most of the water and acetic acid, a small quantity of light oil being removed simultaneously.

Physical Properties.

The more important physical properties of this tar are given in Table I, and for comparison a specification of the British Road Tar Association for a tar suitable for use on roads is adjoined. The viscosity was determined by the modified Redwood viscometer (*cf.* Butterfield, *J.S.C.I.*, 1928, **47**, 298T), free carbon by extraction with toluene, and phenols by treatment with sodium hydroxide.

TABLE I.

Properties of Refined Tar.

	Wood Tar	B. R. T. A. Tar No. 2
Specific gravity	1.156 (24°)	1.150—1.240
Viscosity at 30° (Mod. Redwood)	45 secs.	40—125 secs.
Flash point (Pensky-Marten)	104°	....
Continuous fire point	135°	....
Water	0.6 per cent.	0.5 per cent.
Distillate below 200°	1.5 ,,	1.0 ,,
,, 200–270°	36.6 ,,	8.0–16.0 ,,
,, 270–300°	Trace. ,,	3.5–12.2 ,,
Phenols and acids	21.9 ,,	4.0 ,, (vol.)
Naphthalene	*Nil.*	5.0 ,,
Free carbon	17.0 ,,	6–21 ,,
Ash	0.5 ,,	....

It is well known that wood tar is not a suitable material for tarring roads and the sample under discussion is no exception, owing to the high proportion of comparatively low-boiling oil and the absence of an intermediate fraction between this and the pitch.

Solvent Extraction.

In order to obtain a general idea of the nature of the tar, portions were extracted with organic solvents and the solutions examined; 250 c.c. were treated with light petroleum (b.p. 40–60°) and the insoluble portion further extracted with benzene. Two samples of 20 c.c. were separately treated with ether and benzene. The petroleum extract was shaken with 10 per cent. sodium hydroxide solution and then with 25 per cent. acetic acid to remove acidic and basic bodies; the neutral oils obtained after washing and removing the solvent were distilled. The phenols and acids were recovered from the sodium hydroxide solution by acidifying with 10 per cent. sulphuric acid after a preliminary washing with ether to remove neutral bodies and extraction with ether. A small quantity of tar bases was obtained from the acetic acid solution by adding 40 per cent. sodium hydroxide solution and extraction with ether. An analogous procedure was followed in the case of the other solvents.

For comparison, 20 g. of tar were treated directly with 10 and 20 per cent. sodium hydroxide solutions, the aqueous solution acidified after shaking with ether, and the neutral bodies taken up in ether and filtered from the solids. Table II gives a resume of the results obtained.

TABLE II.

Extraction of Tar.

	Solvent	Petrol	Benzene	Petrol & benzene	Benzene	Ether	NaOH 20%	NaOH 10%
(*a*)	Total extract ..	35.4	44.4	79.8	87.1	84.2	68.8	70.0
(*b*)	Solid residue ..	..	18.7	18.7	12.8	15.8	11	10
(*c*)	Acidic bodies ..	10.1	33.3	43.4	..	49.2	69	70
(*d*)	Neutral oils ..	24.7	10.1	34.8	..	35.0	20	20
(*e*)	Resin on distilling (*c*)	0.8	14.3	15.1	..	19.2	39	34

The petroleum ether extract contained 0.66 per cent of bases. The neutral oils obtained from this solvent boiled at 160–300°, had a density of 0.817 at 24° and n_D^{24} 1.4820. Those insoluble in this solvent but soluble in benzene had a similar range of boiling point, but the refractive index was 1.5000. The acidic bodies soluble in petroleum ether boiled from 180 to 270° at atmospheric pressure and those obtained directly with sodium hydroxide between the same temperatures. The constituents of the two liquids were, however, very different, the former distilling almost completely and yielding a distillate with density 1.06 while the latter, when about half had been distilled, left a resinous mass which decomposed on further heating. The amount of residue calculated for 100 g. of original tar is shown in row (*e*). The reason for this difference in behaviour appears to be the presence of ulmins and rhetinols which together with other neutral substances dissolve very readily in aqueous sodium phenate solution, and are not easily removed by washing with ether. If sodium hydroxide is added to a solution of the phenol in benzene or ether the sodium phenate is less contaminated than it is when no solvent is present (*cf.* Edwards, *J.S.C.I.*, 1924, **43**, 143T; Parish and Rowe, *ibid.*, 1926, **45**, 99T).

A second factor is probably the decomposition of some of the neutral oils by the aqueous sodium hydroxide in absence of a solvent giving rise to substances partly or wholly soluble in alkali. Experimental evidence on this point is not definite, but if some such action does not take place it is difficult to explain why the aqueous solution after washing with ether should contain as much as 20 per cent. more soluble matter than a solution obtained by adding sodium hydroxide to the ethereal extract.

On distilling the phenolic bodies obtained by means of aqueous sodium hydroxide either alone or in presence of an organic solvent, a distillate equivalent to about 30 per cent. of the original tar is obtained, whereas if the tar itself is distilled and the distillate extracted with sodium hydroxide solution (see next section) the yield of phenols is only 22 per cent. The former procedure would appear preferable, but in practice it is difficult to follow owing to the formation of emulsions. The yield of neutral oils is, as may be seen from Table II, much larger when a solvent is used, being 35 per cent. as compared with 20 per cent. for sodium hydroxide alone. If the tar is distilled before extraction this figure is reduced to 15 per cent.

Distillation of Tar.

At first, 500 g. portions of the tar were distilled from a glass distilling flask at atmospheric pressure (680 mm.), so that the course of the distillation might be watched. Subsequently a 3-litre iron retort heated in a fusible metal bath was employed enabling 1500 g. to be treated at once. It was found that at atmospheric pressure the temperature of the vapour rose slowly as distillation proceeded until about 220°, when it became irregular, sometimes rising to 260° and sometimes falling as low as 200° owing to decomposition of the higher boiling portions. By continuing the distillation until the distillate practically ceased, it was possible to obtain 36–37 per cent. of a yellow oil. At reduced pressure there was a steady temperature rise and little or no decomposition. Table III shows some of the results obtained.

TABLE III.

Yield of Tar Distillate at Different Pressures.

Pressure mm.	100	115	135	150	150	160	680
Max. temperature	153	164	170	170	170	170	260
Distillate per cent.	30.4	33.1	33.2	35.0	34.0	34.7	37.3

The temperatures at which distillation started were somewhat indefinite owing to the presence of small quantities of water, but were in the neighbourhood of 130° at 150 mm.

Separation into Constituent Groups.

Extraction of Acids.—1750 g. of the crude distillate were redistilled at 150 mm. pressure and the product shaken in two batches with 250 c.c.

of 10 per cent. sodium carbonate solution for half an hour. The aqueous solution was separated and washed with ether and the acids liberated with sulphuric acid and extracted with ether.

Extraction of Phenols.—The residual oil from the last operation was treated with 1250 c.c. of 20 per cent. sodium hydroxide solution and ether added. Some sparingly soluble sodium salts were dissolved in the minimum quantity of water and the whole of the aqueous liquid well washed with ether. Addition of ether precipitated a small quantity of a dark brown solid which was probably a mixture of resinols. The phenols were liberated by sulphuric acid, redissolved and reprecipitated, the aqueous solutions being extracted with ether.

Extraction of Bases and Neutral Oils.—The ethereal solution of oils insoluble in sodium hydroxide solution was shaken with excess of sulphuric acid, the aqueous solution made alkaline and extracted with ether yielding 8 g. of bases. The remaining neutral oils were freed from ether and distilled.

The Acids.

Acids (32 g.) were obtained representing 1.66 per cent. of the tar distillate. 10 g. were steam distilled and silver salts prepared from the four fractions in which the distillate was collected. The equivalents of the acids in each fraction were found to be 93.8, 100.2, 105.6 and 106.8, indicating that they might be mixtures of butyric (88) and valeric (102) acids with small quantities of higher acids.

After a preliminary fractionation at 35 mm., 20 g. of the acids were refractionated at a pressure of 27 mm. with the results shown in Table IV, the refractive index and equivalent of each fraction being determined, the latter by titration.

TABLE IV.

Fractionation of Acids : 20 g., 27 mm.

Fraction	Temp.	Distillate g.	n_D^{30}	Equivalent	Acid	n_D^{30}	Equivalent
1.	55— 60	0.5	1.3825	*n.d.*	C_3	1.383	74
2.	60— 70	1.5	1.3880	80.4			
3.	70— 80	1.0	1.3970	79.4			
4.	80— 90	1.0	1.4055	88.0	C_4	1.393	88
5.	90—100	0.5	1.4100	96.5			
6.	100—105	2.0	1.4200	95.0			
7.	105—110	2.0	1.4345	98.4	C_5	1.400	102
8.	110—115	1.0	1.4415	112.0			
9.	115—120	1.5	1.4500	113.4			
10.	120—125	1.0	1.4610	115.4	C_6	1.410	116
11.	125—130	1.0	1.4780	121.3			
12.	130—135	0.5	1.4905	129.7	C_7	1.417	130

Their general properties such as smell and solubility suggested that these acids might be the lower members of the aliphatic series, the equivalents of which are given in the last column. Comparison of the refractive indices showed however that this was not so in all cases, as the differences were far too great to be accounted for by experimental error. The first three fractions were readily soluble in water but the rest were not, while all except the first two smelt very strongly of butyric acid. The later fractions gave a slight yellow colour with ferric chloride and decolorized permanganate slowly in the cold. It is thus probable that the fractions 1 to 5 consisted mainly of propionic and butyric acids.

A review of the refractive indices of all the aliphatic acids with molecular weights below 130 revealed none approaching 1.47. Tiglic acid (m.w. 100) which has been observed in wood tar has a refractive index of 1.451 and may have been present in the middle fractions, but it could not be isolated. On precipitating the silver salt from fraction 12 and regenerating the acid, an impure solid melting at 62–65° was obtained, the quantity being too small for identification.

It would thus appear that in order to account for the high refractive index, aromatic compounds must have been present, and since even benzoic acid has a molecular weight of 122, the low equivalents must have been due to the presence of more than one acidic group. The higher fractions, therefore, probably contained dibasic aromatic acids, phenolic acids or even the higher phenols, since several of these are soluble in sodium carbonate solution. With the quantities available, further separation and identification were not possible.

The Bases.

The bases, 8 g. or 0.41 per cent. of the distilled tar, formed an extremely nauseous liquid. They were colourless, lighter than water and miscible with it, the higher boiling fractions only partially. They gave the carbylamine reaction and contained nitrogen. On distillation at atmospheric pressure 1.5 g. was obtained boiling between 40° and 100°, and 5.5 g. between 100° and 220°. The latter fraction had $n_D^{22}=1.3760$ and $d^{22}=0.984$, and yielded a solid picrate melting at 160–165°. Pyridine and its homologues were probably present, but in view of the obvious complexity of the mixture further investigation with the small quantities available appeared of no value.

The Phenols.

Fractionation.—The phenols isolated as already described and forming 59.7 per cent. of the redistilled tar were submitted to a preliminary fractionation at a pressure of 20 mm. in portions of 400 g. using 3 types of fractionating columns for comparative purposes. Table V gives the results of 3 distillations.

TABLE V.

Distillation of Phenols : 20 *mm.*

		Widmer			Young 4-bulb		Lebel-Henninger 3-bulb		
Fraction	Temp.	Dist.%	n_D^{30}	d_{30}^{30}	Dist.%	n_D^{30}	Dist. %	n_D^{30}	d_{30}^{30}
A	100–110	29.5	1.5300	1.064	6.2	1.5295	8.7	1.5290	1.064
B	110–120	16.7	1.5280	1.055	29.1	1.5305	30.7	1.5305	1.064
C	120–130	7.6	1.5250	1.046	13.5	1.5290	12.4	1.5280	1.061
D	130–140	4.5	1.5274	1.058	14.5	1.5308	6.8	1.5285	1.071
E	140–150	6.1	1.5400	1.115	6.2	1.5355	8.5	1.5360	1.096
F	150–160	13.6	1.5455	1.145	10.9	1.5440	19.7	1.5450	1.139
G	160–170	4.5	1.5435	1.137	7.5	1.5460			
H	170–180	3.8	1.5330	1.116	2.6	1.5470	3.4	1.5480	1.129

The Widmer column (*Helv. Chim. Acta*, 1924, **7**, 59) appeared to give the best separation and was used in subsequent distillations. Distillation at atmospheric pressure was found unsatisfactory as there was much resinification and a residue of 14.7 per cent., more than twice the amount under reduced pressure.

Fractions A and B were mixed and 740 g. were twice refractionated and collected in 12 fractions boiling between 86° and 121°/20 mm. Measurements of refractive index showed a considerable variation in the nature of these fractions. On nitration, picric acid was obtained from the first fractions and trinitro-*m*-cresol from those boiling between 90° and 103° but attempts to prepare other derivatives with acetic anhydride, chloracetic acid, benzoyl chloride, picric acid and *p*-nitrobenzoyl chloride were unsuccessful. Steam distillation was found of no value for effecting a separation. Qualitative tests showed a fairly regular gradation in properties ; for example, ferric chloride gave a yellow colour and barium hydrate no reaction with the first 7 fractions, while with the remaining 5, red and blue colorations were produced with these reagents. Silver nitrate was not reduced by the first 4 fractions but was acted upon slowly by the rest. It was thus evident that the mixture, consisting probably of mono-, di- and trihydroxyphenols, cresols, xylenols and their partly methylated derivatives was too complex to resolve by fractionation alone. It was therefore decided to demethylate each fraction so that only the phenols would have to be identified.

Demethylation.—Preliminary experiments showed that the fractions boiling up to 130° could be demethylated by heating with concentrated hydrochloric acid in sealed tubes at 120°. The higher-boiling fractions, however, did not yield so readily to this treatment, a prolonged heating period being required, the result of which was resinification. Better results were obtained by boiling the phenol with 6 times its volume of mixed acetic and hydrobromic acids in equal parts for 8 hours (*cf.* Stoermer, *Ber.*, 1908, **41**, 321). The whole of the phenols boiling below 140° were consequently treated by the former method and the remainder by the latter. In both cases the products were poured into water and the phenols extracted with ether and washed with sodium carbonate solution. After removing the solvent the residue was steam distilled and the phenols recovered with ether. This effected a separation of the monohydroxyphenols which are volatile in steam and the polyhydroxy-compounds which are non-volatile. Table VI shows the percentage methoxyl content of the fractions before and after treatment with acid and the approximate composition. Demethylation was not quite complete in the case of the higher fractions but was sufficient to permit of tests for the components of the mixture.

TABLE VI.

Composition of Phenol Fractions.

Fractions	A+B	C	D	E	F	G+H
Initial OMe ..	7.8	6.8	9.0	11.9	16.0	4.0
Final OMe	0.0	0.0	0.6	1.4	2.0	*n.d.*
Monohydroxyphenols per cent. on total phenols.	15.3	4.3	2.2	1.4	1.8	1.0
Polyhydroxyphenols and derivatives ..	16.8	6.3	8.4	4.5	5.8	2.4
OMe in above ..	16.8	14.4	15.5	16.0	18.6	16.7
Decomposed, per cent. ..	3.9	2.8	4.0	0.3	3.8	6.7

The quantities of monohydroxyphenols are those actually found, calculated as percentages on the total phenols. The amounts of polyhydroxyphenols and derivatives are calculated from the quantity of polyhydroxyphenols obtained after demethylation assuming that the whole of the methoxyl in the fraction was originally combined with them. The methoxyl content of these compounds in all the fractions calculated with the same assumption is not far from 17 per cent. indicating that the constituents are mainly monomethoxy-compounds mixed with smaller amounts of polyhydroxyphenols. All the figures are necessarily very approximate as a comparatively large proportion of each fraction decomposed during the operation of demethylation, as shown in the last line of the table.

Identification of Phenols.

(*a*) *Monohydroxyphenols.*—The steam-volatile products obtained after demethylation were separately fractionated at atmospheric pressure and the density and refractive index of each fraction measured. The results are shown in Table VII.

The first column gives the total weight of the original fraction after distillation with the Widmer column. In several cases only a portion was demethylated and steam distilled, but the weights of monophenols are calculated for the whole fraction from the weights actually obtained. In the same way the figures in the last column give the values which would have been obtained had the whole original fraction been demethylated and distilled.

With the exception of the first two fractions which appeared to contain an impurity with low refractive index (possibly small quantities of acids not extracted by sodium carbonate), the physical properties of the lower boiling fractions indicated that they consisted mainly of the three cresols with, perhaps, a little phenol.

Phenol was identified in fractions 1, 2 and 3 by preparation of the benzoate and by nitration to picric acid ; *o*-, *m*- and *p*-cresols were distinguished by condensation with chloracetic acid and fractional crystallisation of the resulting oxyacetic acids from cold benzene (*cf.* Lederer, *D.R.P.*, 79514). The sparingly soluble acid melting at 151–152° corresponding with *o*-cresol (mixed melting point with *o*-cresoxyacetic acid 151°) was found in fractions 2, 3 and 4 ; the more readily soluble derivative of *p*-cresol m.p. 135–136° (mixed m.p. 135°) in fractions 3 and 4, while fractions 4, 5, 6, 7 and 8 yielded the *m*-cresol derivative, m.p. 102° (mixed m.p. 102°; $C=65.1$, $H=6.0$; $C_9H_{10}O_3$, *m*-cresoxyacetic acid, requires $C=64.9$, $H=6.4$ per cent.). Nitration of these fractions gave trinitro-*m*-cresol m.p. 105°, and the benzoate of *p*-cresol was obtained from fractions 3 and 4. It appeared probable that the higher-boiling fractions might contain xylenols, but their identification was a matter of some difficulty owing to the small quantity of material available and the conflicting data found in literature regarding their properties. An indication of those which were present in appreciable quantities was obtained by brominating the mixture in carbon tetrachloride solution, distilling the solvent and leaving the product in the ice chest until crystallisation took place. The crystals were separated and submitted to a number of fractional crystallisations from alcohol. In this way two substances melting at 179–180° and 165° were obtained from

TABLE VII.

Distillation of Steam-Volatile Phenols: 680 mm.

Fraction	Wt. distilled g.	No.	B.P.	d_{30}^{30}	n_D^{30}	FeCl$_3$	Wt. of distillate	Percentage on total distilled phenols.
A+B. 461 g. Monophenols 197 g.	68	1	160–180	1.037	1.4930	Violet.	1	0.3
		2	180–185	1.039	1.5250	Blue.	2	0.6
		3	185–190	1.036	1.5355	,,	9	2.7
		4	190–193	1.033	1.5380	,,	11	3.3
		5	193–195	1.028	1.5370	,,	3	0.9
		6	195–200	1.025	1.5370	,,	9	2.7
		7	200–205	1.018	1.5345	,,	5	1.5
		8	205–215	1.017	1.5320	Bl.-gr.	10	3.0
			Residue				13	3.9
C. 75 g. Monophenols 24.5 g.	24.5	9	190–198	1.007	1.5185	Gr.-y.	2	0.2
		10	198–200	1.014	1.5275	Blue.	4	0.4
		11	200–205	1.017	1.5300	,,	3	0.3
		12	205–210	1.016	1.5280	Bl.-gr.	4	0.4
		13	210–215	1.018	1.5290	,,	3	0.3
		14	215–220	1.016	1.5280	,,	3.5	0.4
		15	220–225	1.013	1.5280	Gr.-y.	2	0.2
		16	225–230	1.040	1.5290	,,	2	0.2
D. 160 g. Monophenols 25 g.	15	17	200–210	1.015	1.5210	Yellow.	1.5	0.3
		18	210–215	1.016	1.5300	,,	3	0.5
		19	215–220	1.015	1.5300	,,	2.5	0.4
		20	220–225	1.015	1.5275	,,	2	0.3
		21	225–230	1.018	1.5280	Gr.-y.	1.5	0.3
		22	230–240	1.031	1.5305	,,	1.5	0.3
E. 60 g. Monophenols 16.5 g.	5.5	23	210–230	1.02	1.5275	Green.	4	1.2
F. 136 g. Monophenols 31 g.	8	24	200–240	1.03	1.5290	,,	6	2.4
G+H. 84 g. Monophenols 6.5 g.	3	25	230–240	1.03	1.5305	,,	2	0.4

fraction 13 (b.p. 210–215°) and one melting at 165° from fraction 14. 1:3:4-xylenol and 1:4:5-xylenol boil at approximately 208° and 210° at 680 mm. and their bromides both melt at 179°. A good yield of an oxyacetic acid m.p. 118° which is the melting point of the oxyacetic acid of 1:4:5-xylenol was obtained from fraction 6 (b.p. 195–200°) indicating the probable presence of this isomer and thus it seems likely that the bromide isolated from fraction 13 is also derived from the 1:4:5-compound. Too much attention must not be paid to the discrepancy in boiling points owing to the complexity of the mixtures which were being distilled. The bromide melting at 165° from fraction 13 was readily soluble in alcohol and appeared to be derived from 1:3:5-xylenol (b.p. 216°) the bromide of which melts at 162.5° according to Noelting and Forel (*Ber.*, 1885, **18**. 2679) and at 166° according to Thol (*Ber.*, 1885, **18**, 362). On the other hand the product melting at 165° from fraction 14 was sparingly soluble in hot alcohol and appeared to be the bromide of 1:2:4-xylenol (b.p. 223°), although recrystallisation failed to raise the melting point, which according to Jacobson (*Ber.*, 1878, **11**. 28) should be 169°.

Although the above evidence cannot be regarded as conclusive, it seems highly probable that 1:4:5-, 1:3:5- and 1:2:4-xylenols were among the phenolic constituents, and 1:3:4-xylenol may have been present as well. All attempts to prepare derivatives from the higher fractions have so far failed and thus it is not possible even to indicate their probable composition.

Quantitative estimation.—Attempts were made to estimate the amounts of different phenols in the lower fractions by the method of Redman, Weith and Brock (*Ind. Eng. Chem.*, 1913, **5**. 831) which depends on the formation of di-iodo-compounds by *o*- and *p*-cresol and tri-iodo-compounds by phenol and *m*-cresol. Even when three phenols are present the method is not one of great accuracy, as small experimental errors are largely magnified in the final results; if there are four phenols, or if impurities are present, it is only possible to form a very rough estimate of the total amount of *o*- and *p*-cresol together and of each of the other two. As the quantities of demethylated monophenols after distillation were small, material for this estimation was obtained from fractions A and B distilled with the Lebel column and weighing 170 g. (Table V) which were refractionated at atmospheric pressure and divided into four fractions boiling over the range 180–190° (10 g.), 190–200° (55 g.), 200-210° (60 g.) and 210–230° (45 g.). The results indicated 82 per cent. of *o*- and *p*-cresol and 18 per cent. of phenol in the first fraction and 86 per cent. of *o*- and *p*-cresol and 14 per cent. of *m*-cresol in the second fraction. *m*-Cresol was estimated independently by Raschig's nitration method in the two middle fractions which were found to contain 14 and 6 per cent. Determinations of the amount of phenol in the first fraction were also made by nitration to picric acid, the result being 21 per cent. Calculated as percentages on the total distilled phenols the quantities found by titration are:—phenol 0.42, *m*-cresol 1.8, *o*- and *p*-cresols 13.0 and by nitration, phenol 0.48, *m*-cresol 2.6. Of these values, those for phenol and *m*-cresol are probably low, as not all the nitro-derivatives could be recovered, while the figure for the two remaining cresols is likely to be high since the titration value for *m*-cresol is low.

An approximation to the quantities of cresols and xylenols present can also be obtained from Table VII, taking as a rough guide the colours with ferric chloride which are blue for cresols and blue-green for xylenols, and noting that xylenol derivatives were isolated from fractions 6, 13 and 14. The density of *o*-cresol at 30° is 1.041, of *p*- and *m*-cresols 1.031 and of the xylenols about 1.017. This enables an estimate to be made of the relative amounts of cresols and xylenols in the rather large fractions 5–8 assuming no other substances to be present. Fractions 1 and 9 appear to contain an impurity with low density and refractive index, possibly acid decomposition products formed on demethylation. Fraction 1 was found to contain 51 per cent. of phenol by nitration. With these premises the quantities of monophenols in the different fractions are as shown in Table VIII.

TABLE VIII.

Quantities of Monophenols as Percentage of Total Phenols.

Fraction	1	2	3	4	5	6	7	8	9	10	11–14	15–17	18–25	Total
phenol ..	0.15	0.35												0.5
o- and *p*-cresol		0.25	2.7	3.1	0.2									6.25
m-cresol ..				0.2	0.5	1.4	0.1	0.1	0.0	0.1				2.4
xylenols ..					0.2	1.3	1.4	2.9	0.05	0.3	1.4	0.3		7.8
other phenols												0.4	5.8	6.2

It will be observed that a considerable proportion of the phenols occurs in the higher boiling fractions, but it has not been found possible to isolate any definite compounds.

(*b*) *Polyhydroxyphenols.*—The non-steam-volatile residue of demethy'ated phenols from fractions A and B (*cf.* Table VI), after extraction with ether and drying weighed 76 g. This was distilled at 20 mm. pressure and gave 42 g. boiling from 130-160° and 8 g. from 160–200°. The first distillate formed a mass of fine crystals on stirring. The whole was extracted with dry benzene and from the concentrated solution crystals were obtained which after two crystallisations from alcohol melted sharply at 104° and gave all the usual tests for catechol. The bromine derivative melted at 139°. The more soluble portion after several crystallisations from alcohol yielded homocatechol m.p. 52° (m.p. of bromine derivative 162–163°). The formation of catechol after demethylation indicates the presence of guaiacol in the tar. This was further confirmed by the preparation of dinitroguaiacol by addition at zero of fuming nitric acid to the phenol fraction boiling at 113–115°/ 20 mm. (*cf.* p. 46) both in glacial acetic acid solution. It was recrystallised from methyl alcohol and melted at 122° (Found: N, 12.82 ; $C_7H_6O_6N_2$ requires 13.08 per cent.). It was evident that other substances were present but it was not found possible to isolate any of them. The higher boiling fraction, 160-200° formed a jelly-like mass which could not be crystallised from any ordinary solvents.

The higher boiling fractions C-H, Table V, were even more troublesome. After refractionation at 680 mm. of a portion of the distillate boiling at 140–180°/ 20 mm., a fraction boiling at 238–240° was obtained which gave the colour tests for coerulignol, $C_3H_7.C_6H_3(OH).OCH_3$ and contained 16.0 per cent. methoxyl, the value for coerulignol being 18.7. It is probable therefore that this substance, which has been previously found in wood tar (Pastrovitch, *Monatsh.*, 1883, 4, 188), was present. The fraction 243–244° after demethylation gave the fluorescein test indicating the presence of resorcinol, although the phenol itself could not be isolated. Resorcinol monomethyl ether (b.p. 240°/680 mm.) appeared to be a likely constituent. The higher fractions gave sodium and potassium salts which became blue in air and deep red on subsequent addition of acid. This reaction is given by pyrogallol and methyl pyrogallol dimethyl ethers and consequently the fraction was demethylated. This caused a considerable amount of resinification and the fraction boiling between 290° and 300° set to a jelly from which it was not possible to obtain crystals. The aqueous alkaline solution, however, rapidly darkened when exposed to air so that pyrogallol was probably present.

In order to form an estimate of the amount of guaiacol, 45 g. of a phenol fraction boiling at 185–215° was redistilled at atmospheric pressure and the methoxyl content of each fraction determined. A higher boiling fraction 220 g. 140–180°/20 mm. was treated in a similar manner. Table IX gives the results and the weight of each fraction.

TABLE IX.

Amount of Methoxy-compounds in Phenol Fractions.

B. P.	Weight g.	OMe per cent.	Guaiacol (202°)	Creosol (217°)
185–190	8	6.1	1.9	
190–195	5	7.4	1.5	
195–200	7	10.3	2.9	
200–205	7	8.0	2.2	
205–210	5.5	7.4	0.8	0.9
210–215	6	11.0	0.4	2.5
			Coerulignol (237°)	Pyrogallol dimethyl ether (249°)
240–245	8	15.6	1.2	2.5
245–250	21	....	1	6
250–255	29	12.8		9.2
255–260	44	10.4		11.5
260–265	34	15.9		13.5
265–270	18	11.8		5.3
270–290	19	....		

Assuming that guaiacol, creosol, coerulignol and pyrogallol dimethyl ether are the only methoxy-compounds present, an approximation to the amount of each may be calculated since their methoxyl values are 25.2, 22.4, 18.6 and 40.2 respectively. The resulting weights in grams are shown in the table, arbitrary values being assigned for the fractions which contain two ethers. Calculated as percentages on the total phenols the amounts are :—Guaiacol 8.6, creosol 3.0, coerulignol 0.32, higher phenols as pyrogallol dimethyl ether 6.9. The middle fractions were not investigated in detail. That boiling from 215 to 230° formed 13 per cent. of the total phenols and probably contained most of the creosol. It corresponded with the fraction 120–130°/20 mm., the methoxyl value of which was 6.8 so that the approximate creosol content was 4 per cent. of the total phenols. The fraction 230–240° was only 3.5 per cent. and its methoxyl value about 9. Assuming coerulignol to be the only ether present, the amount would be 1.7 per cent. The total quantity of creosol would thus be 7 per cent. and of coerulignol 2.0. A mixture containing these amounts and the quantities of the other two ethers already given, namely, 8.6 and 6.9, would have a methoxyl value of 6.9, corresponding closely with the value 7.0 calculated for the total phenols from the methoxyl values of the different fractions given in Table VI. It was found however that the methoxyl value of the mixed phenols before fractionation was 11.0. This indicates that there is decomposition on distillation and that the residual products contain a high proportion of methoxyl.

The Neutral Oils.

The neutral oils which formed 37 per cent. of the tar distillate were pale brown, had $d_{30}^{30}=0.980$, $n_D^{30}=1.4985$ and a methoxyl content of 4.4 per cent. On distillation at 680 mm., the boiling point ranged from 120° to 300°, the density at 25° of fractions collected every 10° rose from 0.947 to 0.990 and the refractive index at the same temperature from 1.479 to 1.549; 11 per cent. distilled between 200° and 210° and 32 per cent. between 230° and 260°. The fractions boiling between 240–280° darkened on exposure to air but the others were unchanged. On treating 25 g. with 80 per cent. sulphuric acid, which according to Egloff and Morrell (*Ind. Eng. Chem.*, 1926, **18**, 354) reacts only with unsaturated bodies, a residue of 14.0 g. was left, and on nitration all dissolved except 0.5 g. To determine the phenolic ethers, 20 g. were demethylated with hydrochloric acid and the resulting phenols extracted with sodium hydroxide, 5 g. of phenols and 13 g. of unattacked residue being obtained. Since the methoxyl content of the original oil was 4.4 per cent. it may be calculated that 29.4 per cent. of phenolic ethers with a methoxy-content of 15 per cent. were present. The latter value is low, the figure for creosol methyl ether being 24.6. It is to be inferred, apart from experimental error which may be large, that the phenolic ethers present were of comparatively high molecular weight or that some bodies soluble in sodium hydroxide were produced by hydrolysis from compounds other than methoxy-derivatives. In either case it is improbable that polymethoxy-compounds were present in appreciable quantity. The composition of the neutral oil thus appears to be: unsaturated compounds 44, phenolic ethers 30, other aromatic derivatives 24, paraffins 2 per cent.

Summary.

1. Bhadravati refined tar has been separated by treatment with organic solvents into (*a*) a brittle solid, 13–18 per cent. according to the solvent used; (*b*) neutral oils, 35 per cent.; (*c*) phenols and other acidic bodies, 51–44 per cent. The latter on distillation yielded 28–30 per cent. of volatile compounds and a resinous residue.

2. Direct extraction of the tar with sodium hydroxide solution gave only 20 per cent. of neutral oils, but the volatile phenols amounted to 30–35 per cent.

3. On distillation at reduced pressure the average amount of distillate was 35 per cent. and on redistillation 33 per cent. This contained acids 1.66, bases 0.41, phenols 60 and neutral oils 37 per cent.

4. About 25 per cent of the acids consisted of propionic and butyric acids the remainder being a complex mixture of phenolic acids and possibly higher aliphatic acids.

5. The phenols which formed the greater part of the distillate yielded after demethylation 26 per cent. of monophenols and 37 per cent. of polyphenols corresponding with 44 per cent. of original phenolic ethers, the loss on demethylation being considerable. Among the monophenols the following were identified :—Phenol (0.5), *o*- and *p*-cresols (6.3), *m*-cresol (2.4), 1:4:5-, 1:3:5-, 1:2: 4-xylenols and probably the 1:3: 4-isomer (7.8 per cent.). The higher monophenols boiling from 215° to 240° and forming 6.2 per cent. of the total phenols could not be separated sufficiently for identification. The polyphenols were present partly as such and partly as methylated derivatives, but the method adopted did not enable a separate examination of the two classes to be made. The more important methylated products were guaiacol (8.6), ✓ creosol (7), coerulignol (2.0), pyrogallol dimethyl ether and higher boiling ethers calculated as this substance (6.9 per cent.). In all cases the figures for the quantities must be regarded as very approximate owing to incomplete separation and the decomposition occurring at every stage.

6. The neutral oils forming 37 per cent. of the distillate were found to contain 44 per cent. of unsaturated compounds, 30 per cent. of phenolic ethers (probably a high value, 20 being more likely), 24 per cent. of other aromatic derivatives and 2 per cent. of paraffins.

II. THE PRODUCTION OF LAMP-BLACK.

A possible method of utilizing the tar or certain fractions of it would be to burn it for the production of lamp-black. Some experiments were consequently made with a view to determining the suitability of the material for this purpose. Small-scale trials showed at once that the incomplete combustion of the tar was difficult to effect. On heating in a crucible to about 140° the vapours could be ignited, and on lowering a water-cooled metallic cup into the flame until the smokiness reached a maximum, a deposit of carbonaceous material was obtained. After a short time, however, a crust formed on the surface of the liquid which had to be broken in order to allow the combustion to proceed regularly and when no more volatile material could be obtained, a large residue remained in the crucible.

Experiments were made with samples of the refined tar used in part I and also with the crude settled tar and a variety described as 'pitch tar'. The average yields were 4.5, 5.5 and 4.0 per cent. respectively, and the products were almost identical in properties, bearing a close resemblance to carbon black of good quality.

The specific gravity of all three samples was 1.70 and the 'free carbon' after toluene extraction 97 per cent., corresponding figures for the carbon black examined being 1.74 and 94.5. The acetone extract was nearly colourless.

Under the microscope the black was seen to consist of fairly uniform, opaque, amorphous particles approximately the same size as those of the carbon black. On attempting to make a comparison with samples of 'lamp black' bought locally it was found that these were grossly adulterated, the ash varying from 15 to 63 per cent.

Comparative measurements of tinting power were made by thoroughly mixing a small quantity of the sample with white lead, moistening with a definite amount of oil and rubbing the mixture for a short time on a porcelain tile. Small squares of each mixture were painted on a white tile and their tints compared, the comparison being facilitated by covering all the squares not under observation and the unpainted portions of the tile with black paper. A sample of the local lamp-black was examined and also a pigment made by grinding the pitch which remained after distilling the tar. Table I shows the percentage of black which was required to produce the same tint as the amount of carbon black given in the first line.

TABLE I.

Percentage of Black required to match Carbon Black White Lead Mixtures.

Carbon Black	..	0.1	0.2	0.3	0.4	0.5
Refined Tar Black	..	0.1	0.2	0.33	0.5	..
Crude Tar Black	..	..	0.1	0.2	0.3	0.4
Pitch Tar Black	..	..	0.1	0.2	0.3	0.4
'Lamp Black'	..	5	..	20	..	..
Pitch ..	..	3	..	5	..	10

It is thus evident that it is possible to prepare in the laboratory a tar black which is of high quality and nearly identical in properties with carbon black, but it does not follow that the same result can be obtained on a large scale. A few attempts were made to burn the tar with a regulated amount of air by means of a variable jet oil burner. This was built into the end of a brick chamber 2×3×5 feet lined with sheet iron, the top being covered with a shallow iron tank containing water. The tar after heating to about 100° was filtered and supplied to the burner at a pressure of about 40 ℔s. per square inch, the feed pipe being heated to 130–140°, the ignition temperature of the tar. Compressed air was supplied to effect atomization. With these arrangements the tar could be burnt when there was a plentiful supply of air, but on reducing the amount it was found very difficult to maintain a flame in spite of a red hot brick upon which the atomized tar was allowed to impinge. Carbonaceous deposits formed on the burner and choked it, while the small quantity of sooty material that formed was so contaminated with hard unburnt particles that it was useless, except possibly for grinding to form a low grade pigment.

It is probable that the tar could be burnt on a rotating drum dipping into a feed tank and furnished with a scraper to remove unburnt matter, but the process would require very close attention and the cost of maintenance would be considerable, so that it is doubtful if lamp-black from this source could compete with that produced from more readily combustible materials.

Summary.

A black practically identical with good quality carbon black can be obtained in the laboratory by the incomplete combustion of wood tar. On a larger scale, difficulties connected with the burning of the tar render it unlikely that the process could be developed commercially.

III. THE DISINFECTING POWER OF THE PHENOLS.

In order to ascertain the value of the phenolic bodies in the distillate when used as disinfectants, determinations of the phenol coefficients of different fractions were made. The Rideal-Walker method (*Amer. J. Public Health*, 1913, **3**, 575) was used and found to give concordant results, the organism being *B. Typhosus* (Hopkins) which was subcultured 4 times from a strain on agar slant. The fifth generation when tested with standard phenol at a dilution of 1 in 105 lived for 5 minutes but was killed in 7½.

The phenols obtained in the manner described in part I and fractionated as shown in Table V (p. 45) were used for the tests. A small fraction boiling from 90–100°/20 mm. was also examined, and for the sake of comparison the coefficient of the unfractionated neutral oils was determined. In all cases a 1 per cent. stock solution was prepared using 1 per cent. soap solution as diluent; these solutions were clear and homogeneous in the case of the first 7 fractions but the last two fractions formed emulsions. The culture (0.5 c.c.) was added to 5 c.c. of the disinfectant at 24° and the greatest dilution which would kill the bacteria in 10 minutes determined in the usual manner. The values of the phenol coefficients calculated from these results are shown in Table I which also gives the boiling point of the fraction at 20 mm. and indicates its main constituents.

TABLE I.

Phenol Coefficients of different Phenol Fractions.

B. P. of fraction, 20 mm.	Main Components	Phenol coefficient
90–100	Phenol, *o*- and *p*-cresols	2.8
100–110	*o*- *m*- *p*- Cresols, guaiacol	4.5
110–120	Guaiacol, xylenols, creosol	7.9
120–130	Do.	8.7
130–140	Creosol, coerulignol, pyrogallol ethers	9.0
140–150	Coerulignol, pyrogallol ethers	10.0
150–160	Pyrogallol ethers and homologues	6.6
160–170	Do.	5.8
170–180	Do.	3.6
Neutral Oil	.. .. ..	2.7

The activity thus rises to a maximum for the fraction boiling between 140° and 150°, or about 250° at atmospheric pressure and the figures confirm the observation of Morgan and Cooper (8th *International Congress App. Chem.*, 1908, **19**, 243) that the bactericidal power is enhanced by the introduction of hydroxy, methoxy and alkyl groups into the benzene nucleus. No reason can be assigned for the decrease of the phenol coefficients of the higher fractions since the constituents of these fractions are not known.

IV. THE CRACKING OF WOOD TAR.

As the quantity of useful constituents of the tar which could be obtained by distillation was comparatively low, it was considered of interest to see if the yield could be increased by cracking. To effect this the tar was run at the rate of about 5g./min. into an iron tube 4 cm. in diameter and 100 cm. long inclined to the horizontal at an angle of 30°, which could be heated electrically. Screw caps were fitted at the ends to enable the tube to be cleaned, an operation which had to be conducted at the end of every experiment as voluminous deposits of pitch were formed which sometimes choked the pipe, particularly in the early experiments in which the tube was less steeply inclined. The products were passed through a condenser and collected in receivers cooled in a freezing mixture. The uncondensed gas was collected in a gas-holder or in some cases partly condensed by cooling to liquid air temperature.

The distillate was separated into acidic bodies and neutral oils by treatment with 20 per cent. sodium hydroxide solution. The gas was analysed for carbon monoxide, carbon dioxide and unsaturated hydrocarbons, hydrogen and saturated hydrocarbons being determined by difference since they could not be estimated by any simple process in the absence of knowledge regarding the actual gases present. Table I shows the weight of products per 100 g. of tar at 4 different temperatures, the pressure being atmospheric. For comparison the average results of distillation are given in the last line, the maximum temperature being about 260°. Table II gives the composition of the gas.

TABLE I.

Cracking of Tar at Different Temperatures.

Temperature		Weight cracked	Distillate	Gas	Residue	Acidic bodies	Neutral oils
400	..	198	72.2	1.9	25.9	43.4	28.8
500	..	220	64.1	4.8	31.1	43.3	20.8
550	..	160	62.5	6.8	30.7	43.2	19.3
600	..	117	62.4	9.2	28.4	44.0	18.4
Distn.	..	..	36	..	64	22	14

TABLE II.

Composition of the Gases.

Temperature		Carbon monoxide	Carbon dioxide	Unsaturated hydrocarbons	Hydrogen and saturated hydrocarbons
400	..	15.8	14.3	7.9	58.6
500	..	20.8	13.2	11.6	54.4
550	..	34.7	10.6	17.8	36.8
600	..	33.5	4.4	20.1	42.0

From these figures it is evident that cracking gives a far larger yield of volatile products than simple distillation. Variation of temperature over the range studied did not produce as much change in the yield of distillate as might have been expected, the amount of acidic bodies remaining nearly constant. The neutral oils appeared to decompose progressively with rise in temperature giving pitch and gas containing increasing amounts of carbon monoxide and unsaturated hydrocarbons. The phenolic bodies obtained at 400° and 600° were fractionally distilled and were found to differ somewhat in composition, those obtained at the lower temperature boiling almost entirely between 210° and 270° (87 per cent.) and the others giving 25 per cent. boiling at 190–210° and 45 per cent. at 250–295°. In the absence of larger quantities of material a more detailed examination was not made.

The high yield of volatile products obtained by passing the tar through a hot tube indicates the advisability of examining the method in greater detail and of determining the effect of pressure.

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