

## SOME ASPECTS OF THE CONSTITUTION OF COAL

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The last ten years have witnessed rapid strides in our knowledge of the complex nature and constitution of coal. The recent contributions from the physical techniques e.g. infra-red, nuclear magnetic resonance, X-ray and van Krevelen et al's statistical approaches have given a new impetus to the study of coal science as a result of which various models<sup>1,2</sup> of the structural 'unit' of coal have been suggested from time to time. However, the problem of coal constitution is ultimately a chemical one and in the long run sanction of chemical approaches have to be sought for any structure proposed for coal, irrespective of the technique employed in formulating the model. In the past, extensive studies on the oxidation, reduction, halogenation, pyrolysis etc. of coal had been carried out but the data, though informative, failed to unravel the intricate chemical structure of coal in the orthodox chemical sense, nor did they yield any significant information on the structural parameters of coal, an essential prerequisite for hypothesizing a model structure. However, as a result of recent studies an attempt may now possibly be made to make tentative proposals based on the information on the state of carbon, hydrogen and oxygen in coal<sup>3-13</sup>.

### Oxygen in Coal

Though there is still divergence of opinion regarding the actual values of hydroxyl, carbonyl and carboxyl oxygen groups in coal, a fair order of estimate particularly for hydroxyl is now available<sup>14</sup>. 50-60 per cent of the total oxygen in coal, at least in lower ranks ( $C < 85-86\%$ ) is found to be in the form of hydroxyl groups, and the rest appears to be present in small amounts as carbonyl, carboxyl and ether and/or heterocyclic oxygen groups. In higher rank coals ( $C > 86\%$ ) few of the functional oxygen groups are believed to be present, but the major part of oxygen remains unaccounted for.

### State of Carbon and Hydrogen in Coal:

Oxidation & Dehydrogenation Studies: The work of Bone, Wheeler and their collaborators<sup>15</sup> in the early twenties and of Horton<sup>16</sup> and others established that aromaticity of coals increased with increase of the rank. But, for precise determination of aromaticity obviously a method of controlled oxidation was needed which would selectively oxidise the non-aromatic part of the coal structure. Such a method of oxidation was recently advanced<sup>4</sup> by the present writers. It was shown that prolonged oxidation of coal in air at 170°C was chiefly restricted to the non-aromatic structures of coal, leaving the aromatic carbon skeleton practically intact. Such an approach, supported by further work<sup>7,17</sup> led to a number of deductions regarding aromaticity, forms of hydrogen, the size of the aromatic nucleus, and an assessment of the dimensions of the aliphatic side-chains in a coal unit. These deductions are presented in Tables 1 and 2.

The recent studies on dehydrogenation<sup>10,11,12,13</sup> of coals have thrown some fresh light on the problem. The non-aromatic carbon structure of coal has so far been assumed to be only aliphatic in nature. Dehydrogenation studies by Vesterberg's technique and with halogens<sup>18</sup>, appear to indicate that the non-aromatic part may be largely constituted of alicyclic carbon. Similar indications have since been obtained by Ergun<sup>19</sup> from x-ray studies.

The presence of hydroaromatic or alicyclic structure was, however, first suggested by Weiler<sup>20</sup> on the score of the dehydrohalogenation phenomenon (which he called "spitting").

Quantitative measurement of alicyclic carbon and hydrogen from dehydrogenation studies show that a considerable proportion of carbon in bituminous coal is in alicyclic form (10-25%) and also that the alicyclicity progressively diminishes with increase in the rank of coal. Anthracite does not contain any alicyclic carbon nor does it undergo any dehydrogenation.

The chief objection<sup>21</sup> to this technique (Vesterberg's) for quantitative measurement of alicyclicity of coals has been that the method may not selectively dehydrogenate alicyclic carbon alone and that aromatic carbon may also be affected to some degree. Further studies<sup>13</sup> have, however, shown that only a minor part of dehydrogenation may be due to some side-reactions (possibly cross-linking) with aromatic positions and there does not appear to be any doubt, that the method is fairly reliable (as far as coal is concerned). Corrections have now been made for such possible stray side-reactions and the new set of values for alicyclicity of coal derived, are presented in Table 3.

It may appear strange, but statistical and experimental facts seem to indicate that the sum of aromatic and alicyclic carbon percentage is virtually constant (0.87 ± 0.03) as will be seen from Table 4.

If this be true, then obviously the value for the percentage of aliphatic carbon can be deduced from experimentally determined values of aromaticity and alicyclicity, and naturally the value for aliphatic carbon percentage in coals will also be nearly constant. This value is between 10-15%: it may, however, be somewhat on the higher side, as it is likely that the values for alicyclicity presented here is likely to err on the minimum side. Be that as it may, the constant nature of the aliphatic carbon in coal (if this be the case) would appear to be a remarkable fact, for which no explanation can be offered at this stage.

It was suggested<sup>9</sup> earlier that the aliphatic side-chains present in coal should be small and even as small as in methyl group, and certainly not longer than in an ethyl group. The estimation of C-methyl content by Kunn and Koth's reaction<sup>22,23,24</sup> yielded a value of 2 to 4% of the carbon present as methyl group in coal. It is possible that this value is also on the lower side, as the aromatically linked methyl group may not be estimated quantitatively by this technique<sup>25</sup>. Exhaustive chlorination<sup>26</sup> on the other hand gave a higher estimate of C-methyl content i.e., 6-7% of the carbon. The agreement between the experimental values and those theoretically deduced as far as the order is concerned may or may not be significant. Further refinement in the techniques of determination of aliphaticity in coals should prove to be of great value.

#### The Alicyclic Structure in Coals

The formation of tar is completely inhibited when a dehydrogenated coal is carbonized. There is, also, a proportionate increase in the yield of char. The additional carbon 'fixed' in the char is apparently proportional and almost equal in value to the alicyclic carbon estimated directly<sup>10,11,13</sup>. Therefore, it may not be illogical to conclude that tar has its origin in the alicyclic structures of coal<sup>12</sup>. The complete inhibition of tar formation by any method of dehydrogenation (even by air/oxygen)<sup>27</sup> is also significant.

van Krevelen and Fitzgerald recently concluded<sup>23</sup> that "that part of coal structure which yields tar must be weakly linked or not at all bonded to the remainder". A study on the extent of the inhibition of tar formation with varying degrees of dehydrogenation (Fig.1) also leads to a similar conclusion<sup>13</sup>. The complete inhibition of tar formation, however, does not appear to depend on the completeness of the dehydrogenation but a minimum quantity of the dehydrogenating agent (sulphur) is apparently needed for the maximum inhibition (Fig.1). It appears probable that simultaneously with dehydrogenation, a condensation reaction (possibly by cyclo-dehydrogenation) between the alicyclic part and the rest of the coal structure is possibly initiated. The action of sulphuric and

phosphoric acids<sup>29</sup>, phosphoryl oxychloride<sup>30</sup>, even Scholl's reagent<sup>31</sup> also appear to have similar effects on inhibition of tar formation and probably through a similar mechanism of condensation reaction, leading to fixation of the alicyclic carbon in the char.

Another significant fact is that on dehydrogenation or even in condensation reactions mentioned above, nearly 92% of the total carbon in coal is found to be retained in the char (600°C) on carbonization, irrespective of the rank of coal so treated from lignite upto the high rank bituminous coals. Normally, in carbonization only 70-80% of the carbon is fixed in the coke or char at 600°C. Thus, the 'extra' carbon retained in char is of the order of 10-22% of the total carbon in coal, which corresponds to the values of alicyclic carbon determined directly by dehydrogenation reactions. The proportion of carbon normally fixed in coke and char on carbonization at 600°C corresponds to the aromatic carbon in coal<sup>32</sup>. The additional carbon fixed on treatments mentioned above and the constancy of the value at about 92%, again, appears to correspond to the sum of aromatic and alicyclic carbon, irrespective of the rank of coal.

This would indicate that in course of coalification enrichment of aromatic carbon takes place at the expense of alicyclic carbon (and possibly derived from it), the sum total of the two being constant.

#### Stages in Coalification :

The progressive increase in aromaticity in coal (at the expense of alicyclic carbon) during coalification must be a very slow process and a gradual one. One may, therefore, envisage a 'parent' coal unit at any particular stage of evolution which will vary in aromaticity, alicyclic carbon and ring size. This concept of the evolution of coal with increasing rank may be hypothetically illustrated in terms of the structural models shown in Fig. 2.

The model I, C = 68%, may be arbitrarily assumed to be the 'parent' structural unit of coal, existing in the lignitic stage (there may be other structural units, but the model I may be conceived to be as the predominant species at this level). Decarboxylation and partial dehydroxylation (which are believed to be the major reactions in the evolution of coal in the lower ranks) of model I can lead to the stage of model II, C = 79%. The model IIIA, C = 91% is envisaged to be the transitional stage marked by the completion of the decarboxylation, dehydroxylation and dehydrogenation of the alicyclic ring and its fusion with the aromatic nucleus. Partial demethylation may also occur between the stage II and IIIA.

The transitory nature of these structures is to be emphasised at any particular stage of the rank evolution of coal. Decarboxylation may be largely completed at or near about 80% carbon coal but the process may continue well after this stage is reached. Small amounts of carboxylic oxygen can still be detected even in 84-85% carbon coal. Dehydrogenation of the alicyclic ring and ring-closure by cyclodehydrogenation (model II & IIIA) may constitute the major steps in the bituminous coal range.

The properties of the three hypothetical structures designed to portray the three important transition steps in rank-evolution may be depicted as in Table 5.

The analysis of structure IIIA (Table 5) broadly represents a typical high rank bituminous coal (C = 91%) having 91% aromatic carbon. This 'unit' given in the model is presumed to be the most predominant one present at 91% carbon level. At any intermediate stage of coalification between lignite and this high rank bituminous coal, a certain fraction of the 'unit' of model I may undergo metamorphosis into the 'unit' of model II which in its turn, under the prevailing geo-chemical condition may undergo further progressive transformation into the model IIIA. The final stage (model IIIA) is, thus, a result of the sum total of decarboxylation, dehydroxylation, dehydrogenation and partial demethylation of the 'parent' unit (model I). The incipient initiation of stage II to IIIA reaction in

the earlier stages is also not precluded. As a result, any transitory stage in rank-evolution may contain a mixture of one or two or all of the above types of units, though one or the other model species may predominate, depending upon the level of geochemical metamorphosis attained in the natural state.

No coal can, therefore, be homogeneous in respect of their unit structures. As an example, a proportion of 10:70:20 of the three structures may represent the typical analysis, both chemical and structural, of a 80% carbon coal (Table 5). Such a plausible structural analysis of a 80% carbon coal would indicate that it has undergone substantial decarboxylation. It would also indicate that dehydroxylation, dehydrogenation, (including cyclo-dehydrogenation) and demethylation processes had been initiated in varying degrees. All the transformations are consistent with the known properties of coal of such a rank. A partial conversion of model II to IIIA (say to the extent of 22% as suggested in the proportion of the units) will lead to an increase in aromaticity and also to the growth of the aromatic nucleus at the expense of alicyclic carbon.

The possibility of a number of model species (units) occurring together at any stage of coalification (though one or the other may be the dominant one) may also explain some of the following observations: (1) the assortment of ring sizes in any coal, (2) the constant trend of the sum of aromaticity and alicyclicity in any rank of coal (lignites and bituminous coal), (3) the constancy of carbon per cent retained in the char of dehydrogenated coal samples of any rank, as well as several other apparently perplexing facts observed in course of our studies on dehydrogenation and cyclo-condensations.

Whereas the transition of stage I to stage IIIA depicts the evolution of normal coals upto the highest rank in the bituminous range occurring under a set of geochemical conditions, the transition of stage III to stage IV (anthracite stage) must, by all accounts, be an abrupt and drastic one, involving a completely new set of geochemical conditions. The evolution of a typical anthracite may be conceived as shown in Fig. 3.

The structural models given here are not intended to actually represent any coal but has merely been used to illustrate the concept of the heterogeneity of the coal structure at any particular stage, and to emphasise the predominant chemical transmutation that may take place in response to geochemical forces in nature at any given level of metamorphic history of coal.

Studies in rank classification of coal have led to the formulation of the well-known coal band, which by itself, emphasises the transitory nature of the metamorphic changes in coal. Whether there are distinct and discretely separate zones of chemical reactions in course of rank-evolution is yet to be established, though the predominance of one set of reactions over another at any stage can not be disputed.

Admittedly, the models, the reactions, and the concept of co-existence of several models may explain many experimentally determined properties of coal, but we do not submit them here as pure "models" of any 'unit' coal; that stage may yet be far off. The number of rings assumed or other structural feature shown in the models (e.g. the disposition of unaccounted oxygen) may be different and still fit into the general picture of evolution of rank, but what is emphasised is that rarely any reaction in nature is ever complete, though the ideal is always towards perfection.

References

1. Dryden I.G.C., J. Inst. Fuel, (1957), 193.
2. Given, P.H., Fuel 39(1960), 147
3. (a) Mazumdar, B.K., Bhangale, P.H. & Lahiri, A., J. Sci. industr. Res., 15B (1956)  
(b) Mazumdar, B.K., Bhangale, P.H. & Lahiri, A., Fuel (Lond.), 36(1957), 254.
4. Mazumdar, B.K., Anand, K.S., Roy, S.N. & Lahiri, A., Brennst-Chemie, 19/20, 38(1957), 305.
5. Mazumdar, B.K., Chakrabartty, S.K., (Mrs.) Saha, M., Anand, K.S. & Lahiri, A., Fuel, 38, 4 (1959), 469.
6. Mazumdar, B.K., Chakrabartty, S.K., & Lahiri, A., J. sci. industr. Res, 16B (1957), 275.
7. Mazumdar, B.K., & Lahiri, A., Fuel, 37 (1958), 495.
8. Chakrabartty, S.K., Mazumdar, B.K., & Lahiri, A., Fuel, 37(1958), 498.
9. Chakrabartty, S.K., Mazumdar, B.K., Roy, S.N., & Lahiri, A., Brennst-Chemie, (in press).
10. Mazumdar, B.K., Chowdhury, S.S., Chakrabartty, S.K., & Lahiri, A., J. sci. industr. Res., 17B (1958), 509.
11. Mazumdar, B.K., Chakrabartty, S.K., Chowdhury, S.S., & Lahiri, A., Proc. Symp. on the "Nature of Coal" Central Fuel Research Institute (India), February, 1959, 219-229.
12. Mazumdar, B.K., Chakrabartty, S.K., & Lahiri, A., Fuel, 38 (1959), 112.
13. Mazumdar, B.K., Chakrabartty, S.K., De, N.G., Ganguly, S, & Lahiri, A., Fuel, (in press).
- 14(a) Halleux, A., Delavarenne, S., Tschamler, H., Fuel (1959), 283.
- 14(b) Brooks, J.D., Proc. Symp. on the "Nature of Coal" Central Fuel Research Institute (India), February, 1959, p. 167-172.
- 15(a) Tidswell, F.V. and Wheeler, R.V., J. Chem. Soc., 1922, 121, 2345.  
(b) Francis, W. and Wheeler, R.V., J. Chem. Soc, 1927, 2958.  
(c) Fischer, F. and Schröder, H., Gas Abh. Kennt. der Kohle, 1919, 4, 342.  
(d) Bone, W.A. and Quarendon, R., Proc. Roy. Soc. A 1926, 110, 537.
16. Horton, L., Fuel, Lond. 1955, 34, S 14.
17. Mazumdar, B.K., Chakrabartty, S.K., Lahiri, A., "Determination of Aromaticity of Coal" - Submitted to the Conference at brussels to be held in Nov., 1960.
18. Mazumdar, B.K., Choudhury, S.S. & Lahiri, A., Fuel, 39 (1960), 179.
19. Ergun, S, & Tiensuu, V.H., Nature, June 13, 1959, 1668.
20. Wieler, J.F., Fuel, 14, 190-6 (1935).
21. van Krevelen, D.H. et al, Fuel, 38(1959), 256.

22. Kinney, C.R., J. Amer. Chem. Soc., 69 (1947), 284.
23. Brooks, J.D., Durie, R.A., Sternhell, S., Aust. J. Appl. Sci., 9, 3, (1958), 303.
24. (Mrs.) Kaiser, F., Rao, H.S., & Lahiri, A., Proc. Symp. on the "Nature of Coal", Central Fuel Research Institute, February, (1959), 245.
25. Kuhn, R. and L'Orsa, F., Angew. Chem., 44 (1931), 847.
26. Bhowmik, J.N., Mukherjee, P.N., Mukherjee, A.K., & Lahiri, A., Proc. Symp. on the "Nature of Coal", Central Fuel Research Institute, February (1959), 242.
27. Chakrabartty, S.K., Mazumdar, B.K. and Lahiri, A., Nature (in press).
28. Fitzgerald, D. and van Krevelen, D.W., Fuel, 38(1959), 17.
29. Mazumdar, B.K., Ganguly, S., De, N.G., & Lahiri, A., Fuel (in press).
30. De, N.G., Mazumdar, B.K., & Lahiri, A., Unpublished work.
31. Mookherjee, S.K., Mazumdar, B.K., & Lahiri, A., Unpublished work.
32. Mazumdar, B.K., Chakrabartty, S.K. & Lahiri, A., Proc. Symp. on "Nature of Coal", Central Fuel Research Institute, February (1959).
33. Mazumdar, B.K., Chakrabartty, S.K. and Lahiri, A., J. sci. industr. Res, 168, 11, (1957), 509.

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Table 1 - Calculation of Aromaticity in Coal from Oxidation Studies  
(based on oxidation of 100 gm. of coal substance)

[ Reproduced from Unkrabarty, S.K., Mazumdar, B.K., Roy, S.N., Lahiri, A., Brennst-Chemie, in press ]

Sample	C %	H %	Gain/ loss in wt. %	Oxygenated groups in oxy-coal			Carbon input gm.	Carbon output gm.	COOH (in oxy- coal) gm.	W aromatic (C <sub>ar</sub> )	C <sub>ar</sub> Total
				COOH %	OH %	COO %					
Lignite	71.53	4.66	-26.4	17.5	7.4	4.0	71.53	45.23	4.83	40.40	0.56
Overall(1)	80.69	5.33	-3.0	14.3	2.3	6.5	80.69	62.38	4.93	57.45	0.71
Vitrain (1)	81.46	5.40	-7.0	16.0	4.0	6.5	81.46	60.82	5.58	55.24	0.68
Vitrain(2)	84.35	5.72	-7.6	16.0	2.6	7.9	84.35	60.56	5.52	55.04	0.65
Overall (2)	85.15	5.70	-5.0	14.3	4.0	5.3	85.15	63.86	5.10	58.76	0.69
Vitrain (3)	87.25	5.27	+0.8	14.0	2.2	8.9	87.25	68.08	5.28	62.80	0.72
Vitrain (5)	89.56	4.93	+8.0	11.2	1.5	11.0	89.56	75.60	4.56	71.04	0.79
Overall (3)	90.31	4.86	-2.9	10.3	3.0	4.4	90.31	73.79	3.75	70.04	0.73
Anthracite	93.20	3.50	+4.0	2.1	2.1	2.4	93.20	91.60	0.83	90.77	0.97

Table 2 - Forms of Hydrogen and Average Ring-size of Coal Units from Oxidation Studies  
 (based on oxidation of 100 gm. coal-substance, d.a.f.)

[Reproduced from Chakrabarty, S.K., Mazumdar, B.K., Roy, S.N., & Lahiri, A., Brennst-Chemie, in press.]

Sample	Rank	Atomic H/C.	Hydrogen input gm.	Hydrogen output gm.	Correction for		H <sub>ar</sub> <sup>+</sup> gm.	H <sub>ar</sub> /H	atomic H/C oxycoal	Atomic H/C (hypothetical hydrocarbon corresponding to the oxy-coal)	*** No. of rings condensed	*** No. of rings pericond.
					H <sub>alip</sub> <sup>*</sup> gm.	H <sub>arom</sub> <sup>**</sup> gm.						
Lignite	71.53	0.78	4.66	1.77	-0.40	Nil	1.36	0.29	0.71	0.75	-	5
Overall (1)	80.69	0.79	5.33	1.93	-0.41	+0.27	1.79	0.32	0.67	0.60	7	5
Vitrain (1)	81.46	0.79	5.40	2.10	-0.47	+0.26	1.89	0.35	0.65	0.63	5	4
Vitrain (2)	84.35	0.81	5.72	2.09	-0.46	+0.43	2.06	0.36	0.64	0.62	6	4
Overall (2)	85.15	0.80	5.70	2.25	-0.43	+0.30	2.12	0.37	0.63	0.63	5	4
Vitrain (3)	87.25	0.72	5.27	2.20	-0.44	+0.50	2.26	0.43	0.57	0.60	7	5
Vitrain (5)	89.56	0.63	4.98	2.41	-0.38	+0.74	2.77	0.55	0.44	0.60	7	5
Overall (3)	90.31	0.65	4.86	2.33	-0.31	+0.25	2.27	0.47	0.53	0.49	7	7
Anthracite	93.20	0.47	3.50	2.70	-0.07	+0.016	2.79	0.80	0.20	0.39	-	12

\* H Corresponding to COOH, See Table 1.

\*\* H replaced by quinone gr., see Table 1.

+ This includes the hydrogen of the phenolic hydroxyl group.

\*\*\* Calculated from the hypothetical atomic H/C ratio corresponding to the 'hydrocarbon' model of the oxidised coal.

Table 3 - Values of alicyclicly determined by dehydrogenation studies  
 (Based on dehydrogenation of 100 gm. coal substance by sulphur)<sup>10,11,13</sup>  
 [Data mostly reproduced from 'Further Studies on Dehydrogenation of Coal'<sup>13</sup>, Fuel, in press]

Sample	C		H		H <sub>2</sub> dehydrogenated from alicyclic positions*	Total alicyclic (Hha)/gm		Total alicyclic (Cha)/gm.		Cha = alicyclic city	% of carbon retained in 600°C		Cha	U
	%		%			Hha	H	Cha	U		Normal coal	dehydrogenated coal		
lignite	71.53		4.66		-	-	-	-	-	-	68	91.0	0.23	
Overall (a)	80.10		5.44		23.5	2.55	0.47	15.30	0.19	0.19	75	92.0	0.17	
Overall (1)	80.69		5.33		22	2.35	0.44	13.50	0.17	0.17	75	95.0	0.20	
Vitrain (1)	81.46		5.40		20	2.16	0.40	12.96	0.16	0.16	74	92.0	0.18	
Vitrain (2)	84.35		5.72		16	1.83	0.32	10.98	0.13	0.13	70	87.0	0.17	
Overall (2)	85.15		5.70		16.5	1.88	0.33	11.28	0.13	0.13	71	87.0	0.16	
Vitrain (3)	87.25		5.27		12	1.27	0.24	7.62	0.09	0.09	78	92.0	0.14	
Vitrain (5)	89.56		4.98		10	1.00	0.21	6.00	0.07	0.07	86	92.0	0.06	
Overall (3)	90.31		4.86		14.5	1.43	0.29	8.58	0.10	0.10	82	95.0	0.13	
Anthracite	93.20		3.50		nil	nil	nil	nil	nil	nil	98	98.0	nil	

\* After correcting for "side-reactions" with aromatic positions shown elsewhere<sup>13</sup>. The corrections may be on the higher side and the values of alicyclicly presented here should be treated as the minimum estimate.

\*\* Taken from earlier papers<sup>10,11</sup>

Table 4 - Structural Parameters from Oxidation<sup>9</sup>, Dehydrogenation<sup>32</sup> and Pyrolysis<sup>32</sup>  
(Typical values of aromaticity, alicyclicity and aliphaticity)

Sample	C %	H %	Distribution of Carbon			Distribution of Hydrogen		
			** Aromaticity $\frac{C_{ar}}{C}$	Alicyclicity $\frac{C_{ha}}{C}$	Aliphaticity $\frac{C_{al}}{C}$ (by diff.)	$\frac{H_{ar}}{H}$	$\frac{H_{ha}}{H}$	$\frac{H_{al}}{H}$ (by diff.)
Lignite	71.53	4.66	0.62	0.22	0.16	0.30	0.50	0.20
Overall (1)	80.69	5.35	0.72	0.18	0.10	0.35	0.45	0.20
Vitrain (1)	81.46	5.40	0.71	0.17	0.12	0.35	0.43	0.22
Vitrain (2)	84.35	5.72	0.68	0.15	0.17	0.34	0.36	0.30
Overall (2)	85.15	5.70	0.70	0.15	0.15	0.35	0.36	0.29
Vitrain (3)	87.25	5.27	0.75	0.11	0.14	0.43	0.30	0.27
Vitrain (5)	89.56	4.98	0.82	0.07	0.11	0.50	0.20	0.30
Overall (3)	90.31	4.86	0.83	0.05	0.12	0.49	0.13	0.38
Anthracite	92.20	3.90	0.97	nil	0.03	0.82	nil	0.18

\*\* Average values on the basis of oxidation<sup>9</sup> and pyrolysis<sup>32</sup> studies.

Table 5 - Comparison of the Chemical and Structural properties of the suggested Structural Pattern with those of a typical Coal

Analysis	Model I	Model II	Model IIIA	Assembly of structure with 10% of Model I, 70% of Model II, 20% of Model IIIA	Coal (Typical value)
Empirical formula	C <sub>24</sub> H <sub>24</sub> O <sub>6.7</sub> N <sub>0.5</sub>	C <sub>23</sub> H <sub>22</sub> O <sub>2.7</sub> N <sub>0.5</sub>	C <sub>22</sub> H <sub>12</sub> O <sub>0.5</sub> N <sub>0.5</sub>	-	-
Unit wt.	426.2	348.2	291	80.4	80.2
C%	67.6	79.3	90.7	5.7	5.4
H%	5.6	6.4	4.1	2.0	1.9
N%	1.6	2.0	2.4	11.9	12.5
O%	25.2	12.3	2.8	0.8	0.9
COOH%	7.5	Nil	Nil	4.4	6.0
OH%	11.3	4.6	Nil	3.6	1.8
CO%	3.8	4.6	Nil	3.1	3.8
*OC-O-%	2.6	3.1	2.8	0.67	0.68
f <sub>a</sub> (aromaticity)	0.58	0.61	0.91	0.24	0.18
** f <sub>ha</sub> (alicyclicity)	0.29	0.30	Nil	0.09	0.14
f <sub>al</sub> (aliphaticity)	0.13	0.09	0.09	0.26	0.35
*** h <sub>ar</sub>	0.21	0.17	0.60	0.44	0.45
H <sub>ha</sub>	0.50	0.55	-	0.30	0.20
H	0.29	0.28	0.40	-	-
H <sub>al</sub>	-	-	-	-	-
H	-	-	-	-	-
Average No. of aromatic Rings	3	3	5	3.5	4

\* In the models, the unaccounted oxygen usually found in coals have been represented as ether linkages: this may not be true. On the other hand, the possibility of the heterocyclic oxygen in coal in the form of flavone structure or similar configuration can not be ruled out (unpublished work : Mazumdar, D.K. et al). No attempt is made now to represent this in the models.

\*\* This includes the bridge methylene group.

\*\*\* This includes the hydrogen of the phenolic hydroxyl group.

+ Proportion of nitrogen assumed; its disposition in the models has not been shown.

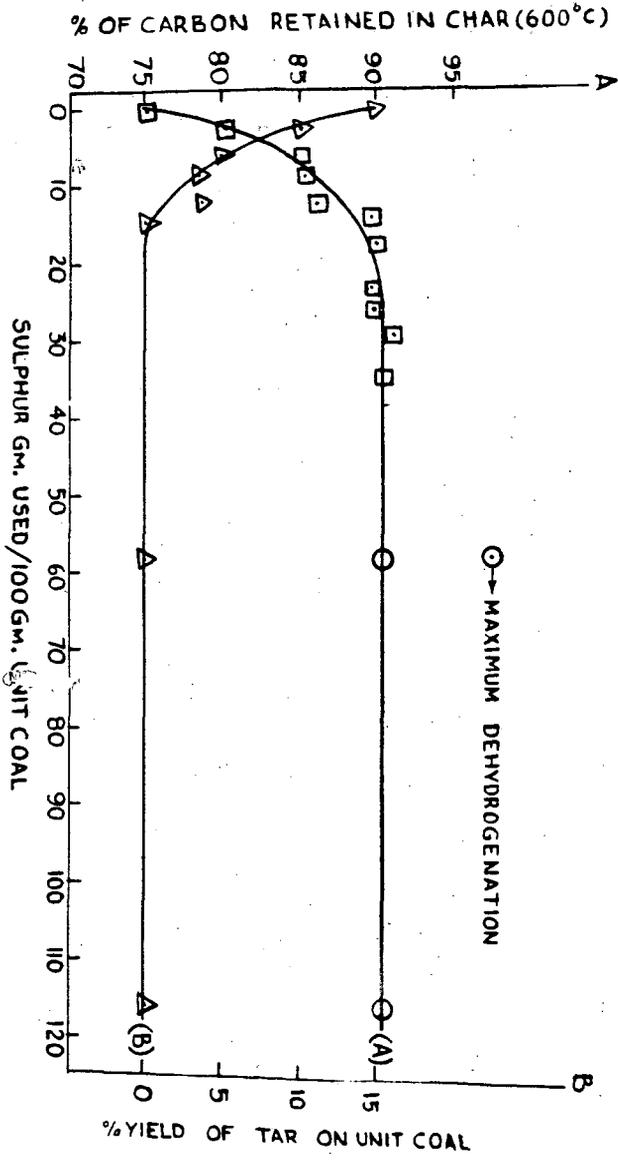
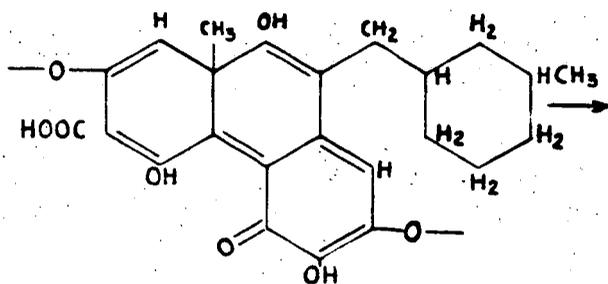
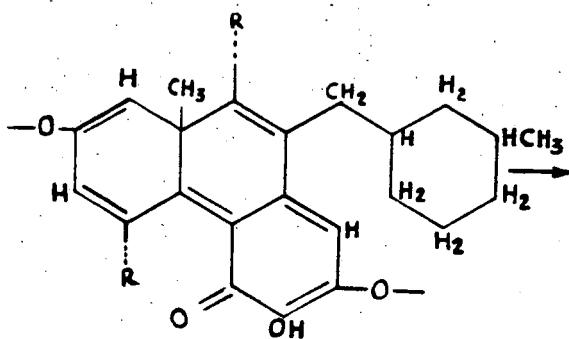


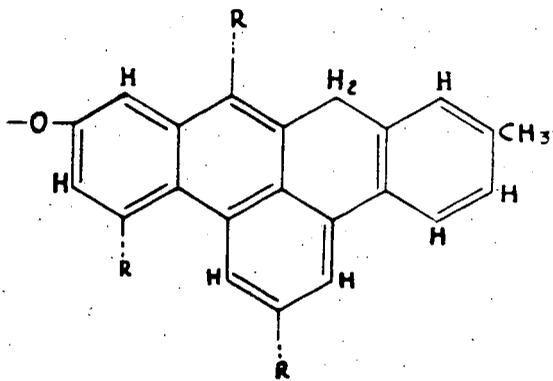
Fig. 1 Inhibition of Tar Formation and Fixation of Additional Carbon in Char consequent on Varying Degrees of Dehydrogenation.



I  
C=67.6%



II  
C=79.3%



III A  
C=91.0%

Fig. 2

Hypothetical model Unit illustrating its Transition from the stage of Lignites to High Rank Bituminous Coal.

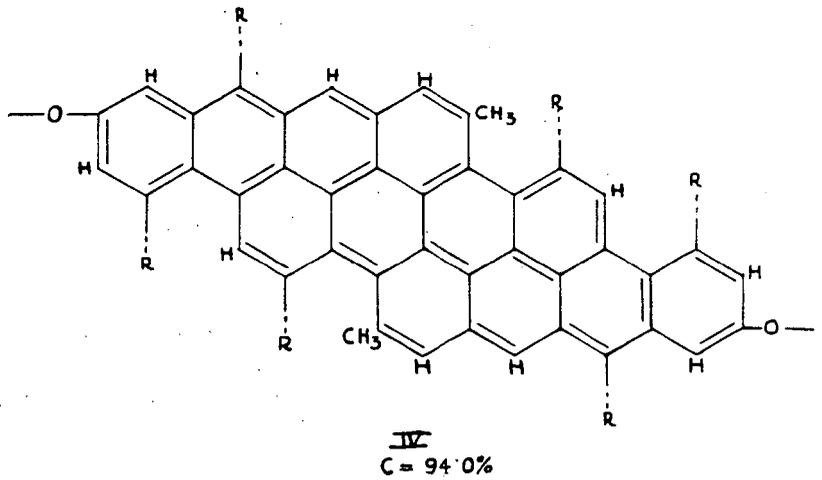
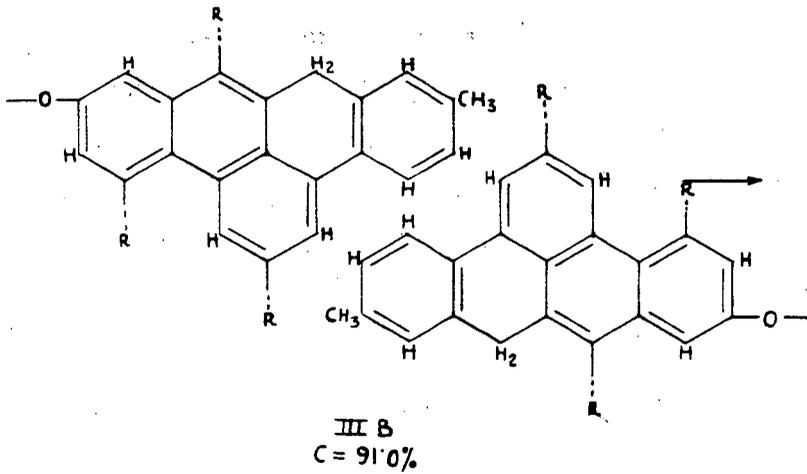


Fig. 3 Hypothetical Model Units depicting the Formation of Anthracite from the Stage of High Rank Bituminous Coal.

Model IV : Empirical formula :  $C_{44}H_{16}O_{.7}N_{.5}$

Unit wt. = 562.2, C = 94.0, H = 2.8  
N = 1.2, O = 2.0,  $f_a = 0.95$ .

Typical analysis of anthracite, C = 94.3, H = 3.0, N = 1.0,  
O = 1.7

## Molecular Weights of Humic Acids in Sulfolane

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### INTRODUCTION

Recent viscosimetric studies by Mukherjee and Lahiri (1) and by Rajalakshmi et al. (2) offer convincing evidence that humic acids behave as polyelectrolytes. Since this behaviour is fundamentally inconsistent with previously reported molecular weights - which range from 160 to 700 when measured cryoscopically in catechol or acetamide (3, 4) - re-examination of the molecular weight of humic acids appears to be fully warranted.

The difficulties inherent in such a study are formidable and have been discussed by several investigators (1, 2, 3, 5, 6, 7). For example, Yokokawa (7) notes that molecular weight determinations on solutions of humic acids in acetamide amount to little more than an estimate of the proportion of functional groups. From conductivity measurements and parallel cryoscopic determinations on potassium humates in aqueous solutions, he concluded that some of his preparations had molecular weights in the thousands rather than in the hundreds. Osmotic pressure techniques (8) have likewise yielded molecular weights estimated in the range of 1200-2200. And Dryden (9), using semi-quantitative diffusion measurements, concluded that some 90% of the ethylene diamine extract of coal\* has a molecular weight in excess of 6000.

Some of the specific problems associated with cryoscopic measurements on humic acids emerge from an analysis of published data, e.g. those of Polansky and Kinney (4). A particularly noteworthy feature of these data is the variation of the cryoscopic constant  $K$  with solute concentration, which suggests some form of molecular association, dissociation or solvation in acetamide. Fig. 1, which reproduces typical results obtained in this laboratory with 1, 2, 4, 5 - benzene tetracarboxylic acid in acetamide, may serve to illustrate the general effect: the curvilinear shape of the graph suggests complex behaviour including probable ionization at low molality and solvation at higher molalities (10). A second difficulty to be overcome in molecular weight determinations by cryoscopic means relates to the removal of water without simultaneous chemical change and loss of solubility. Finally, it should be recognized that humic acid preparations, particularly those obtained by oxidative degradation of coal, may show a wide distribution of molecular weights. In order to attach real significance to a number-average molecular weight of such materials, and permit a meaningful comparison of  $M_n$  with weight-average molecular weights obtained by other methods, it is, therefore, important to undertake appropriate fractionation of the sample.

To a considerable degree, however, it appears that most of these difficulties can now be eliminated. Burwell and Langford (11) recently suggested that tetramethylene sulfone (sulfolane) because of its low latent heat of fusion and resulting high cryoscopic constant ( $K$ ) might represent a good medium for the cryoscopic determination of molecular weights, and this suggestion seems to have real merit. It has been found that sulfolane is not only a reasonably good solvent for humic acids, but that it behaves as an essentially ideal solvent for a variety of solids with normally quite distinct associative and dissociative tendencies. The detailed findings are reported below.

\*While humic acids need not necessarily have similar molecular weights, some preparations or fractions of humic acids prepared from coal might be expected to be in such a range.

## EXPERIMENTAL

### Materials

Acetamide used was Fisher certified reagent dried in an oven at 60°C/20 mm. for 24 hours and stored in a desiccator over phosphorous pentoxide until used.

Sulfolane was the product of Shell Development Co., Emeryville, California. This material was distilled from powdered sodium hydroxide under reduced pressure and the portion boiling at about 100°C/0.01 mm. retained for use.

1, 2, 4, 5 - Benzene tetracarboxylic acid (mp. 177-8°C) was obtained from Aldrich Chemical Co., dried and stored in the same manner as the acetamide.

$\beta$ -Naphthalene sulfonic acid was recrystallized from an alcohol-benzene mixture as the hydrate, but no attempt was made to dry it as this was accomplished in the course of its use (see below).

Humic acids were derived from two sources. One was commercially available Baroid Carbonox, a naturally oxidized (i.e. weathered) North Dakota Lignite, and the other a weathered sub-bituminous coal from the upper seam at Sheerness, Alberta. Each was extracted with sodium hydroxide solution, filtered, precipitated with hydrochloric acid, washed until nearly free of salts, and finally electro-dialyzed until the current had fallen to a minimum.

### Cryoscopic Procedure

Cryoscopic measurements were carried out in an apparatus similar to that employed by Smith and Howard (3) and Polansky and Kinney (4) and flooded with purified nitrogen to exclude moisture. Measurements in acetamide were performed following the procedure of Polansky and Kinney (4). When sulfolane (mp. 28.2°C) was used, the bath was slightly cooled by a cold water-coil in order to permit operation of the heater-controller.

Materials such as biphenyl and benzoic acid, which did not present a significant drying problem, were weighed out and directly dissolved in sulfolane for cryoscopic constant determinations. In the case of  $\beta$ -naphthalene sulfonic acid, it was found more convenient to dissolve a roughly weighed sample in more sulfolane than actually required and subsequently to distill off part of the solvent (and all water) at 100°C/0.01 mm. The acid concentration was then determined by titrating an aliquot of the solution with standard alkali.

### Molecular Weight Determinations

Since humic acids did not dissolve rapidly in sulfolane, and since it was also necessary to use a drying technique on the resultant solution, it was found most convenient to dissolve the sample (300-500 mg.) in 20-30 ml. of a 3:1 acetone-water mixture, add this to 55-60 ml. sulfolane, filter the mixture repeatedly (5-8 times) through a Seitz bacterial (sterilizing) filter (previously found adequate to render the filtrates optically void) and remove the acetone, water and some sulfolane under reduced pressure (with the final conditions not exceeding 100°C/0.01 mm.). After determination of the freezing point depression, the weighed sulfolane solution was diluted with sufficient benzene to precipitate the humic acid, which was then removed by centrifugation, washed free of sulfolane with more benzene, dried and weighed. In the case of lower molecular weight humic acids, a significant amount of material remained in solution in the mother liquor after the first precipitation; this was recovered by concentrating the solution to a very small

volume under reduced pressure and further dilution with benzene. The precipitate was then treated like the first one and added to it.

The techniques described above for sample drying eliminate the water problem entirely. Because of the large difference in the boiling points of sulfolane (278°C/700 mm.; 100°C/0.01 mm.), and water it was possible to remove water entirely by vacuum distillation prior to the freezing point determination. Caution is, however, necessary in the case of humic acid solutions, whose exposure to temperatures much in excess of 100°C results in the formation of anhydrides with consequent changes in solubility. This aspect will be discussed in another paper.

#### The Cryoscopic Constant of Sulfolane

The average cryoscopic constant of sulfolane ( $K = 65.5^\circ\text{C}/\text{mole}/\text{kg.}$ ), which agreed well with the figure of  $66.2 \pm 0.6^\circ\text{C}/\text{mole}/\text{kg.}$  quoted by Burwell and Langford (11), was established by measuring the freezing point depression ( $\Delta T$ ) for various concentrations of benzoic acid, biphenyl and  $\beta$ -naphthalene sulfonic acid. The results are shown in Fig. 2 and indicate that the constant is valid for use with materials of vastly differing dissociative and associative potentialities.

#### Fractionation

Humic acids were prepared for molecular weight determination by two fractionation techniques, one involving successive extractions with an alcohol-benzene mixture and the other precipitation from sulfolane solution with benzene as the non-solvent. In the former case, 14.18 g. of Carbonox humic acid (average m.w. 1570) was extracted in a soxhlet apparatus with the azeotrope of alcohol and benzene for 25 days; the results are set out in Table I. Infrared spectra were obtained for each fraction, typical ones being shown in Fig. 3. Apart from small variations in the carbonyl band, which are listed in Table I, all spectra were similar.

In the second method, a 10 g. sample of Sheerness, Alberta, humic acid (average m.w. 4600) was dissolved in 200 ml. of sulfolane by the acetone-water technique described above, filtered through a Seitz (sterilizing) filter until optically void and then diluted with 130 ml. of benzene. The resultant precipitate was removed in the centrifuge, washed with benzene and dried at 60°C/20 mm.

The remaining solution was treated with more benzene to produce a second precipitate and so on. The general procedure is summarized in Table II.

#### DISCUSSION

A number of factors combine to make sulfolane a peculiarly attractive solvent for cryoscopic measurements. Its cryoscopic constant (65.5 degrees per mole) is very much higher than those of other readily available solvents (thus permitting accurate measurements of freezing point depressions at low solute concentrations). It has good solvent properties for humic acids and a wide variety of simpler materials. It permits effective drying of hygroscopic materials and also allows their concentration to be determined quantitatively after drying. And most important, sulfolane appears to eliminate disturbing effects arising from association or dissociation of solute molecules.

Fig. 2 supports this last contention by showing that sulfolane exhibits ideal cryoscopic behaviour - cf. Spauschus (10) - with  $K$  values independent of concentration for benzoic acid,  $\beta$ -naphthalene sulfonic acid and biphenyl. It should be emphasized that this constancy of  $K$

Table I  
 Fractionation of Carbonox Humic Acid with Alcohol-Benzene  
 (Average molecular weight of starting material 1570)

Fraction	Incremental Extraction Time	Extract (% of original sample)	%C*	%H	E <sup>0.4%</sup> ** 0.09 cm.	Molecular Weight
1	2 hours	8.21			19.4	600
2	3 hours	6.77	56.98	4.39	23.9	970
3	12 hours	24.75	57.46	4.26	21.0	1546
4	48 hours	6.19	58.30	4.30	18.2	
5	12 hours	1.61	57.84	3.95		
6	24 hours	1.01	57.32	4.40	18.3	
7	24 hours	0.95	57.76	4.19	19.9	
8	4 days	5.39	58.40	4.02	18.3	5370
9	7 days	1.07	58.96	4.04	19.1	
10	7 days	1.01	58.78	4.15	19.3	
Residue		45.46	57.91	3.19	13.4	
Total		102.42				

\* Carbon and hydrogen analyses were performed by Micro-Tech Laboratories, 8000 Lincoln Avenue, Skokie, Illinois.

\*\* E<sup>0.4%</sup><sub>0.09 cm.</sub> = extinction coefficient of carbonyl band (1720 cm.<sup>-1</sup>)  
 (determined in KBr)

Table II  
 Fractionation of Sheerness Humic Acids by Precipitation from Sulfolane (200 ml.)  
 (Average molecular weight of starting material 4600)

Fraction	Incremental Volume of Benzene added	Precipitate (% of original sample)	%C	%H	Molecular Weight
1	130	66.13			See note A
2	100	9.98	56.8	4.58	
3	100	3.77	58.6	4.43	1, 260
4	400	0.64	57.95	4.90	
5	material remaining in solution	2.21	59.37	4.66	460
Total		82.72*			

\* A material balance shows that some 17% of this initial sample were lost during fractionation. We are inclined to the view that this loss accrues from partial peptization of this humic acid and elimination of the peptized material with the washings.

Note A

Fraction 1 was dissolved in 200 ml. of sulfolane and 100 ml. benzene added. The fraction which precipitated (3.55 g.) had molecular weight 8,500, and contained 52.1% C, 4.00% H.

would not be observed if the carboxylic or sulfonic acid groups were to ionize or associate in sulfolane solution. Burwell and Langford (11) cite three other examples of this ideality in sulfolane solution, the most interesting from the standpoint of the present study being acetic acid, which they describe as behaving as a monomer when dissolved in sulfolane.

That sulfolane solutions of humic acid also yield concentration-independent results is illustrated by the fact that the observed molecular weights of a humic acid preparation over the 0.01-0.005 molal range varied only between 1520 and 1560. This variation is considered to lie within the normal experimental error incurred in the measurement.

On the assumption that association would be at a maximum in the solid state and at a minimum in dilute solution, further evidence for the absence of association in sulfolane solution can be derived from infrared data, in particular from analysis of the carbonyl stretching frequency between 1733 and 1695  $\text{cm.}^{-1}$  and from the -OH stretching frequency between 3700 and 2500  $\text{cm.}^{-1}$ .

When benzoic acid is examined in a Nujol mull, the carbonyl absorption band appears at 1695  $\text{cm.}^{-1}$ , while a 0.5% solution in sulfolane shows this band at 1733  $\text{cm.}^{-1}$ . Since such a shift is known to be associated with a change from the dimeric to the monomeric form of the acid (12), molecular association in sulfolane solution would imply a progressive shift of the carbonyl band towards 1695  $\text{cm.}^{-1}$  or the appearance of a second band there (12) as the solute concentration increases. This does not occur: even for a 5% solution of benzoic acid in sulfolane, the carbonyl absorption was found to remain at 1733  $\text{cm.}^{-1}$ .

The same conclusion can be derived from the position of the -OH stretching band. According to Bellamy (13) and Flett (12) absorption between 2700 and 2500  $\text{cm.}^{-1}$  is commonly taken as evidence for the existence of dimeric carboxylic acid groups. This is observed in the solid state spectrum of benzoic acid, but is absent in spectra of sulfolane solutions. The -OH band which did appear occurred at 3226  $\text{cm.}^{-1}$ . This is too low for completely free -OH (3700-3500  $\text{cm.}^{-1}$ ) but is in the region of weak hydrogen bonding. Since the cryoscopic results showed no variation with concentration, and since the carbonyl absorption showed no indication of dimerization of the benzoic acid molecules, this shift does not appear to be caused by inter-action between the acid molecules. It is possible that the -OH group is hydrogen-bonded to an oxygen atom of the sulfolane, cf. Jones (14). This would remove some of the solvent molecules from that role and make them in effect part of the solute. However, over the concentration range here studied this has been calculated to exert a negligible influence on the effective concentration.

The unsuitability of acetamide as a cryoscopic solvent is borne out by the variation of its cryoscopic constant (determined with 1, 2, 4, 5 - benzene tetracarboxylic acid solute) with solute concentration (Fig. 1). Spauschus (10) reported similar behaviour for high molecular weight esters in benzene and discussed the large departure from ideality in the region of low concentration. Assuming that a similar behaviour to that seen here for benzene tetracarboxylic acid would be exhibited by humic acids in acetamide solution, it is likely that previously reported measurements were carried out in the region of large deviations from ideality (below 0.03 molal), since the materials used probably had number average molecular weights in excess of 1000.

Further evidence for the unsuitability of acetamide for cryoscopic work is offered by Magne and Skau (15) who note that the molar depressions of closely related fatty acids in acetamide vary widely. They suggest that differing degrees of dissociation of the molar complexes of these materials with acetamide may explain this phenomenon.

Considerable errors would also be introduced if insufficiently dried humic acids were used. For example, 1% water in a material of m.w. 1500 would double  $\Delta T$ . The same impurity would result in a 3-fold increase in  $\Delta T$  if the molecular weight were 5000.

In order to show that the humic acids here studied were also subject to these uncertainties in acetamide, a sample of molecular weight 970 (determined in sulfolane) was found to give a value of 230 in acetamide (using  $K = 3.58$ ).

The fractionation procedures described above provided samples which, from several standpoints, are more appropriate for molecular weight studies than an aggregate, unfractionated sample. For example, in order to compare values obtained by number and weight average techniques, as small a range of molecular sizes as possible is desirable.

There is reason to believe that further fractionation is possible and that the molecular weights of humic acids may extend well beyond the upper limit reported here. The method adopted in this study is limited by the fact that acids of high equivalent weight and/or very high molecular weight are difficultly soluble in sulfolane.

In the case of fractionation by extraction with an alcohol-benzene mixture, attempts to determine the molecular weight of the residue encountered difficulties. The sample would only incompletely dissolve in either acetone-water or in this mixture plus sulfolane, and each attempted molecular weight determination accordingly resulted in different  $\Delta T$ 's with calculated molecular weights ranging from 985 to 1510. We venture to suggest that this behaviour is intimately connected with particular properties of the residue. While a residue fraction with an apparent molecular weight of 985 was shown by sodium aminoethoxide titration to have an equivalent weight of 240, previously separated alcohol-benzene soluble fractions, irrespective of their molecular weights, had equivalent weights of about 140. It is, therefore, reasoned that the residual material includes both high and low molecular weight fractions characterized by a relative lack of polarity. This view is consistent with the low carbonyl extinction coefficient of  $E_{0.09}^{0.4\%} = 13.4$  for the whole residue as compared with an average of  $E_{0.09}^{0.4\%} = 19.6$  for the soluble fractions.

It has thus been shown that the molecular weights of humic acids dissolved in sulfolane, and thoroughly freed from water, can be determined satisfactorily by the cryoscopic method. The resultant measurements appear to have resolved the apparent inconsistencies between previously determined cryoscopic values and those obtained by other methods.

#### Acknowledgment

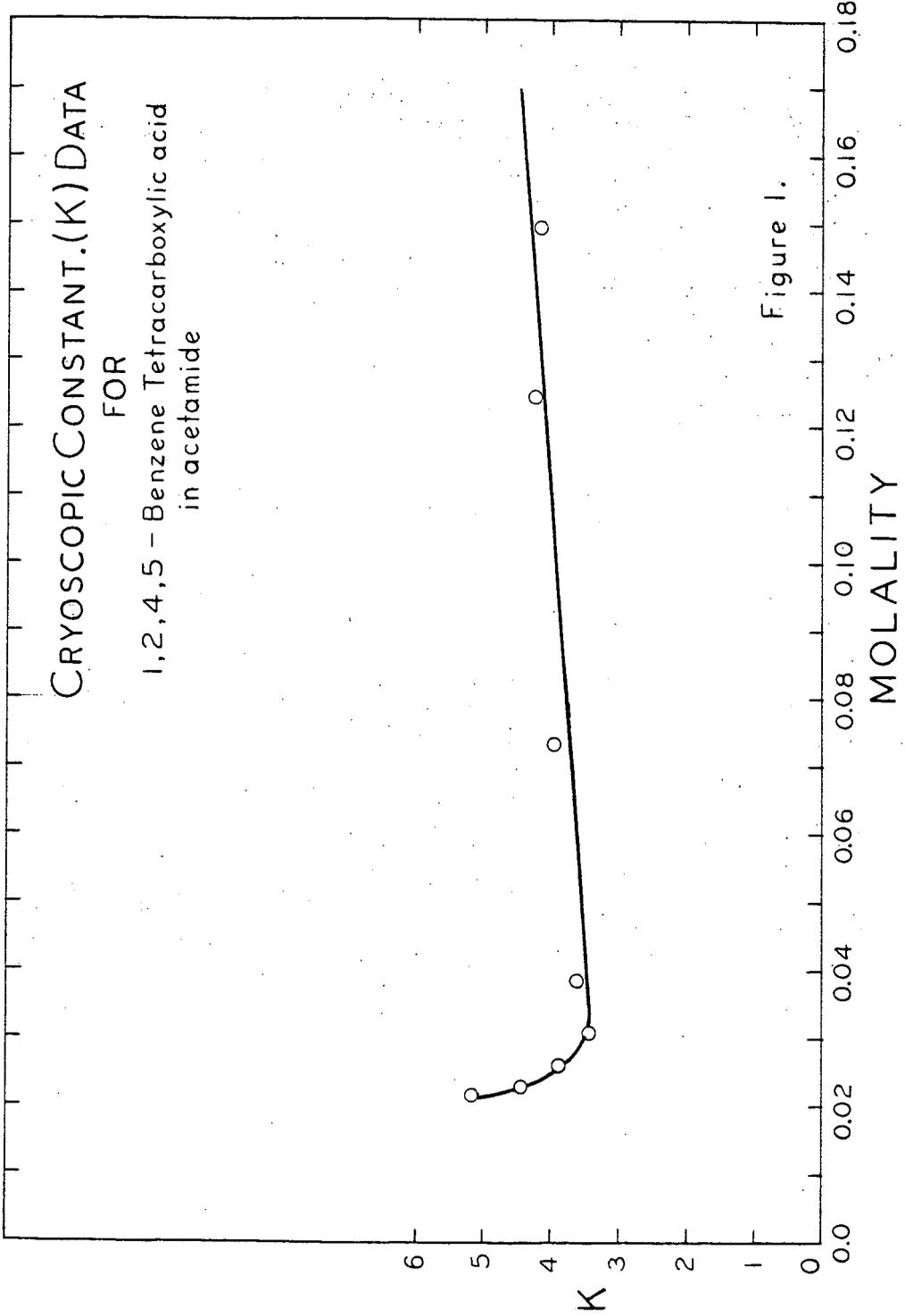
The authors wish to express their thanks to Drs. H. W. Habgood and N. Berkowitz for their assistance and encouragement throughout this work.

Thanks are also extended to the Shell Development Co. of Emeryville, California, for samples of sulfolane, with which this work was begun.

#### References

- (1) Mukherjee, P.N., Lahiri, A., J. Colloid Sci., 11, 240 (1956).
- (2) Rajalakshmi, N., Sivarajan, S.R., Vold, R.D., J. Colloid Sci., 14, 419 (1959).
- (3) Smith, R.C., Howear, H.C., J. Am. Chem. Soc., 57, 512 (1935); *ibid.* 58, 740 (1936).
- (4) Polansky, T.S., Kinney, C.R., Fuel, 31, 409 (1952).

- (5) Howard, H. C., "Chemistry of Coal Utilization", H. H. Lowry, ed., Vol. I, John Wiley & Sons, Inc., New York, 1945, p. 352.
- (6) Yohe, G. R., Illinois State Geol. Survey, Rep. Invest. No. 207, 21 (1953).
- (7) Yokokawa, C., "Chemical Constitution of Coal", Dept. of Fuel Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan, 1958, p. 10.
- (8) Wynne-Jones, W. F. K., Blayden, H. E., Shaw, F., Brennstoff Chem. 32, 201 (1952).
- (9) Dryden, I. G. C., Fuel, 31, 176 (1952).
- (10) Spauschus, H. O., J. Chem. and Eng. Data 5, 201 (1960).
- (11) Burwell, R. L. Jr., Langford, C. H., J. Am. Chem. Soc., 81, 3799 (1959).
- (12) Flett, M. St. C., J. Chem. Soc., 962 (1951).
- (13) Bellamy, L. J., "The Infrared Spectra of Complex Molecules", John Wiley & Sons, Inc., New York, 1954, p. 142.
- (14) Jones, R.N., "Chemical Applications of Spectroscopy", W. West, ed., Interscience Publishers, Inc., New York, 1956, p. 427.
- (15) Magne, F. C., Skau, E. L., J. Am. Chem. Soc., 74, 2628 (1952).



# CRYOSCOPIC CONSTANT.(K) DATA FOR

- Benzoic Acid ..... O
- Biphenyl..... x
- Naphthalene Sulfonic Acid. Δ
- in sulfolane

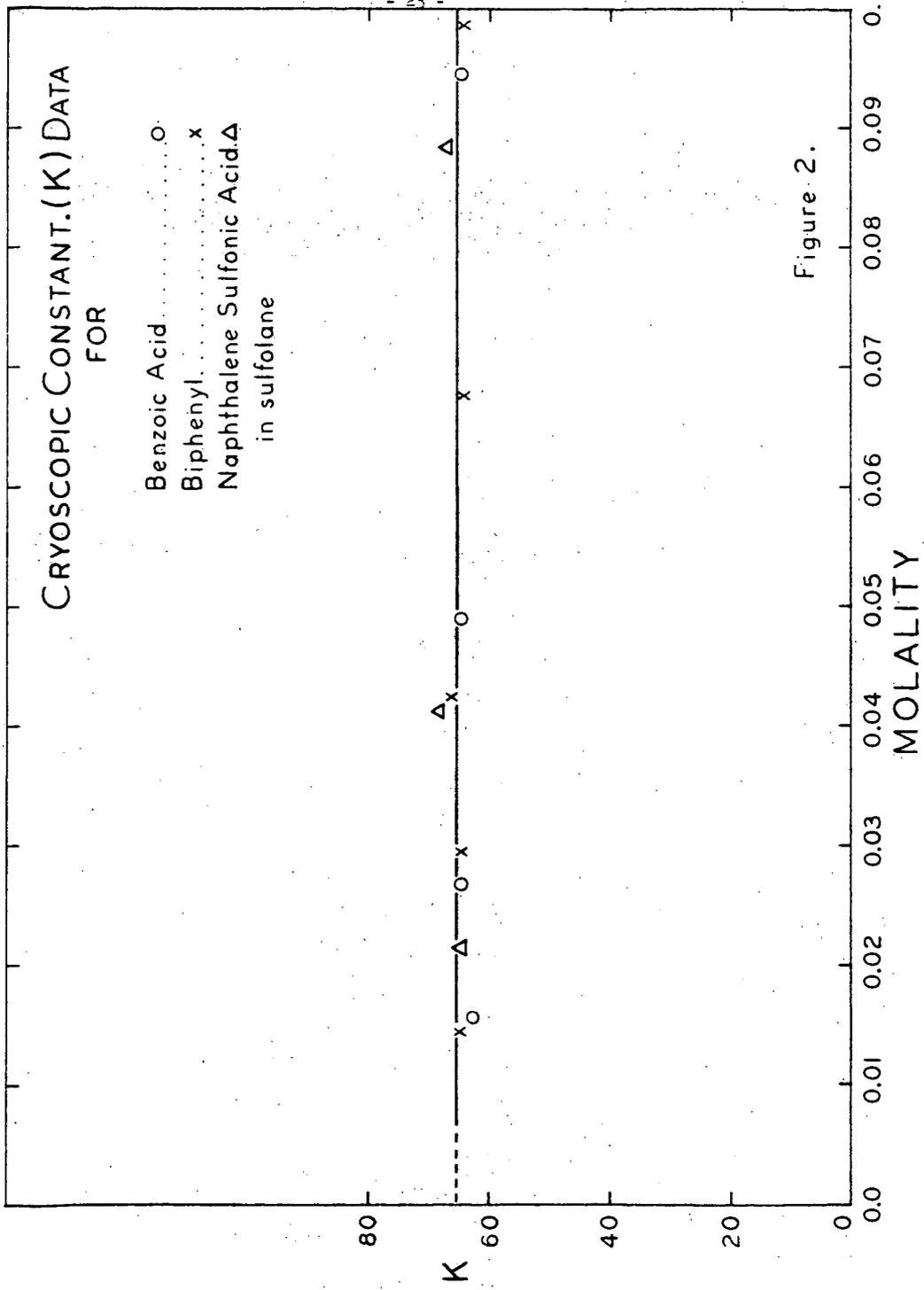
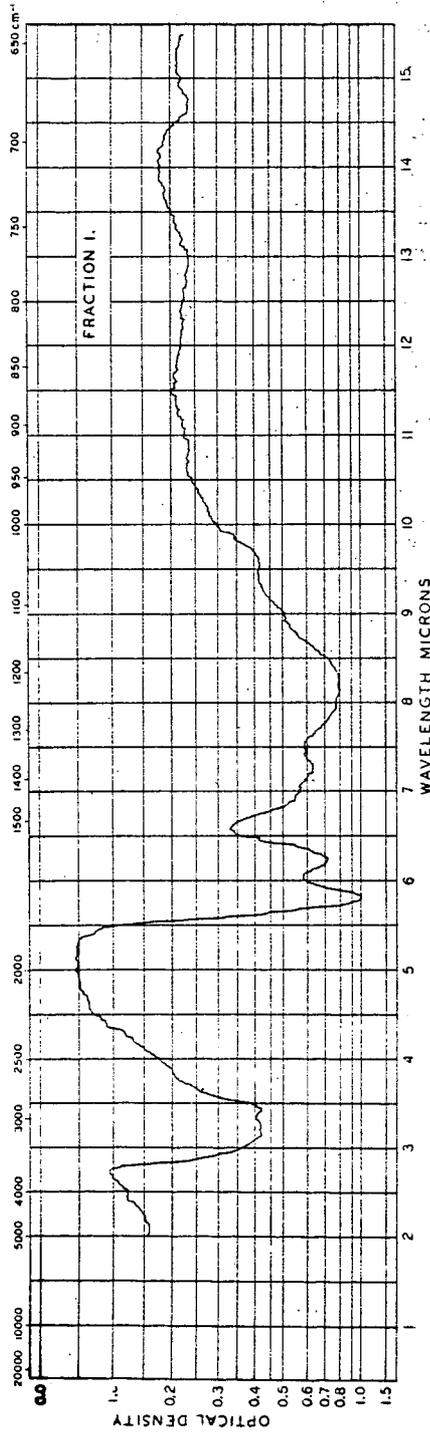
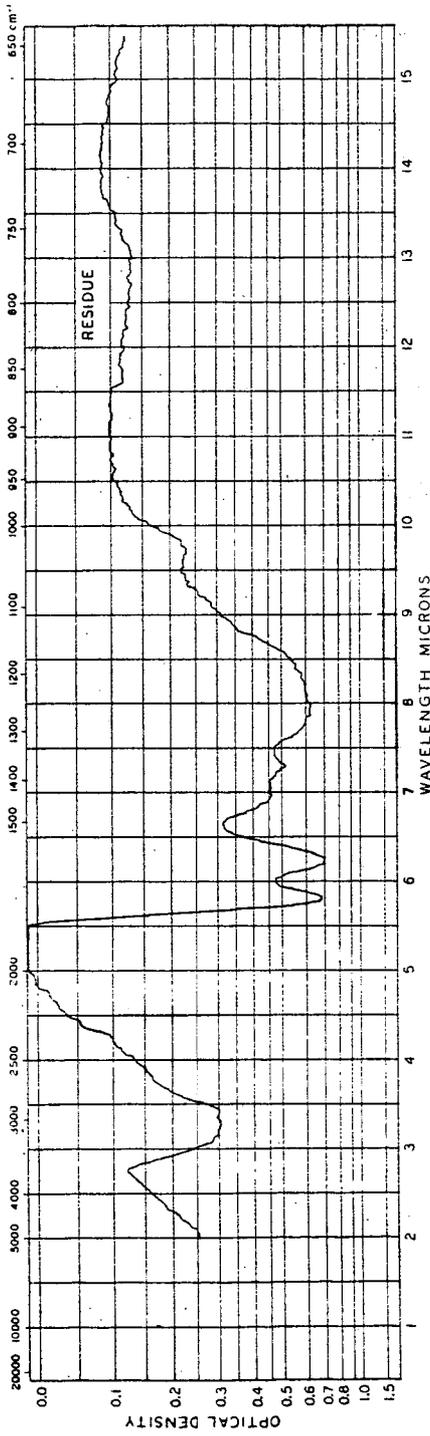


Figure 2.

Figure 3.



✓ 7 11 14 15 16 17 18 19 20 21 22 23 24

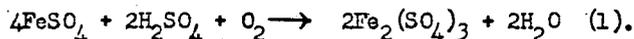
## THE ELIMINATION OF SULFUR FROM COAL BY MICROBIAL ACTION

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### INTRODUCTION

The sulfur present in coals in the form of iron pyrites is of interest for at least three reasons: (1) as a contaminant in coals used for the preparation of metallurgical coke, (2) as a contaminant in coal used for power purposes, and (3) as the ultimate source of the sulfur appearing as sulfuric acid in the effluents of mines producing acid waters. Certain bacteria are known which, when grown in the presence of pyrites, copper sulfides, or molybdenum sulfides, catalyze the formation of sulfuric acid with concurrent release of the metallic cation in a soluble form (1-3). Microbiological studies have thus far shown that one of these organisms, Ferrobacillus ferrooxidans, catalyzes the reaction:



Experimentally, it has been demonstrated that iron- and/or sulfur-oxidizing organisms catalyze the production of acid and soluble iron from coal sulfur ball material (1) or from the sulfidic constituents of finely ground coal (2). It is therefore believed that a thorough microbiological study of the oxidation of pyrites would not only clarify the role microorganisms play in the process but conceivably, through strain selection, determination of nutritional requirements, and control of the physical environment, a method for the removal of pyritic sulfur from coal by a microbial process might be devised. Such a study would also clarify the role of microorganisms in the formation of acid mine waters. A related problem, the treatment of acid waters by a microbial process utilizing the unique abilities of the bacterium Desulfovibrio desulfuricans to reduce sulfates to elemental sulfur and/or sulfide, might possibly be carried out by extension of the aforementioned line of attack.

There is very little known concerning the activities and abilities of microbes which may attack organic sulfur-containing compounds other than the naturally-occurring amino acids and vitamins. A study of the oxidation of aromatic sulfur compounds by microorganisms has been initiated in the hope of finding a way of eliminating organic sulfur from coal.

### EXPERIMENTAL

#### A. Materials and Methods

1. Stock Cultures. Stock cultures of the following autotrophic strains of bacteria have been obtained from the Syracuse University Culture Collection. (a) Ferrobacillus ferrooxidans - Culture capable of oxidizing ferrous iron to ferric state. Maintained on medium 9K (see below) containing  $\text{FeSO}_4$  as energy source. (b) Thiobacillus thiooxidans - Culture capable of oxidizing elemental sulfur to sulfate. Maintained on medium 9KS<sup>o</sup> and ThS. Strains of the heterotrophic Pseudomonas aeruginosa were those reported previously (4).

2. Media Used. The following media are used for the routine culture of the above bacteria and/or were used in the screening studies with the acid mine water samples:

(a) Medium 9K (5) for iron bacteria: Solution A - Basal Salts -  $(\text{NH}_4)_2\text{SO}_4$ , 3.00 g.; KCl, 0.10 g.;  $\text{K}_2\text{HPO}_4$ , .50 g.;  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , .50 g.;  $\text{Ca}(\text{NO}_3)_2$ , .01 g.;  $10\text{NH}_2\text{SO}_4$ , .10 ml.; distilled water, 700 ml. Solution B - Energy Source -  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ : 300 ml. of a 14.74% (w/v) solution is added to 700 ml. of the basal salts solution to make one liter of medium. The pH is 3.0 to 3.6 without further adjustment.

(b) Medium 9KS 0 - For sulfur oxidizers. As in (a) with 1-2% elemental sulfur (sterilized separately by autoclaving at 100° C. for 3 hours) replacing the iron salt as source of energy; pH adjusted to 3.5.

(c) Medium 9KS - For sulfur oxidizers. As in (a) with 1.0%  $\text{Na}_2\text{S}$  as  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) as source of energy.

(d) Medium 9KP - For iron or sulfur oxidizers. As in (a) with 5% pyrite (Sample No. PS-34-6008 obtained in a pulverized form from Bituminous Coal Research, Inc.) as source of energy. This medium was prepared at two pH levels: 3.5 and 7.0.

(e) Medium ThS - For sulfur oxidizers (6).

(f) Medium SS-1 - For sulfate reducers (6).

### 3. Bacteriological Methods

Standard plate count methods for numbers of heterotrophs were used with nutrient agar (Difco) or Czapek's medium in Petri plates. Tubes of media for determination of autotrophs were examined visually or subjected to microscopic examination. Liquid media for isolation of sulfate-reducing bacteria were prepared in Virtis anaerobic tubes. Agar media were prepared as deep tubes or drawn into foot lengths of 4 mm. OD pyrex tubing. The ends of the latter were sealed with paraffin wax. Growth in these tubes is recognized visually by the production of a black precipitate of iron sulfide.

### 4. Cultures for Manometric Experiments

Preparations of resting cells of iron and sulfur oxidizers were made according to the methods of Silverman and Lundgren (5,7); heterotrophs were grown as previously noted (4). The Warburg apparatus was used in the conventional manner to measure oxygen uptake (8). Description of the flask contents for any particular experiment is found in the figure legend.

5. Determinations of iron were made by the colorimetric o-phenanthroline method, as described in ASTM methods. A standard curve for concentrations between 20 to 240  $\mu$  of iron was prepared, reading optical density at 500 m $\mu$  in a Beckman Spectronic 20 spectrophotometer-colorimeter.

6. The source, description, and analyses of the pyritic materials is shown in Table I. The material was used as originally received (passing 65 mesh) or ground in an agate mortar to pass a 325-mesh screen. The crystalline form of the sulfuritic material in these samples was verified as pyrite by X-ray diffraction. In addition, samples of museum-grade pyrite and marcasite ground to -325 mesh were used.

Table I. Analyses of pyritic material

Sample No.	Description and source	Percent pyrite
29	Waste material—pyrite concentrate from coal from Tabo bed, Power Mine, Montrose, Henry County, Missouri.	77.0
30	Waste material—pyrite concentrate from Illinois #6 coal, Peabody #10 Mine; Christian County, Illinois.	60.0
34	Pyrite concretion (sulfur ball) from Pittsburgh bed, Osage #3 Mine, Monongalia County, West Virginia.	54.4 <sup>a</sup>
35	Pyrite concretion (sulfur ball) from Meigs Creek #9 coal, Bradford #1 Mine, Harrison County, Ohio.	74.5

a Contained 13.8% CaCO<sub>3</sub> in the form of calcite.

B. Procedures and Results

Samples of acid mine muds were obtained from shafts of the Hutchinson Mine near Irwin, Pa., and waters and bottom muds from the point of exit of the mine waters, and the acid swamp these waters form (Marchand Pool). The pool empties into Sewickley Creek, from which samples were obtained upstream from the pool entry. The samples collected are listed in Table II.

Table II. Samples of acid mine waters and related materials

Sample No.	Source	Description	pH
1	Hutchinson Mine	Acid gob (yellow mud)	2.9
2	Hutchinson Mine	Alkaline gob (orange mud)	6.3
3	Sewickley Creek,	Surface water	3.8
4	upstream from	Bottom mud	4.1
5	Marchand Pool	Green algal streamer	too small
6	Exit point of	Surface water (clear)	5.3
7	acid waters	Bottom water (clear)	5.5
8	from mine	Bottom mud (orange)	4.9
9	Junction of mine water and Marchand Pool	Bottom water (clear)	5.7
10	Marchand Pool	Top scum (oily)	4.6
11	Marchand Pool	Surface water (orange)	5.7
12	Marchand Pool	Bottom mud (orange)	5.8
13	Marchand Pool	Bottom water (green-brown)	4.9
14	Marchand Pool	Bottom water (green)	5.0
15	Pool spillway to Sewickley Creek	Bottom water (green)	5.0

After collection, the samples, were examined microscopically. The presence of viable bacteria was noted in samples 1, 2, 4, and 12. Sample 5 contained not only bacteria but green streamers recognizable as algae; numerous protozoa and planarians were present. The samples were used to inoculate duplicate tubes of culture media.

The various media were incubated at room temperature with the exception of 4 mm. OD pyrex tubes of agar medium SS-1, which were incubated at 30°C. Tubes of medium 9KS<sup>o</sup> were incubated on the shaker. The subcultures to the various media were observed daily and examined microscopically as required.

Observations made on the various media after one week of incubation at room temperature are summarized in Table III. Microscopic observations were made on the pyrite and iron media (9KP and 9K), although in some cases, simple visual examination was sufficient to recognize the deep red-orange precipitate formed by iron oxidation.

Table III. Growth in various culture media one week<sup>a</sup> after inoculation with acid mine water samples

Growth in media containing the energy sources designated							
Sample	S <sup>=</sup>	Pyrite	Pyrite	Fe <sup>++</sup>	SO <sub>4</sub> <sup>=</sup> (anaerobic tubes)	SO <sub>4</sub> <sup>=</sup> (capillary tubes)	S
1	-	+	+	+	-	-	+
2	-			+	+	+	+
3	-			+			+
4	-	+	+	+	+	+	+
5	+			+	-	-	+
6	-	-	-	-			+
7	-	+	+	+			+
8	+	+	+	+	+	+	+
9	-	-	-	-			-
10	-			+			-
11	-			+			+
12	+	+	+	+	+	+	+
13	-	-	-	-	-	-	-
14	-			-	-	-	+
15	-	-	-	-			+

a Medium 9KS<sup>o</sup> examined after 10 days of shaking.

The cultures were carried through serial transfer on the appropriate media; determination of growth was made by a combination of microscopic examination and visual inspection.

The activity of resting cells of Ferrobacillus ferrooxidans on pyrites was tested by means of the Warburg technique. This technique is excellent for the determination of: (1) the ability of selected cultures to oxidize pyrite, (2) differences in the susceptibility of the various pyrites to oxidation, and (3) the physiology of pyrite oxidation by bacteria in short-term experiments. Pyrite samples (65 mesh) were weighed and placed in the Warburg vessel with sufficient cell suspension (pH 3.5) and water (pH 3.5) to bring the volume to a predetermined value. Cell suspensions for the experiments were adjusted to 0.4 mg. bacterial-N/ml. Oxygen uptake was measured in the conventional manner. Results of two such experiments with concentration of pyrites and cells as variables are shown in Figures 1 and 2. The rate of pyrite oxidation was increased only two-fold by a twenty-fold increase in pyrite concentration with these 65 mesh samples.

A series of Warburg experiments demonstrated the role of particle size of the substrate on oxidation rates. The results (shown in Table IV) demonstrate that reduction in particle size enhanced bacterial action six-fold in the case of the pyrite concretion and 35- to 70-fold when the pyrite concentrates were used as substrates. Oxidation with the bacteria was 20 to 40 times that of the controls for 3 of the 4 pyrites tested.

Table IV. Oxidation of pyritic material of two particle sizes in the presence of Ferrobacillus ferrooxidans

Sample No.	Microliters oxygen taken up in three hours <sup>a</sup>			
	Approximately 65 mesh		Passing through 325 mesh	
	No cells	Cells	No cells	Cells
29	28 <sup>+</sup>	40	60	1342
30	12	16	51 <sup>+</sup>	1137
34	23 <sup>+</sup>	11 <sup>+</sup>	91	29 <sup>+</sup>
35	24 <sup>+</sup>	336	46	2040

a Oxygen uptake/1.2 mg. bacterial-nitrogen/three hours.

+ Apparent evolution of gas.

In separate shaken-flask experiments the release of hydrochloric acid-soluble iron was determined instead of oxygen uptake, as a means of demonstrating oxidation of the pyrites. Results of iron determinations in one such experiment are shown in the following table (Table V). The 25 ml. conical flask used contained 100 mg. of pyritic material, an aliquot of cell suspension containing 0.84 mg. bacterial nitrogen and sufficient H<sub>2</sub>SO<sub>4</sub>-acidified water, pH 3.5, to bring the total volume to 4.0 ml. After 24 hours, 4.0 ml. of 2.0N HCl was added and the mixture heated 30 minutes on a steam bath. The HCl-soluble iron content of suitable filtered aliquots was determined as given in the section on Methods.

TABLE V. Production of hydrochloric acid-soluble iron from pyritic material in the presence of Ferrobacillus ferrooxidans

Sample No.	Cells	Micrograms HCl-soluble iron released <sup>a</sup>			
		Initial	24 hours	Net	Pyrite oxidized, %
29	+	1024 <sup>b</sup>	4400	3376	9.42
	-	808	1080	272	0.76
30	+	1250	4000	2750	9.34
	-	1034	1376	342	1.22
35	+	3040	7200	4160	11.99
	-	2824	3140	316	0.91

a Production of iron from 100 mg. pyritic material in the presence of 0.84 mg. bacterial-N.

b 216  $\mu$ g. Fe were carried over with the cell suspension.

The ability of Thiobacillus thiooxidans to accelerate the oxidation of the pyrite samples was also tested in Warburg experiments. It was found that this organism was unable to accelerate oxidation rates over those of control vessels. The ability of T. thiooxidans and F. ferrooxidans to accelerate oxidation of museum grade samples (large crystals free of inclusions and contaminating materials) of pyrite and marcasite was tested. It was found that both strains attacked the marcasite, Ferrobacillus being more effective; neither culture accelerated the oxidation of museum grade pyrite. Results of these experiments are seen in Table VI.

Table VI. Effect of Thiobacillus thiooxidans or Ferrobacillus ferrooxidans on the oxidation of museum grade sulfide minerals  
Microliters oxygen taken up in 3 hours per mg. bacterial-nitrogen

Sample	Cells	Microliters oxygen taken up in 3 hours per mg. bacterial-nitrogen	
		<u>T. thiooxidans</u>	<u>F. ferrooxidans</u>
Pyrite	-	15	38
	+	70 <sup>a</sup>	19 <sup>a</sup>
Marcasite	-	82	209
	+	128	734

a Apparent gas evolution.

Efficacy of use of a mixture of the two strains was also tested. In these Warburg experiments a resting cell suspension of Ferrobacillus was placed in the vessel and oxygen uptake was measured for one hour. At the end of this time the sulfur-oxidizing Thiobacillus was tipped into the reaction mixture. The effect on oxidation of samples 29, 30, 35, and museum grade marcasite was determined. The effect of addition of Thiobacillus is seen in Figure 3.

The rate of oxidation of ferrous iron and elemental sulfur by the strains of Ferrobacillus ferrooxidans and Thiobacillus thiooxidans in use in the experiments has been calculated from the data obtained in the preceding experiments. These are presented in Table VII.

Table VII. Rates of oxidation of ferrous iron and elemental sulfur by Ferrobacillus ferrooxidans and Thiobacillus thiooxidans

Organism	$Q_{O_2} (N)^a$	
	S (1000 $\mu$ moles)	Fe <sup>++</sup> (500 $\mu$ moles)
T. thiooxidans	557	0
F. ferrooxidans	148	3672

a  $Q_{O_2} (N)$  represents  $\mu$ liters oxygen uptake/mg. cell-nitrogen/hour.

Other manometric experiments with polycyclic aromatic hydrocarbon-grown cells of a strain of Pseudomonas aeruginosa were carried out to study the activity of bacteria regarding sulfur-containing organic compounds. It was found that cells grown with phenanthrene as source of carbon would take up more oxygen than cells grown on naphthalene when benzthiophene was provided them as a substrate. Benzthiophene was chosen as a model sulfur containing aromatic of the type thought to be present in coal. If oxygen uptake of both crops with naphthalene as substrate is calculated to a value of 1.0, then uptakes on benzthiophene were: naphthalene-grown, 0.3; phenanthrene-grown, 1.3.

Benzthiophene was provided at a concentration of 3.3  $\mu$ moles/ml. At 6.6  $\mu$ moles/milliliter, less oxygen was taken up than at the lower concentration. At 3.3  $\mu$ moles/ml, addition of benzthiophene to the flask contents served to lower oxygen uptake of cells metabolizing naphthalene and 2-methylnaphthalene (Figure 4). Thus it seems that a competitive inhibition or perhaps simple toxicity of the compound may be evident except in the case of cells grown on or metabolizing phenanthrene (Figure 5).

#### DISCUSSION OF RESULTS

Results obtained on examination of the microflora of acid mine drainage showed that top waters and rapidly running waters (green) were almost sterile in all cases. The best sources of microorganisms are the muds, which are apparently rich in all forms tested for. The bottom muds (orange) collected at the pool accumulate only where the water is not turbulent or flowing too rapidly. Where water flow is rapid, bottom mud does not accumulate, the orange color of oxidized iron products is absent, and the number of microorganisms present is quite small. In the laboratory, samples of such moving clear water after two weeks of incubation give evidence of iron oxidation (orange precipitate, heavy). The reason for their clarity is probably that they are simply flowing too rapidly for oxidation of iron to occur. Thus, clarity of water is no criterion of its potential yield of ferruginous mud under non-agitated conditions.

The finding that all types of bacteria tested for appear to be present in the samples illustrates that those chemicals present in an environment are usually accompanied by bacteria capable of utilizing them. The importance of these particular types found, in regard to the problems of sulfur removal from coal and treatment of acid mine waters, is as follows:

(1) The same organisms which play a role in the production of acid mine waters, and in whose presence oxidation of large sulfidic concretions, pyrite, and marcasite has been demonstrated are precisely those forms whose abilities must be exploited in any attempt to desulfurize coal by microbiological means.

(2) In any plan for disposal of sulfuric acid microbiologically, the use of anaerobic sulfate-reducing bacteria to convert sulfuric acid to elemental sulfur and/or hydrogen sulfide must be considered. The isolation of such bacteria from the bottom mud samples collected gives hope that strains of these organisms able to tolerate the acid environment necessitated by the use intended can be found or developed. Acid conditions are known not to be optimum for their growth, but their presence in samples 4 and 5 at pHs of 4.1 and 4.9, respectively, indicate they may be more tolerant of acid than previously assumed.

(3) The presence of sulfur oxidizers, iron oxidizers, and sulfate reducers in a given environment (ferruginous mud) indicates that all three forms may participate in a cyclical process for sulfur. Thus, it appears that previous testing of pyrite oxidation with pure cultures of bacteria may not provide the best means possible for carrying out the process. It may well be better to try the natural flora for most efficient activity, although mixed cells of Ferrobacillus and Thiobacillus did not have the desired effect on pyrite (Figure 3).

The manometric studies (Figures 1 and 2) with 65 mesh sample #35 demonstrated that oxygen uptake is significantly greater than that required solely for the oxidation of ferrous iron initially present in the pyrite sample as determined by our extraction procedure.

Significantly higher oxidation rates were obtained when the sulfidic materials were ground to pass 325 mesh (Table IV). The ability of Ferrobacillus to accelerate the oxidation of the pyrite in samples 29 and 30 is encouraging as regards microbial coal desulfurization. These samples are pyrite concentrates from coal. These contain minute crystals of pyrite embedded in the coal with perhaps only one face exposed for oxidation. Yet in the presence of the bacteria oxidation proceeds at a rapid rate as compared to the rates in the absence of the organisms.

Based on the results found in these studies (Tables III-VII, Figures 1-5) certain generalizations regarding microbial processes for coal desulfurization may be drawn. These are that: 1. The rate of pyrite oxidation depends upon available, that is, exposed pyrite. As a corollary to this, the coal must be in a finely divided state in order to expose a maximum of the embedded pyrite. 2. The rate of oxidation of pyrite depends upon the "type" of pyrite present. The word type is used for want of a better description, since X-ray diffraction patterns are identical for the pyrite of samples 29, 30, 34, 35, and museum-grade pyrite.

Only sample #34 and museum-grade pyrite resisted oxidation in the presence of F. ferrooxidans. Sample #34 contained considerable calcite. Preliminary experiments after the calcite had been removed (neutralizing effect of  $\text{CaCO}_3$ ) gave indication of oxidative activity.

The ubiquitous presence of Thiobacillus thiooxidans in acid-mine waters is as yet unexplained. Our results show that only marcasite, a substance rarely present in acid-producing areas, can be attacked by this organism, raising the question of a possible energy source for the organism. The production of free sulfur during the oxidation of pyrite is one explanation. However, the ability of the iron-oxidizing F. ferrooxidans to oxidize elemental sulfur suggests another explanation.

The three organisms found in acid mine waters are listed below together with their proposed energy sources.

<u>Organisms</u>	<u>Energy source</u>
<u>Thiobacillus thiooxidans</u>	Elemental S
<u>Thiobacillus ferrooxidans</u>	Ferrous iron; thiosulfate
<u>Ferrobacillus ferrooxidans</u>	Ferrous iron

The three are morphologically indistinguishable; the chief criteria for their description being energy source. During isolation procedures, it is entirely possible that F. ferrooxidans will grow in an iron medium and be identified as F. ferrooxidans and also be isolated in an elemental S medium and be identified as T. thiooxidans. Thus, F. ferrooxidans may really be a variant of T. thiooxidans and exists in acid-mine waters by virtue of its iron oxidizing capacity. The inability of Thiobacillus thiooxidans to oxidize iron may be due to the loss of adaptive iron-oxidizing enzymes upon growth in elemental sulfur.

The ability of bacteria to accelerate the oxidation of sulfuritic material has been studied primarily by investigators at the Mellon Institute (1) and West Virginia University (9). Their studies involved testing for the production of free iron, sulfate, or increased acidity from insoluble pyrite materials in the presence or absence of bacteria in experiments of long duration. The development of methods and media for the propagation in high yield of the relevant bacteria (5, 7) has enabled us to utilize the manometric method for examining the role of bacteria in the oxidation of pyrites, thus enabling us to accumulate comparable data in a short time. A comparison of the results obtained with those of the Mellon Institute and West Virginia University is given in Table VIII. In general, our findings agree most closely with those of the Mellon Institute.

Table VIII. Acceleration of the rate of oxidation of different pyritic materials by iron- and sulfur-oxidizing bacteria

	<u>Ferrobacillus ferrooxidans</u>			<u>Thiobacillus ferrooxidans</u>			<u>Thiobacillus thiooxidans</u>		
	M.I.	W.V.U.	B.M.	M.I.	W.V.U.	B.M.	M.I.	W.V.U.	B.M.
Sulfur ball	+	N.T. <sup>a</sup>	+	N.T.	+	N.T.	-	+	-
Waste material	N.T.	N.T.	+	N.T.	N.T.	N.T.	N.T.	N.T.	-
Museum-grade marcasite	+	N.T.	+	N.T.	N.T.	N.T.	+	+	+
Museum-grade pyrite	-	N.T.	-	N.T.	+	N.T.	-	N.T.	-

a N.T. = not tested.

#### ACKNOWLEDGMENTS

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#### Literature Cited

- (1) Leathen, W.W., Microbiological Studies of Bituminous Coal Mine Drainage. Mellon Inst. of Ind. Res. Special Summary Report (1952) 64 pp.
- (2) Ashmead, D., Influence of Bacteria in the Formation of Acid Mine Waters. Coll. Guard., 190, 694-698 (1955).
- (3) Bryner, L.C., and Anderson R., Microorganisms in Leaching Sulfide Minerals. Ind. Eng. Chem., 49, 1721-1723 (1957).
- (4) Rogoff, M.H., and Wender, I., Methyl-naphthalene Oxidation of Pseudomonads. Jour. Bact., 77, 783-788 (1959).
- (5) Silverman, M.P., and Lundgren, D. G., Studies of the Chemoautotrophic Iron Bacterium Ferrobacillus ferrooxidans I. Jour. Bact., 77, 642-647 (1959).
- (6) Starkey, R.L., Isolation of Some Bacteria Which Oxidize Thiosulfate. Soil Sci., 39, 197-219 (1935).
- (7) Silverman, M.P., and Lundgren, D.G., Studies on the Chemoautotrophic Iron Bacterium Ferrobacillus ferrooxidans II. Manometric Studies. Jour. Bact., 78, 326-331 (1959).
- (8) Umbreit, W.W., Burris, R.H., and Stauffer, J.F., Manometric Techniques, (1957), Burgess Publishing Co., Minneapolis.
- (9) Temple, K.L., and Koehler, W.A., Drainage from Bituminous Coal Mines. West Virginia Univ. Bull. No. 25, 1954.

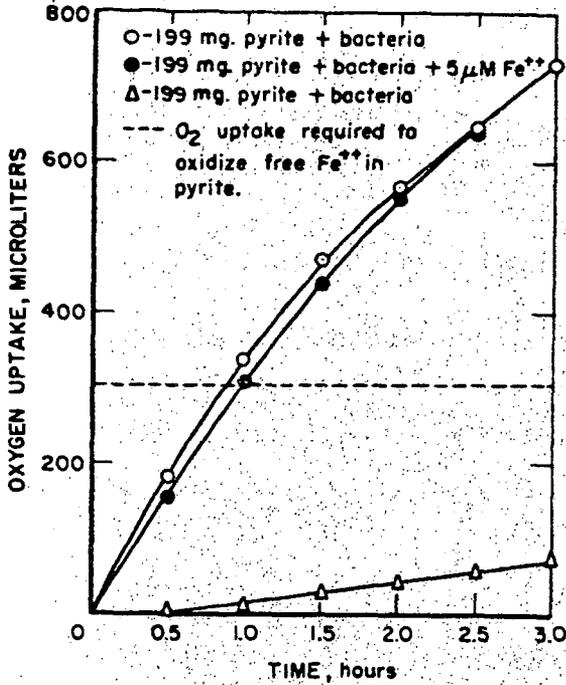


Figure 1.-Oxidation of sulfur ball (199 mg.) by *Ferrobacillus ferrooxidans*.

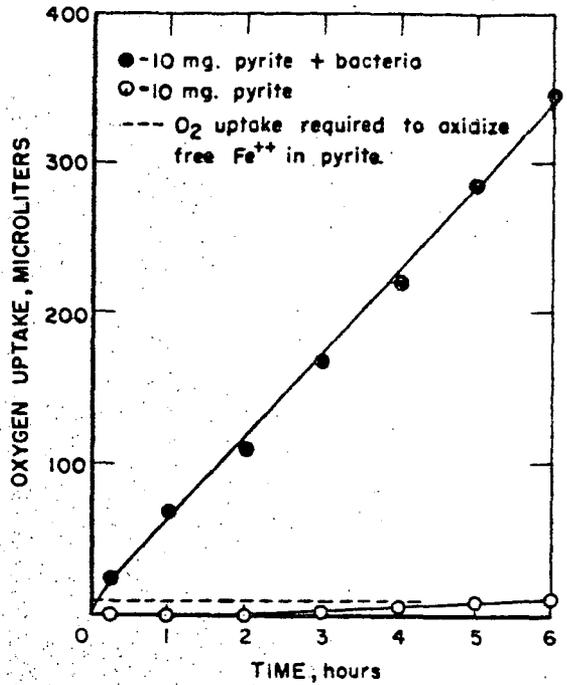


Figure 2.-Oxidation of sulfur ball (10 mg.) by *Ferrobacillus ferrooxidans*.

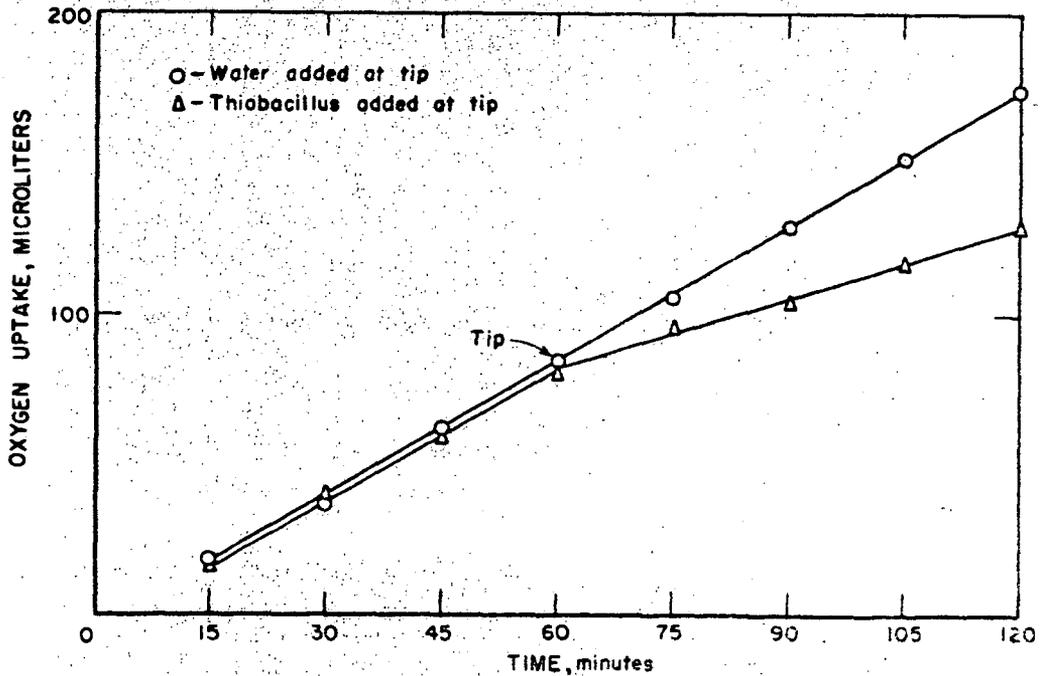


Figure 3.-Oxidation of sulfur ball (20mg.) by *Ferrobacillus ferrooxidans*.

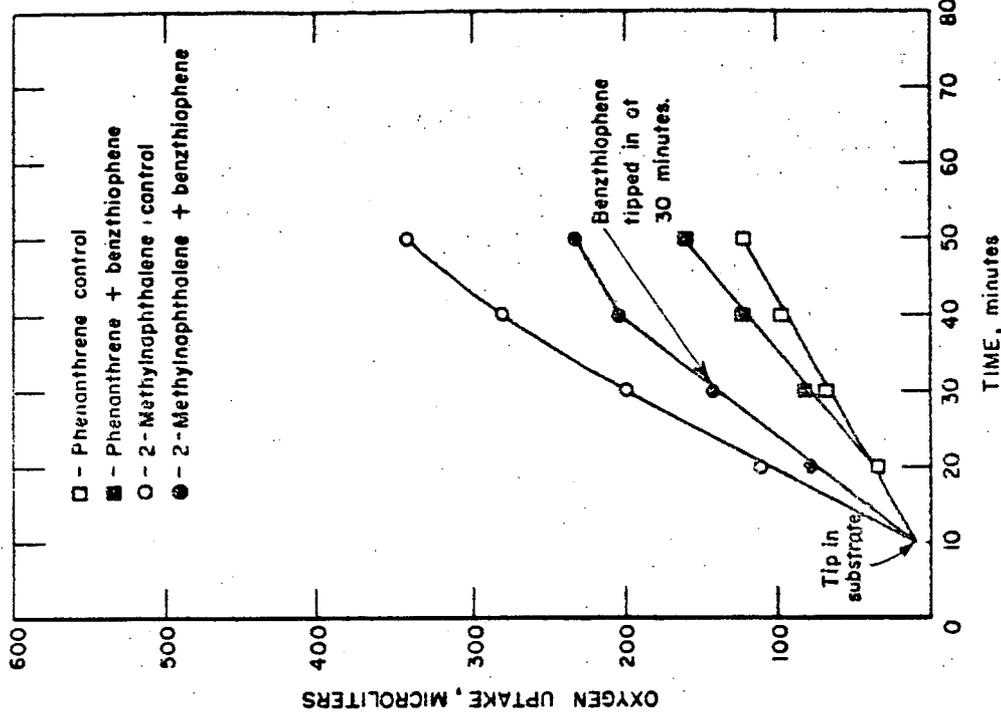


Figure 5.-Oxidation of aromatic hydrocarbons by strain PM-1.

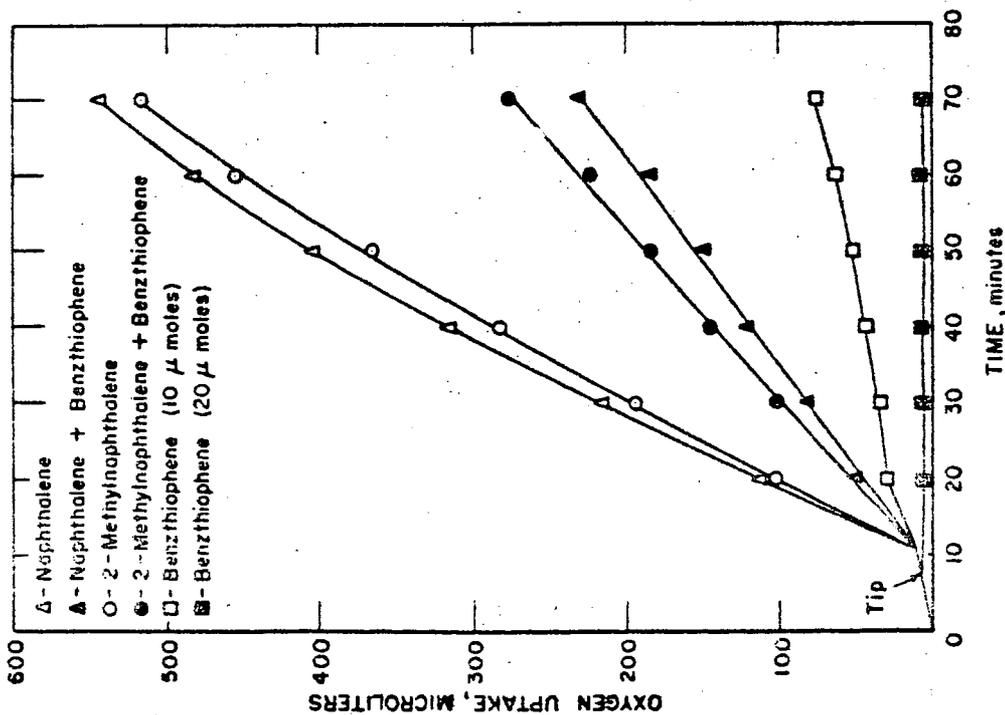


Figure 4.-Oxidation of aromatic hydrocarbons by strain PM-1.

CONSTITUTION OF HYDROCARBON-LIKE MATERIALS DERIVED FROM  
KEROGEN OXIDATION PRODUCTS

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Oxidation is one method of converting the insoluble organic material (commonly called kerogen) present in oil shale to soluble degradation products for constitutional studies. The amount of degradation and the molecular weight of the products depend upon the extent of oxidation and severity of the reaction conditions. A variety of oxidants can be used to accomplish this degradation, but some are more suitable than others.

In a previous study (6), organic material from Colorado oil shale was oxidized to high-molecular-weight acids by a boiling solution of alkaline potassium permanganate under controlled conditions, and to carbon dioxide and oxalic acid by exhaustive oxidation for 100 hours. By choosing different ratios of  $KMnO_4$  to kerogen, large or small amounts of intermediate acids were obtained. However, it was not possible to obtain complete conversion to intermediate acids without simultaneously producing carbon dioxide and oxalic acid. In general, small yields of final oxidation products were associated with large yields of high-molecular-weight intermediate acids and vice versa.

In another report (5), the nature of the organic acids that were obtained by oxidizing raw oil shale from the Mahogany-zone beds of the Green River formation near Rifle, Colo., was studied. The oil shale assayed approximately 66 gallons of oil per ton of shale and contained about 34% kerogen. An oxidation product was prepared by treating each part of organic carbon present in the kerogen with eight parts of  $KMnO_4$ . The organic acids obtained were converted to n-butyl esters, fractionated by distillation, and identified, where possible, by mass and infrared spectra of the esters and by X-ray diffraction of selected derivatives. A total of 59% of the organic acids in the oxidation product was identified as  $C_2$  to  $C_8$  difunctional acids of the alkane series. The remaining 41% of the organic acids were not identified by this method because of their complex nature. Identification or classification of this material would contribute to the knowledge of the structure of kerogen and might suggest new commercial uses for oil shale.

In this study by the Federal Bureau of Mines, characterization of the remaining 41% of the organic acids in this oxidation product was accomplished by reducing the carboxyl groups of the acids through a series of reactions. The resulting hydrocarbon-like materials were amenable to fractionation and characterization. Some of the usual methods of decarboxylation were tried, but extensive thermal degradation resulted.

The oxidation product also contained n-paraffinic, isoparaffinic, aromatic, naphthenic, and heterocyclic acids. The naphthenic and heterocyclic acids predominated, which suggested that the structure of Colorado kerogen is mainly alicyclic and heterocyclic, with smaller amounts of straight-chain and aromatic structures.

#### EXPERIMENTAL PROCEDURE

Preparation of Organic Acids. Kerogen oxidation products were prepared from raw oil shale using a method described in earlier reports (5,6). The raw oil shale was oxidized in two steps by an aqueous solution of alkaline  $KMnO_4$ . The first step was treatment of 1 part of organic carbon of the kerogen with 6 parts of  $KMnO_4$ , 1.6

parts of KOH and 34 parts of water at 70° to 90° C. until the  $\text{KMnO}_4$  was reduced. The treatment was repeated in the second step except that only 2 parts of  $\text{KMnO}_4$  were used. The alkaline solution was separated from the shale residue, acidified with 1 to 1 sulfuric acid and evaporated to dryness. Nonvolatile organic acids were extracted from this dried product using methyl ethyl ketone. Based upon total carbon, the kerogen was oxidized to 58% nonvolatile acids, 15% carbon dioxide, a trace of volatile acids, and 27% remained unoxidized.

Preparation of n-Butyl Esters. The nonvolatile organic acids were converted to n-butyl esters by reacting 250 grams (0.8 mole) of the acids with 1275 ml. (14 mole) of n-butyl alcohol and 25 ml. (0.5 mole) of concentrated sulfuric acid under reflux conditions for about 100 hours. Water was removed by using an enlarged Dean-Stark tube mounted above the reaction flask. After completion of the reaction, the n-butyl alcohol was removed by distillation. The resulting product was dissolved in ether, was washed free of acid with a solution of sodium carbonate, and finally was dried over anhydrous sodium sulfate and recovered.

Preparation of Alcohols. All the recovered n-butyl esters were reduced to alcohols in the following manner (1): The esters were treated with a total of 61 grams (1.6 mole) of  $\text{LiAlH}_4$  in 2500 ml. (23.6 mole) of anhydrous ether in five different batches. An ether solution of the esters was added slowly to an ether solution of  $\text{LiAlH}_4$ , then refluxed 4 to 5 hours. Excess hydride was decomposed by cautiously adding water to the reaction mixture. After gas stopped evolving, the complex was treated with 10% sulfuric acid and the reduced product was recovered from the ethereal layer.

Preparation of Iodides. The alcohols were converted to iodides by reacting the alcohols with 115 grams (0.8 mole) of  $\text{P}_2\text{O}_5$ , 216 ml. (3.2 mole) of 85%  $\text{H}_3\text{PO}_4$  and 530 grams (3.2 mole) of KI (7). After the reaction mixture was heated at 100° to 120° C. for 3 to 5 hours, the iodides were extracted with ether. The ether solution was washed with sodium thiosulfate and sodium chloride solutions, dried over anhydrous sodium sulfate, and the ether was distilled from the iodides.

Reduction of Iodides. The resulting iodides were reduced with zinc and hydrogen chloride gas (2). Zinc dust was added over a period of 2 hours to a warm glacial acetic acid solution of the iodides, which was constantly stirred. The reaction mixture was stirred and heated at 90° to 95° C. for an additional 24 hours and was saturated with dry HCl gas every 4 hours. A trap, submerged in a dry ice and acetone bath, was connected to the exit gas tube to condense any hydrocarbons with low boiling points formed during the reduction. After completion of the reaction, the mixture was diluted with water, and the product was extracted with ether. After the ether solution was washed free of acid, it was dried over anhydrous sodium sulfate, and the ether was partly distilled from the product.

Fractionation of the Reduced Product. The product and a small quantity of ether were placed in a spinning band distillation column and distilled at atmospheric pressure (580 mm. mercury) up to a head temperature of 70° C. (pot temperature of 175° C.). After the reduced product cooled to room temperature, the distillation was continued at 1 mm. mercury pressure with a head temperature up to 130° C. and a pot temperature of 200° C.

A flow diagram of the fractionation of the distillate and distillation residue is shown in figure 1. The distillate and residue fractions were dissolved in a 40 to 1 volume ratio of pentane, allowed to stand overnight at 0° C., and then filtered. The insoluble material was washed with a small quantity of cold pentane, freed of solvent, and weighed. The pentane-soluble material was fractionated on pretreated columns of alumina (25 to 1 weight ratio of Alcoa XF-21 alumina) using pentane, benzene and a 10% methanol-90% benzene mixture as eluting solvents. The benzene-eluted material, referred to as nonpolar resins, and the benzene-methanol eluted resins, referred to as polar resins, were freed of solvent and weighed.

Wax was separated by dissolving the pentane-eluted fraction (oil plus wax) in a 40 to 1 volume ratio of methyl ethyl ketone (MEK), allowing it to stand at  $-5^{\circ}\text{C}$ . for 1 hour. The wax was filtered from the MEK-soluble oil, freed of solvent, and weighed. Urea adducts were prepared by reacting each gram of wax with 21 ml. of a saturated solution of urea in methanol. Excess urea, 1.5 grams per gram of wax, and 6 or 7 drops of benzene, were added. This mixture was stirred at room temperature for 24 hours. The adduct and nonadduct waxes were separated by filtration; the adduct was then decomposed with hot water and extracted with ether. Both fractions were freed of solvent by distillation. Wax was not separated from the distillate fraction.

The distillate oil, the wax fraction, and the distillation residue oil were fractionated by a method similar to that reported by Mair, Marculartis and Rossini (3). Each fraction was placed on a pretreated column of silica gel (25 grams of Davidson analytical grade silica gel to 1 gram of sample) and eluted successively with 2,2,4-trimethyl pentane, benzene, and 2-propanol. The fractions were freed of solvent, weighed and identified as paraffin oil, aromatic oil, and polar oil respectively. The paraffin oil from the distillation residue was adducted with urea by the same technique used for waxes. The aromatic oil from the distillation residue was further fractionated on a pretreated column of alumina using a 25-to-1 ratio of alumina to sample. Eluting materials were a mixture of iso-octenes, benzene, and 2-propanol.

Reduction with Hydriodic Acid. The wax and paraffin oil fractions were completely reduced by concentrated hydriodic acid. Samples of 0.1 to 0.5 gram were reduced by sealing them in glass ampoules with 15 ml. of concentrated hydriodic acid (sp. gr. 1.9) and heating at  $175^{\circ}\text{C}$ . for 24 hours. The treated samples were dissolved in benzene and washed free of iodine with a solution of sodium thiosulfate. The benzene solution was washed with water and finally dried over anhydrous sodium carbonate. Benzene was distilled from the reduced product at reduced pressure.

Physical and Chemical Properties. The elemental composition and functional groups of the fractions were determined by macro methods at the Bureau's laboratory and by micro methods at a commercial laboratory, using conventional methods. Carbon and hydrogen were determined by combustion, nitrogen by the Kjeldahl or Dumas methods, sulfur by ignition in a Parr oxygen bomb, oxygen by difference or by the Unterzaucher direct method, saponification equivalents by hydrolysis and hydroxyl groups by acetylation. Molecular weights were determined from mass spectra and by the rise-in-boiling-point method using benzene as solvent. Infrared and mass spectra, as well as X-ray diffraction, were used to characterize the various fractions.

## RESULTS AND DISCUSSION

The total yield of reduced product from 250 grams of kerogen acids amounted to 36 grams after removal of all solvents, or approximately 15 weight percent. The theoretical yield, based on data from a previous study (5), was 198 grams or 79 weight percent. However, approximately 50% of the oxidation product consisted of difunctional acids containing 2 to 4 carbon atoms per molecule. The reduction method used in this study converted these acids to gases that were not recovered in the reduced product. Because of this loss, the overall yield of reduced product was 36% of the theoretical. Typical yields were: esters - 95%, alcohols - 75%, iodides - 95%, and hydrocarbons 50%. Losses were probably due to handling rather than to unreactivity of the components. However, the possibility of fractionation occurring did exist and some unreactive parts of the oxidation product may have been eliminated from the reduced material. Vacuum distillation of the reduced product resulted in a yield of 8.5% distillate and 91.5% distillation residue.

Composition of the Distillate Fraction. In addition to the solvents used, the distillate obtained by atmospheric distillation contained trace amounts of pentanes, hexanes, hexenes, and cyclohexanes. The distillate obtained by vacuum distillation (8.5% of the total reduced product) was fractionated by the method described earlier

and shown in figure 1. Nearly equal amounts of five fractions were obtained, namely paraffin oil, aromatic oil, polar oil, nonpolar resins, and polar resins.

Mass spectra analysis of the paraffin oil fraction showed that it consisted of isoparaffins and cycloparaffins, with the latter predominating. The cyclic part contained 1 to 5 rings per molecule with dinuclear material constituting the largest single type material. The major components of the aromatic fraction were benzenes, indanes/tetralins and naphthalenes.

Infrared analysis of the nonpolar resins, polar resins, and polar oil indicated that these fractions were predominantly cyclic because absorption in the 13.7 and 13.9 micron region was very weak. They also appeared highly saturated as shown by strong absorption in the 3.45 and 6.84 micron regions. The presence of considerable terminal CH<sub>3</sub> groups was suggested by medium to strong absorption in the 7.3 micron region. Absorption in the aromatic region was weak. There was indication of the presence of OH groups and other oxygen functionals; however, the strong absorption in the 5.70, 5.78, and 5.95 micron region may be due to C=O groups of unreduced esters.

Composition of the Distillation Residue. The amount of each of the various fractions from the distillation residue, which represented 91.5% of the reduced product, is shown in table 1. The major fractions consisted of resins and paraffin oil, while wax, aromatic oil, polar oil, and pentane-insoluble material were present in smaller amounts. Molecular weights ranged from about 300 to 1200.

Table 1. Distribution and Molecular Weights of the Distillation Residue Fractions

	Percentage of Total Distillation Residue	Percentage of Total Reduced Product	Molecular Weights
Pentane-insoluble material	3.0	2.7	1220
Resins			
Nonpolar resins	11.9	10.9	530
Polar resins	25.9	23.7	800
Wax			
Urea adduct	3.0	2.7	405
Urea nonadduct	10.4	9.5	400
Oil			
Paraffin oil adduct	1.5	1.4	310
Paraffin oil nonadduct	30.5	27.9	410
Aromatic oil (iso-octene eluted)	9.5	8.7	270
Aromatic oil (benzene eluted)	0.3	0.3	340
Aromatic oil (2-propanol eluted)	0.3	0.3	345
Polar oil	<u>3.7</u>	<u>3.4</u>	-
Total	100.0	91.5 <sup>a</sup>	

<sup>a</sup>The remaining 8.5% consisted of the vacuum distillate fraction.

Ultimate analyses shown in table 2 indicated that the recovered fractions contained appreciable amounts of oxygen. It was necessary to determine the nature of

this oxygen and to eliminate the oxygen from portions of the fractions by HI reduction, so that mass spectra data for ring analysis and carbon chain length would have meaning.

Table 2. Elemental Analyses of Distillation Residue Fractions

	C	H	O	N	S	Atomic H/C
<b>Wax</b>						
Urea adduct	83.6	14.2	1.8 <sup>a</sup>	0.2	0.2	2.04
Urea nonadduct	82.9	11.1	5.4 <sup>a</sup>	0.2	0.4	1.61
<b>Oil</b>						
Adduct paraffin	84.2	14.3	1.2 <sup>a</sup>	0.2	0.1	2.04
Nonadduct paraffin	81.1	11.1	7.6 <sup>b</sup>	0.0	0.2	1.64
Mono/di-aromatic	86.2	11.2	-	2.6 <sup>c</sup>	-	1.56
<b>Resins</b>						
Nonpolar	78.9	10.1	9.4 <sup>b</sup>	0.4	1.2	1.54
Polar	70.2	9.6	19.1 <sup>b</sup>	1.0	0.1	1.64

<sup>a</sup>Direct oxygen (Unterzaucher).

<sup>b</sup>Oxygen was determined by difference.

<sup>c</sup>Total oxygen, nitrogen, and sulfur determined by difference.

An estimate of the type and amount of oxygen functional groups for various fractions was obtained by analyses for hydroxyl, ester, and alkoxy oxygen. Other ether, carbonyl and unaccounted for oxygen was determined by difference. As this difference value was large in all cases, infrared analyses was used to indicate the most likely type oxygen present.

Mass spectra data reported for the oil and wax fractions were obtained from the HI-reduced material. By contrast, infrared spectra was determined on the oil, wax, and resin fractions before reduction with hydriodic acid; also the aromatic oil was not reduced with HI.

**Adduct Wax.** Based on mass spectra data, this fraction, which represented 2.7% of the total reduced product, contained mostly isoparaffins and normal paraffins with smaller amounts of cycloparaffins (table 3). Isoparaffins appeared to predominate over normal paraffins; the normal paraffins ranged from C<sub>13</sub> to C<sub>36</sub> carbon chains with an average chain length of C<sub>26</sub>. (Average carbon chain length of this wax, determined by X-ray diffraction, was 28.) These data showed the presence of long carbon chains, which suggested that the original oxidation product contained a small amount of fatty acids.

Ultimate analyses (table 2) showed that the adduct wax was highly saturated with hydrogen and contained 1.3% oxygen. Infrared analyses of the fraction before reduction with HI, shown in table 4, confirmed the presence of a predominance of chain structures. The average molecular weight of the adduct wax before reduction with HI was 405.

**Nonadduct Wax.** By contrast, the nonadduct wax fraction, which represented 9.5% of the total reduced product, contained predominantly cyclic structures and only a small amount of normal paraffins and isoparaffins (table 3). The cyclic portion

consisted of aromatic and naphthenic rings with a predominance of the naphthenic rings. The number of rings per molecule ranged from 1 to 6 with an average of 2 to 3 rings per molecule.

Table 3. Constitution of the HI-reduced Wax and Paraffin Oil Fractions Obtained from the Distillation Residue

	Average Composition, mole % <sup>a</sup>			
	Wax		Paraffin Oil	
	Adduct	Nonadduct	Adduct	Nonadduct
n-Paraffins	27	4 <sup>b</sup>	84	6 <sup>b</sup>
Isoparaffins	66	-	7	-
Naphthenes				
Mono and noncondensed naphthenes	3	11	-	18
Condensed naphthenes				
2 rings	1	19	1	22
3 rings	1	14	2	13
4 rings	1	5	2	3
5 rings	1	19	2	7
6 rings	-	6	2	6
Aromatics	-	22	3	25
Total	100	100	100	100

<sup>a</sup>Determined from mass spectra.

<sup>b</sup>Total normal and isoparaffins.

Oxygen functional groups were determined by the methods described earlier and the results are shown in table 5. The fraction contained 5.4% oxygen (table 2), which appeared to be mostly in the form of ether or carbonyl oxygen with smaller amounts of ester, but no hydroxyl oxygen. Infrared spectra before reduction with HI, shown in table 4, indicated medium to weak absorption for ester, ketone, alcohol, and anhydride oxygen suggesting a predominance of ether oxygen. The presence of only small amounts of long carbon chains was also confirmed by infrared analyses; however, strong absorption in the 7.3 micron region indicated the presence of considerable terminal CH<sub>3</sub> groups. This fraction had an average molecular weight of 400 before reduction with HI and 360 after reduction.

Adduct Paraffin Oil. The adduct paraffin oil, one of the smaller fractions representing only 1.4% of the reduced product, was composed largely of normal paraffins with smaller amounts of cycloparaffins and isoparaffins (table 3). The normal paraffins ranged from C<sub>15</sub> to C<sub>30</sub> carbon chains with an average chain length of C<sub>23</sub>. (The average chain length determined by X-ray diffraction was C<sub>22</sub>.) The naphthenic material contained 2 to 6 rings per molecule.

Ultimate analyses (table 2) showed that this fraction was highly saturated with hydrogen and contained 1.2% oxygen. Because of limited size of the fraction, oxygen functional groups were not determined by chemical methods. Infrared spectra of this fraction, shown in table 4, indicated the presence of very little oxygen functional groups. This suggested that most of the oxygen was ether oxygen. Strong absorption in the 13.7 and 13.9 micron region confirmed the presence of considerable

Table 4. Infrared Spectra of Wax and Oil Fractions Obtained From the Distillation Residue

Band Locations, Microns	Intensity <sup>a</sup>				Possible Interpretations
	Adduct Wax	Nonadduct Wax	Adduct Paraffin Oil	Nonadduct Paraffin Oil	
2.9	W	W	W	W	OH (bonded)
3.45	S	S	S	S	CH <sub>2</sub> , CH <sub>3</sub>
5.70	M-W	M-W	W	W	C=O (ester)
5.78	M-W	M	W	M-W	C=O (ester)
5.95	None	M-W	W	W	C=O, aromatic
6.25, 6.35	W	M-W	W	M-W	C=C (aromatic), carboxylate ion
6.84	S	S	S	S	CH <sub>2</sub> , CH <sub>3</sub>
7.30	M-W	S	M	S	CH <sub>3</sub>
7.55	W	M	W	W	-
8.10	W	M	None	None	Ester,
8.45	W	M	None	None	ketone, alcohol,
8.55	W	M	W	None	anhydride
11.25	W	M-W	M-W	W	-
11.5	W	M	W	M-W	Aromatic
12.7	M	M	M	M-W	-
13.45	None	None	None	None	Aromatic
13.7, 13.9	S	W	S	W	Alkyl chains

<sup>a</sup>W - weak, M- medium and S - strong.

Table 5. Oxygen Functional Groups of Various Fractions

	Percent of Total Oxygen			
	Hydroxyl	Ester	Alkoxy	Ether, Carbonyl and Others <sup>a</sup>
Nonadduct wax	0	36	-	64
Nonadduct paraffin oil	2	27	3	68
Nonpolar resins	0	45	15	40
Polar resins	6	27	3	64

<sup>a</sup>Determined by difference.

normal paraffins. There was also some evidence for the presence of terminal CH<sub>3</sub> groups. The molecular weight of this fraction was 310 before reduction with HI.

Nonadduct Paraffin Oil. This fraction, which was the largest single fraction and amounted to 27.9% of the original reduced product, was predominantly naphthenic with smaller amounts of aromatic and paraffinic constituents (table 3). The naphthenic material had 1 to 6 rings per molecule with an average of 2 to 3 rings per molecule. The normal paraffinic and isoparaffinic constituents represented only a small portion of the total fraction; however, about 25% of the material was of aromatic composition.

Oxygen functional groups were determined by the methods described earlier and the results are shown in table 5. Of the 7.6% oxygen present in this fraction (table 2), the majority appeared to be present in the form of ether or carbonyl oxygen with smaller amounts of ester, hydroxyl and alkoxy functional groups. A predominance of ether oxygen was indicated by infrared analyses (table 4) since the absorption for carbonyl and other oxygen was weak. Also, weak absorption in the 13.7 and 13.9 micron region indicated the absence of long alkyl chains; however, strong absorption in the 7.3 region indicated the presence of considerable terminal  $\text{CH}_3$  groups. This fraction contained very little nitrogen and sulfur and had an average molecular weight of 410 before reduction with HI and 350 after reduction.

Aromatic Oil. The aromatic fraction, which represented 9.3% of the total reduced product, was separated into 3 additional fractions; namely, iso-octenes, benzene, and 2-propanol eluted material (figure 1). These fractions are referred to as mono/di, tri, and tetra nuclear aromatics, respectively. Piperonal chloride color tests indicated that the iso-octene eluted material, which was the major aromatic fraction (table 1), was predominantly mono/di nuclear aromatics. This was confirmed by mass spectra data shown in table 6, which indicated that the material was mostly indanes and tetralins with smaller amounts of the other series of aromatic compounds. The benzene series had large peaks at m/e 268 and m/e 259. The m/e 288 peak was a parent peak that lost an ethyl radical to form m/e 259 and may represent the molecular weight of 1 compound or several isomeric compounds. A molecular weight of 288 indicated that 15 carbon atoms in alkyl groups larger than n-propyl were attached to the benzene ring. Considering all possible substitutions and eliminating some by infrared analyses, 3-ethylpropyl substitution appeared most likely. In addition to tri-substituted benzenes (Mol. wt. 288) there was evidence of di-substituted benzenes (Mol. wt. 216), di-substituted indanes (Mol. wt. 258)/di-substituted tetralins (Mol. wt. 272), and di- and tri-substituted indenenes (Mol. wt. 256, 326). These substitutions are shown diagrammatically in figure 2. The location of the substituted groups is not known; however, there is some evidence for the presence of symmetrical tri-substituted benzenes. Also, it is not meant to imply that other series of aromatics with the same "X-number" are not present, but the ones indicated appeared to be the best possibilities. It was assumed that the aromatic compounds isolated were degraded from kerogen and were not formed during the oxidation or reduction procedures. Therefore, each substituted group may represent a ruptured ring or ring system and suggests the presence of carbon skeleton structures in kerogen similar to that present in these compounds. Ring systems that would be readily ruptured by  $\text{KMnO}_4$  to produce similar substitution on aromatic nuclei after reduction are cyclopentanone, cyclopentanol, cyclopentene or others.

Table 6. Constitution of Aromatic Oil Fractions From the Distillation Residue

	Volume, % <sup>a</sup>	
	Iso-octene eluted <sup>b</sup>	Benzene eluted <sup>c</sup>
Benzenes	12	16
Indanes and tetralins	41	29
Indenes and dihydronaphthalenes	14	16
Naphthalenes	10	10
Acenaphthenes	8	10
Acenaphthylenes	5	3
Anthracenes and phenanthrenes	10	11
Total	100	100

<sup>a</sup>Determined from mass spectra.

<sup>b</sup>The ratio of calculated to observed total ionization was 0.65.

<sup>c</sup>The ratio of calculated to observed total ionization was 1.09.

Resins. The resinous material obtained from the original product consisted of nonpolar (Mol. wt. 530) and polar resins (Mol. wt. 800) and represented 12 and 26% of the total material, respectively. Elemental analyses (table 2) of each fraction showed that they contained large amounts of oxygen and smaller amounts of nitrogen and sulfur. Oxygen functional groups were determined by the previous methods (table 5) and appeared to be present as ester and ether or carbonyl oxygen with smaller amounts of alkoxy oxygen. The polar resins contained some hydroxyl and little alkoxy oxygen. Infrared analyses of the two resin fractions are shown in table 7. Both fractions showed weak or no absorption in the 13.7 and 13.9 micron region, indicating few carbon chains with more than four methylene groups. Strong absorption in the 7.3 micron region indicated the presence of considerable terminal CH<sub>3</sub> groups. Absorption in the aromatic region was weak; consequently, these materials appeared to be composed predominantly of saturated cyclic structures. Infrared spectra showed evidence for hydroxyl, carbonyl and other oxygen functional groups, some of which was due to unreduced ester groups.

Table 7. Infrared Spectra of Resin Fractions Obtained From the Distillation Residue

Band Location, Microns	Intensity <sup>a</sup>		Possible Interpretation
	Nonpolar Resins	Polar Resins	
2.9	M-W	M-W	OH (bonded)
3.45	S	S	CH <sub>2</sub> , CH <sub>3</sub>
5.75	S	S	C=O (ester)
5.95	W	None	C=O, aromatic
6.25, 6.35	M-W	W	C=C (aromatic), carboxylate ion
6.84	S	S	CH <sub>2</sub> , CH <sub>3</sub>
7.30	S	S-M	CH <sub>3</sub>
8.10	W	S-M	Esters, ketones,
8.9	S	None	alcohols, anhydrides
11.4	W	None	Aromatic
11.5	None	W	Aromatic
13.45	S	None	Aromatic
13.7, 13.9	W	None	Alkyl chains

<sup>a</sup>W - weak, M - medium and S - strong.

Polar Oil and Pentane-insoluble Material. No analytical data were obtained for these fractions.

Composition of the Original Acids. Approximately 59% of the original acid fraction was identified by a previous study (4). In the present study, the remaining 41% was characterized as shown in table 8. These complex acids, whose molecular weights have a maximum of more than 1200, consisted of small amounts of straight-chain and aromatic acids, but were predominantly saturated cyclic and heterocyclic acids.

There was evidence that the oxidation product contained appreciable amounts of ether oxygen. Fractions of the material obtained by the reduction of the oxidation product contained 7 to 19% oxygen, of which 40 to 70% may be ether oxygen. A quantitative estimate was obtained from the remainder of the reduced product and a comparison of the oxygen present in the original kerogen from which these products were obtained. The total oxygen accounted for in the reduced product equaled 22% of the oxygen present in the original kerogen, which indicated that at least 10 to 15% of the oxygen present in kerogen may be ether oxygen.

Table 8. Composition of Acid Fraction Obtained from Kerogen by Alkaline Permanganate Oxidation

	Percentage of Reduced Product <sup>a</sup>	Percentage of Total Acids <sup>b</sup>
Normal paraffin acids (C <sub>2</sub> to C <sub>8</sub> )	-	59
Normal paraffin acids (C <sub>16</sub> to C <sub>38</sub> )	2	1
Isoparaffin acids	2	1
Cycloparaffin acids (1 to 6 rings)	34	14
Aromatic acids (1 to 2 rings)	15	6
Heterocyclic acids	<u>47</u>	<u>19</u>
Total	100	100

<sup>a</sup>Determined from mass spectra.

<sup>b</sup>Based on analyses obtained from data presented in this report and a previous report (4).

By choosing other oxidation conditions different yields of complex acids could have been obtained. For example an 8-step-oxidation procedure produced 4% oxalic acid, 17% CO<sub>2</sub>, 2% volatile acids and 77% complex organic acids. About 50% of the organic acids had molecular weights from 1200 to 1400 and did not undergo the reactions used in this study. Consequently, the oxidation used in the present study appeared to be a compromise between the two extremes and no attempt was made to obtain maximum yield of any one type of constituent.

#### SUMMARY AND CONCLUSIONS

The oxidation product obtained from Colorado oil-shale kerogen consisted of n-paraffinic, isoparaffinic, aromatic, naphthenic and heterocyclic structures; the naphthenic and heterocyclic types predominated.

The n-paraffins ranged from C<sub>2</sub> to C<sub>38</sub> compounds. The cycloparaffins contained 1 to 6 rings per molecule with di- and tri-nuclear material being most prevalent. Also, mono/di-nuclear aromatics appeared to predominate over compounds having more rings. The aromatic fraction contained nuclei with 3-ethylpropyl substitution at two and three points. The presence of this type of compound in the degradation products suggested that the permanganate oxidation cleaved 5-membered ring systems such as cyclopentene, cyclopentanone, or cyclopentanol that were substituted on benzene, tetralin, indane or indene nuclei. This structure has not been identified previously in kerogen degradation products.

Evidence was found for the presence of ether oxygen in the original kerogen. The four major fractions obtained by the reduction of the oxidation product still contained appreciable amounts of oxygen, most of which was unreduced ester and ether

oxygen. This indicated that Colorado kerogen contains some cyclic or bridge ether oxygen. It seems unlikely that stable ether groups would have been formed during any of the treatment procedures.

In general, these data show that Colorado oil-shale kerogen is predominantly a cyclic material, highly saturated with hydrogen and contains oxygen, nitrogen and sulfur atoms associated with ring structures. There is evidence for the presence of some aromatic and long-chain structures, each representing small portions of the kerogen. The nature of the oxidation products suggests that the kerogen is composed mostly of ring systems connected through short carbon chains, bridges or hetero atoms and is not composed of highly condensed ring structures (2 to 3 rings predominate). These conclusions are in agreement with those obtained from previous studies (4,5,6).

#### ACKNOWLEDGMENT

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#### LITERATURE CITED

- (1) Adams, Roger, "Organic Reactions," vol. VI, pp. 469-509, John Wiley and Sons, Inc., New York, N. Y., 1951.
- (2) Blatt, A. H., "Organic Synthesis," Collective vol. II, pp. 320-1, John Wiley and Sons, Inc., New York, N. Y., 1943.
- (3) Mair, B. J., Marculartis, W. J., Rossini, F. D., Anal. Chem. 29, 92 (1957).
- (4) Robinson, W. E., Cummins, J. J., J. Chem. Eng. Data 5, 74-80 (1960).
- (5) Robinson, W. E., Cummins, J. J., and Stanfield, K. E., Ind. Eng. Chem. 48, 1134-38 (1956).
- (6) Robinson, W. E., Heady, H. H., and Hubbard, A. B., Ind. Eng. Chem. 45, 788-91 (1953).
- (7) Schreiber, R. S., "Organic Synthesis," vol. 31, pp. 31-2, John Wiley and Sons, Inc., New York, N. Y., 1951.

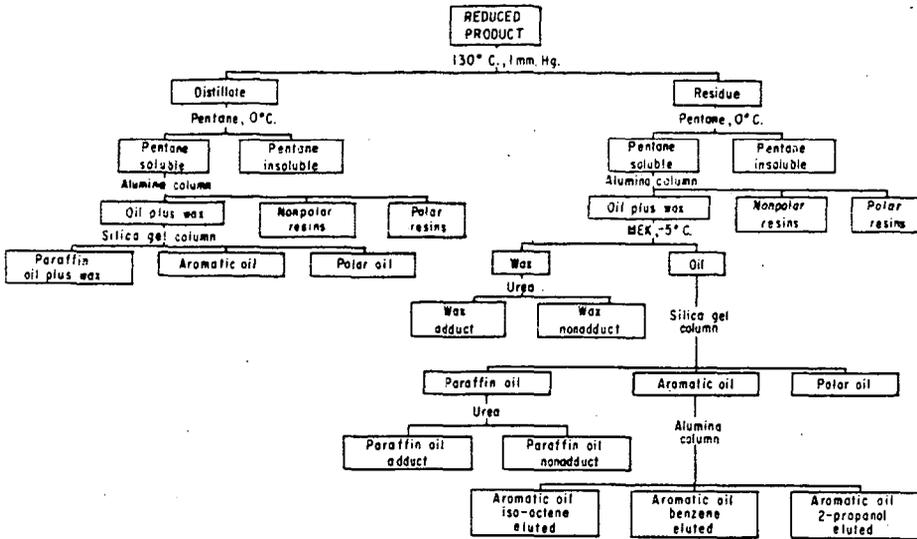


FIGURE 1.- FRACTIONATION OF REDUCED PRODUCT

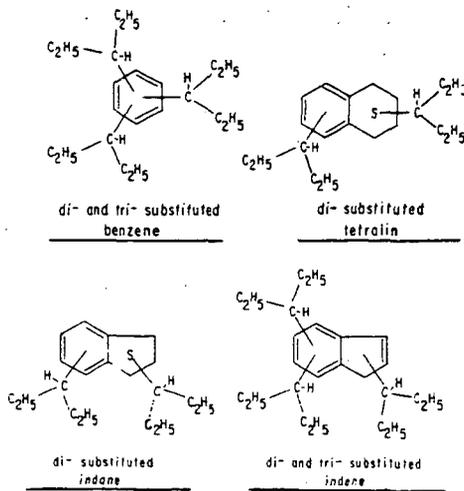


FIGURE 2.- POSSIBLE STRUCTURES PRESENT IN THE MONO/DI-NUCLEAR AROMATIC OIL.

COMPRESSIBILITY FACTOR OF NATURAL GASES  
AT 60°F AND ONE ATMOSPHERE

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INTRODUCTION

Modern analytical techniques have markedly improved the accuracy with which the composition of a gas can be measured. For many years fuel gases were analyzed by volumetric techniques, such as the Orsat or Podbielniak. Heating values and specific gravities were also determined at atmospheric conditions for pure components and fuel gas mixtures, thus resulting in real gas values. However, because of low accuracy in the analytical methods, particularly with respect to determination of the heavier hydrocarbons, differences between calculated and observed heating values were generally ascribed to experimental techniques, and not interpreted on the basis of gas law deviations.

With the advent of the mass spectrometer, more accurate and complete analyses of gas mixtures may be obtained. These analyses are on a true mole fraction, or ideal gas, basis. Also, accurate ideal gas heat of combustion values can now be derived from the work of Rossini et al., API Project 44<sup>9</sup>. However, full utilization of this improved accuracy can not presently be obtained in the calculation of real gas heating values and specific gravities. The lack of sufficient data to permit accurate prediction of the compressibility factor for real gas mixtures may result in significant differences between measured values and those calculated from the gas analysis. Largest deviations occur in fuel gases containing appreciable quantities of heavier constituents.

An experimental program was therefore planned to obtain compressibility factor data at 60°F and one atmosphere on fuel gas components and mixtures. It was anticipated that these data would provide the basis for development of generalized procedures for prediction of compressibility factors of gas mixtures. This project was undertaken as part of the continuing basic research program of the Institute of Gas Technology, and was sponsored by The Peoples Natural Gas Company. The results obtained for natural gas components and mixtures are reported here.

Methods used for determination of gas compressibility factor fall into two groups: 1) gas density, and 2) pressure-relative volume measurement. In the first group of methods, gas density is measured by gas balance or by direct weighing in a bulb. The compressibility factor is calculated from the expression:

$$z = \frac{pV}{RT} \quad (1)$$

where  $V$  is the volume of one mole calculated from the density and molecular weight of the gas. The accuracy of this method depends on absolute values of pressure, volume and temperature.

In the second group of methods, measurements of pressure and relative volume are made over a range of pressure, and  $pV$  or a related parameter is extrapolated to zero pressure, as in the Burnett method.<sup>2</sup> A method of this kind for use at pressures near atmospheric was described by Jessen and Lightfoot.<sup>6</sup> Data are obtained at two or three different pressures by confining the sample of gas in progressively larger volumes over mercury. The compressibility factor is calculated by fitting the  $pV$  measurements ( $V$  is the measured volume here) with an equation such as:

$$pV = (pV)_0 \quad z = (pV)_0 (1 + \beta p) \quad (2)$$

Here the accuracy depends primarily on relative volume and pressure measurements, and constancy of temperature, rather than on absolute values of these quantities. Absolute values of pressure and temperature affect the result in a much less critical way; that is, by the dependence of  $z$  on pressure and temperature, and not by the dependence of  $pV$  and  $RT$ . Similarly the accuracy of  $z$  for mixtures is not affected by the dependence of gas density on composition. However, the method is dependent on the linearity of  $z$  with pressure.

According to the statistical mechanical expressions for virial coefficients in the equation

$$pV = RT (1 + Bp + Cp^2 + \dots) \quad (3)$$

the second virial coefficient,  $B$ , represents the deviation from ideal behavior involving collisions between two molecules.<sup>5</sup> From this theory it also follows that the second virial coefficient for mixtures involves only binary interaction terms, and is of the form:

$$B_m = x_1^2 B_1 + x_2^2 B_2 + x_3^2 B_3 + \dots \\ + 2x_1 x_2 B_{12} + 2x_1 x_3 B_{13} + 2x_2 x_3 B_{23} + \dots \quad (4)$$

where  $B_1, B_2, B_3, \dots$  are second virial coefficients of the pure components, and  $B_{12}, B_{13}, B_{23}, \dots$  are interaction coefficients. The latter can be evaluated by experimental determination of  $B_m$ 's on binary mixtures, together with knowledge of the  $B$ 's for pure components. The effect of the third virial coefficient at one atmosphere is very small and is considered later.

Five components usually occur in natural gases in concentrations of 5% or more: methane, ethane, propane, carbon dioxide and nitrogen. Minor amounts of isobutane, *n*-butane, isopentane and *n*-pentane also occur, together with traces of heavier hydrocarbons. A review of the literature indicated that sufficiently reliable values of atmospheric pressure compressibility factors are available for the major components,<sup>1,4</sup> but not for the minor components. Also, although only very limited data were available on mixtures of these components, the data indicated that composition had a very sizeable effect on compressibility factor.

Therefore, compressibility factor measurements were made on the pure butanes and pentanes, and on a series of selected mixtures. The interaction coefficients among the five major components, and of methane with the four minor components, were determined. In addition, the interaction coefficients of n-butane with all major components was measured to provide a basis for prediction of those not determined experimentally.

#### APPARATUS

The apparatus is shown in Fig. 1. The mixture preparation system, gas expansion system, mercury reservoir and the lower part of the mercury manometer are mounted in a water bath with a plate-glass front. The temperature of the bath was maintained within  $0.05^\circ$  of  $15.55^\circ\text{C}$  ( $60^\circ\text{F}$ ), and did not vary more than  $0.01^\circ\text{C}$  during any one run.

A and B are Hoke stainless steel cam-closing valves. Connection to glass parts is made through stainless steel Swagelok fittings and 1/8-in. stainless steel tubing sealed to the glass with Dekhotinsky cement. Other valves are Hoke toggle or needle valves. The upper part of the long manometer arm extends out of the bath and is equipped with a jacket for water circulation. Manometer arms and jacket are constructed of precision bore tubing; arms 1 and 2, 12 mm ID; arm 3, 13.8 mm ID. Vacuum is maintained at 0.02 mm or less with a mechanical vacuum pump and dry ice cold trap, and is read with a tilting McLeod gage sensitive to 0.01 mm Hg. Mercury levels are read to 0.05 mm with a Gaertner 100 cm cathetometer.

The mixture preparation bulbs, gas expansion bulbs, and manometer arm 1 were calibrated by weight of mercury delivered. The volume of valve B and the capillary manifold in the expansion system, and the volume between valves A and B and the top of the upper bulb in the mixture preparation system, were determined with a 10 cc gas burette. The volume between the top and bottom menisci of the manometer arm 1, and corrections for capillary depression, were taken from Kistemaker<sup>7,8</sup>.

#### MATERIALS

The hydrocarbons used were Phillips research grade. According to the supplier, purity of the methane was 99.68 mole %, with impurities of ethane and nitrogen. Purity of the other hydrocarbons was 99.9% or better. The carbon dioxide was Matheson, bone dry grade; the nitrogen was Matheson prepurified. Components other than nitrogen and methane were condensed in the freezeout trap to remove air. The part of the apparatus being filled was flushed with the component before filling.

#### PROCEDURE

In making binary mixtures the first component was measured in the gas expansion system. The second component was measured in the mixture preparation system by means of manometer arms 2 and 3. Then valve A was closed and the gases were mixed by being forced from one buret to the other several times. A similar procedure was followed in making multicomponent mixtures, except that the intermediate components were measured one at a time in the mixture preparation buret and transferred to the gas expansion buret. Gas

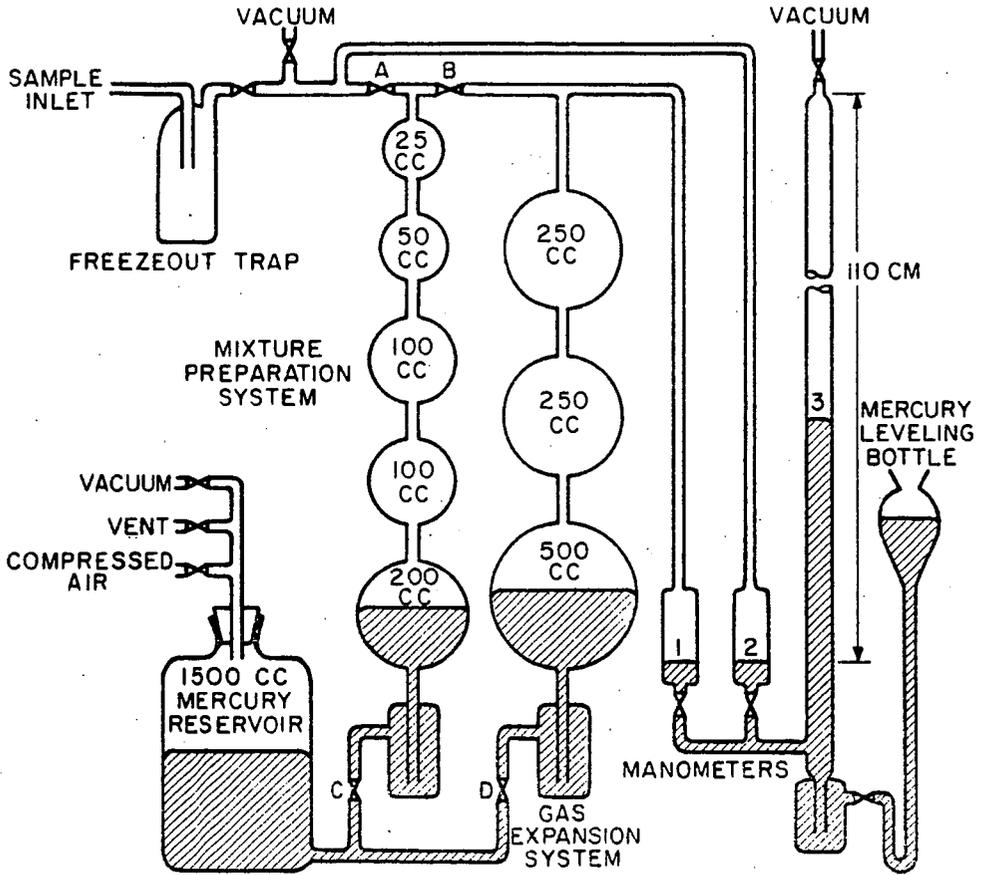


Fig.1.-SCHEMATIC DIAGRAM OF LOW PRESSURE P-V APPARATUS WITH INTEGRAL VOLUMETRIC MIXTURE PREPARATION SYSTEM

remaining in the section between valves A and B after the transfer was discarded.

In most cases, the two upper bulbs of the gas expansion buret were filled to a pressure of about 950 mm Hg. Three to five readings of the top and bottom of the mercury menisci in the two arms of the manometer, and of a reference point on manometer arm 1 were taken. The position of the mercury was changed a millimeter or so for each reading, to minimize the effect of local imperfections of the manometer tubing and plate glass window. Similar readings were taken after the gas was expanded to fill all three bulbs. Measurements on C<sub>5</sub> hydrocarbons had to be taken at lower pressures; a maximum of about 80% of saturation pressure was used.

The apparatus was constructed with three bulbs to allow measurements at three different pressures on the same charge of gas in order to detect variation of the slope  $\beta$  in equation (2) with pressure. However, from variances of the pV measurements at different pressures, it was concluded that better accuracy might be obtained if only the larger volumes were used since volume measurement as well as pressure measurement contributed to the error. Accordingly, data at lower pressures was obtained by removal of part of the sample and repeating measurements on the same two combinations of bulbs.

Data were fitted to equation (2) by least squares computation on an Alvac III digital computer.

#### COMPRESSIBILITY FACTORS OF PURE COMPONENTS

Results for the coefficient  $\beta$  equation (2) obtained on C<sub>4</sub> and C<sub>5</sub> paraffin hydrocarbons are presented in Table 1. Determinations at lower pressures were made as a part of Runs 2 and 6 on n-butane, and of Runs 3 and 4 on isobutane, to detect the change of coefficient with pressure. A trend in the direction of smaller numerical values of the coefficient at lower pressures is evident. Such tests were confined to the C<sub>4</sub> hydrocarbons, since the effect is barely detectable with them and is likely to be less with lighter hydrocarbons and with mixtures. Determination on the C<sub>5</sub> hydrocarbons at necessarily lower pressures would not yield significant results on this question.

In order to obtain the best value of 1-z (1 atm, 60°F), the third virial coefficient was introduced to account for the observed trend of  $\beta$  with pressure:

$$\frac{pV}{(pV)_0} = z = 1 + Bp + Cp^2 \quad (5)$$

An approximation formula was derived from which values of B and C/B could be evaluated from two measured values of  $\beta$  and the average initial and final pressures, p<sub>1</sub> and p<sub>2</sub> of each run

$$B = \beta \left[ 1 - \frac{C}{\beta} (p_1 + p_2) \right] \quad (6)$$

The ratio C/B was evaluated by application of formula (6) to the data from pairs of runs on the same sample, one made at normal pressures

Table 1. GAS LAW DEVIATIONS OF C<sub>4</sub> AND C<sub>5</sub> PARAFFIN HYDROCARBONS  
AT 60° F.

Run No.	$\beta$ (atm <sup>-1</sup> )	$p_1 + p_2$ (atm)	Atmospheric Gas Law Deviation $b = 1 - 2$
<u>n-Butane</u>			
1	-0.03413	1.901	0.03361
2a	-0.03466	1.826	0.03417
2b	-0.03433	1.437	0.03410
2c	-0.03422	1.044	0.03419
3	-0.03423	1.849	0.03374
4	-0.03453	1.830	0.03404
5	-0.03411	1.846	0.03362
6a	-0.03437	1.862	0.03387
6b	-0.03397	1.458	0.03370
6c	-0.03416	1.027	0.03414
			Weighted Avg. $\pm$ 0.03394
			-0.00008 (a)
<u>Isobutane</u>			
1	-0.03022	1.894	0.02982
2	-0.02993	1.891	0.02953
3a	-0.03013	1.889	0.02973
3b	-0.02973	0.937	0.02970
4a	-0.03022	1.881	0.02982
4b	-0.02942	0.895	0.02947
			Weighted Avg. $\pm$ 0.02971
			-0.00010 (a)
<u>n-Pentane</u>			
1	-0.05504	0.578	0.05570
2	-0.05632	0.525	0.05703
			Weighted Avg. $\pm$ 0.0565
			-0.0007 (b)
<u>Isopentane</u>			
1	-0.05199	0.723	0.05236
2	-0.05076	0.766	0.05107
			Weighted Avg. $\pm$ 0.0518
			-0.0005 (b)

(a) From pooled variance of b values for both butanes.

(b) From variance of the pV measurements.

and the other at about half the normal pressures. Runs 2a with 2c, and 6a with 6c, on n-butane, and Runs 3a with 3b, and 4a with 4b, on isobutane, give C/B ratios of 0.016, 0.007, 0.014 and 0.026, respectively. The average of the four, weighted according to the variance of the pV measurements, was 0.016; its standard deviation, also calculated from the variance of the pV measurements, was 0.006.

It was desirable to apply similar corrections to our results for C<sub>5</sub> hydrocarbon and mixtures. However, the C/B ratio for lighter gases at 60°F is smaller than those observed for the butanes, e.g., ethane, 0.006<sup>1,3</sup>, while higher ratios are theoretically expected for heavier hydrocarbons<sup>3</sup>. The observed ratio of C/B for the butanes was approximately equal to B/2. In order to correct our results on a consistent basis over the complete range of deviations, we adopted a C/B ratio of B/2 for all the hydrocarbons and mixtures.

Gas law deviations of the C<sub>4</sub> and C<sub>5</sub> hydrocarbons, in the form of 1-z for easy comparison with the uncorrected  $\beta$  values, are shown in Table 1. Maximum error of the compressibility factors of the butanes is estimated to be 0.03%, and for the pentanes, 0.1%.

Values of gas law deviations for pure components used in the calculation of data on mixtures are collected in Table 3.

#### BINARY INTERACTION COEFFICIENTS

Interaction coefficients determined by measurement of the compressibility factors of binary mixtures of natural gas components are presented in Table 2. These have been calculated by means of the mixture rule of equation (4) but using the gas law deviation (1-z) rather than actual second virial coefficients. Since the third and higher virial coefficients make only a small contribution (maximum about 1%) to the deviation, error from this approximation should not be significant.

Estimated standard deviations of the methane - n-butane and methane - n-pentane averages are 0.00034 and 0.00045, respectively. The estimated standard deviation of other average interaction coefficients is 0.00022.

Agreement of experimental gas law deviations with the mixture rule was tested by determinations of interaction coefficients on 1:3 and 3:1 mixtures of methane with n-butane, and of carbon dioxide with n-butane. On the carbon dioxide - n-butane system, agreement is within experimental error and no trend is apparent. On the methane - n-butane system, a trend of increasing interaction coefficient with increasing methane content is noticeable; however, the difference between 3:1 and 1:3 coefficients is not significant at the 90% confidence level. Compressibility factors of the methane - n-butane mixtures calculated from the average interaction coefficient reported in Table 2 agree with the determined values within 0.06% maximum deviation, and agree to 0.03% on the average.

Table 2.-COMPRESSIBILITY AND INTERACTION COEFFICIENT OF BINARY MIXTURES OF NATURAL GAS COMPONENTS

Mixture	Composition Mole % First Component	Gas Law Deviation $b_m^*$	Interaction Coefficient $b_{1,2}^*$	Mixture	Composition Mole % First Component	Gas Law Deviation $b_m^*$	Interaction Coefficient $b_{1,2}^*$
Methane-Ethane	50.6 50.7	.00472 .00441	.00436 .00376 AVG .00406	Nitrogen-Methane	50.0 50.6	.00091 .00093	.00072 .00078 AVG .00075
Methane-Propane	49.7 50.3	.00798 .00771	.00590 .00558 AVG .00574	Nitrogen-Ethane	50.1 50.3	.00344 .00334	.00254 .00236 AVG .00245
Methane-Isobutane	48.6 49.9	.01155 .01137	.00651 .00688 AVG .00669	Nitrogen-Propane	48.4 48.4 48.4	.00682 .00650 .00682	- - - - - - - - -
Methane-n-Butane	72.1 74.8 75.1 48.5 48.7 23.6 23.7 24.6	.00702 .00626 .00583 .01326 .01323 .02251 .02190 .02174	.00843 .00806 .00711 .00765 .00773 .00724 .00567 .00634	Nitrogen-n-Butane	49.7 49.8 49.3	AVG .00622 .01039 .01070	.00374 .00348 AVG .00367
Methane-Isopentane	59.8 59.7	.01345 .01358	.00917 .00933 AVG .00925	Carbon dioxide-Methane	49.6 49.5	.00318 .00323	.00260 .00270 AVG .00265
Methane-n-Pentane	59.2 60.5 59.9	.01542 .01479 .01544	.01107 .01103 .01180 Weighted AVG .01132	Carbon dioxide-Ethane	49.5 49.1	.00630 .00602	.00532 .00494 AVG .00523
Ethane-Propane	50.5 50.2	.01266 .01259	.01222 .01162 AVG .01192	Carbon dioxide-Propane	49.0 50.1	.00977 .00992	.00744 .00800 AVG .00777
Ethane-n-Butane	49.9 49.8	.01830 .01859	.01542 .01592 AVG .01567	Carbon dioxide-n-Butane	74.5 49.5 50.2 24.6	.00924 .01498 .01456 .02322	.00975 .00990 .00942 .01021 AVG .00978
Propane-n-Butane	50.4 49.6	.02504 .02499	.02426 .02388 AVG .02407	Carbon dioxide-Nitrogen	49.6 50.0	.00220 .00259	.00144 .00218 AVG .00181

\*  $b_m = x_1^2 b_{11} + 2 x_1 x_2 b_{12} + x_2^2 b_{22}$  where  $b_1, b_2$  are gas law deviations (1-2) at one atmosphere for the mixture, pure component 1, and pure component 2, respectively, at mole fractions  $x_1$  and  $x_2$  of the components in the mixture.

### COMPLEX MIXTURES

In the Benedict-Webb-Rubin equation the linear square root combination is used to predict constants for mixtures from constants for the pure components for the second virial terms. Applied to our parameter this yields:

$$b_m = \left[ \sum_i x_i b_i^{1/2} \right]^2 = \sum_i x_i^2 b_i + 2 \sum_{i \neq j} x_i x_j b_i^{1/2} b_j^{1/2} \quad (7)$$

Comparison with equation 4 indicates that interaction coefficients for a given component  $i$  should lie on a straight line of slope  $b_i^{1/2}$  if plotted against  $b_j^{1/2}$ . This plot is shown in Fig. 2. Experimental points fall reasonably close to the predicted value, except for carbon dioxide mixtures. In order to retain the advantages of the linear square root combination for calculating the compressibility factor of complex mixtures, a pseudo  $b$  value for carbon dioxide has been calculated (Table 3).

Two four-component mixtures were prepared and their gas law deviations measured to test methods of predicting the compressibility factors of complex mixtures. The measured values are presented in Table 4, together with values calculated by:

- 1) Linear combination of gas law deviations of components,
- 2) Mixture rule with binary interaction coefficients, equation (4), and
- 3) Linear square root combination of gas law deviations of pure components equation, (7), with the pseudo deviation for carbon dioxide.

These results indicate that the compressibility factor of complex mixtures can be calculated by either 2) or 3) with an accuracy of 0.03% or better. This represents a distinct improvement over the linear combination.

Heating values of gas mixtures are sometimes calculated by a summing of terms of the form  $x_i H_{g,i}$ , where  $H_{g,i}$  is the real gas heating value of the pure component. This formula yields values for the two mixtures in Table 4 which are about 3 Btu per SCF, or almost 0.3%, too high. As a result of this study it is recommended that the heating value be calculated on the basis of the ideal gas heating values, and be corrected for nonideality by the mixture compressibility factor, calculated by either of the recommended combining rules, methods 2) or 3). By this procedure the error of calculation for the mixtures in Table 4 is reduced to only 0.3 Btu/SCF, or 0.03%.

### ACKNOWLEDGMENT

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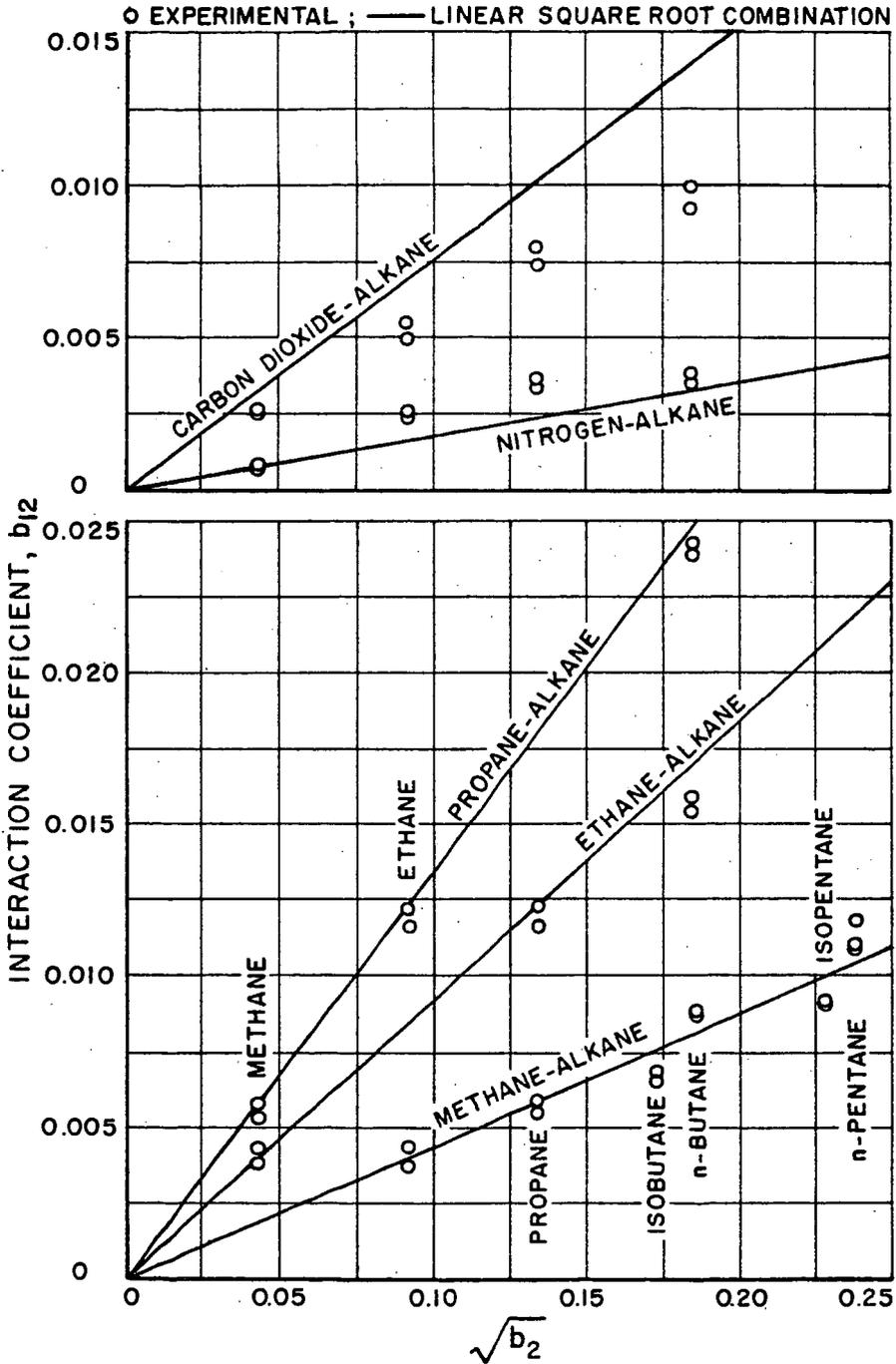


Fig. 2.- COMPARISON OF EXPERIMENTAL AND CALCULATED INTERACTION COEFFICIENTS OF NATURAL GAS COMPONENTS

Table 3. GAS LAW DEVIATIONS OF NATURAL GAS COMPONENTS AT 60°F AND ONE ATMOSPHERE

<u>Hydrocarbon</u>	<u>Gas Law Deviation b = 1 - z</u>	<u>Source</u>
Methane	0.0019	API <sup>1</sup>
Ethane	0.0084	API <sup>1</sup>
Propane	0.0180	API <sup>1</sup>
Isobutane	0.0297	IGT
n-Butane	0.0339	IGT
Isopentane	0.0518	IGT
n-Pentane	0.0565	IGT
Nitrogen	0.0003	NBS <sup>4</sup>
Carbon Dioxide	0.0057*	NBS <sup>4</sup>

\* For calculation by linear square root combination, use the pseudo value, b = 0.0041.

Table 4. GAS LAW DEVIATIONS OF FOUR-COMPONENT MIXTURES AT 60°F AND ONE ATMOSPHERE

	<u>Mixture 1</u>	<u>Mixture 2</u>
Methane, mole %	67.44	64.14
Ethane, mole %	16.37	20.68
Propane, mole %	5.30	5.02
Nitrogen, mole %	10.89	0.00
Carbon Dioxide, mole %	0.00	10.16
b <sub>m</sub> measured	0.00274	0.00331
b <sub>m</sub> calculated*	(1) 0.00364	0.00444
	(2) 0.00292	0.00357
	(3) 0.00285	0.00362

\* b<sub>m</sub> calculated from (1)  $b_m = \sum x_i b_i$   
 (2)  $b_m = \sum x_i^2 b_i + \sum 2x_i x_j b_{ij}$   
 (3)  $b_m = (\sum x_i b_i^{1/2})^2$

LITERATURE CITED

- (1) American Petroleum Institute, "Selected Values of Properties of Hydrocarbons and Related Compounds," API Research Project 44. Pittsburgh: Carnegie Institute of Technology, October 31, 1958.
- (2) Burnett, E. S., J. Applied Mechanics 3, A-136-40 (1936).
- (3) David, H. G. and Hamann, S. D., in Institution of Mechanical Engineers, "Thermodynamics and Transport Properties of Fluids," 74-78. London: The Institution, 1958.
- (4) Hilsenrath, J. et al., "Tables of Thermal Properties of Gases." NBS Circular 564. Washington, D. C.: Govt. Print. Office, 1955.
- (5) Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., "Molecular Theory of Gases and Liquids," 132. New York: John Wiley and Sons, Inc., 1954.
- (6) Jessen, F. W. and Lightfoot, J. H., Ind. Eng. Chem. 28, 870-71 (1936) July.
- (7) Kistemaker, J., Physica 11, 270-76 (1945) December.
- (8) Kistemaker, J., Physica 11, 277-86 (1945) December.
- (9) Rossini, F. D. et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44. Pittsburgh: Carnegie Press, 1953.

THE DISTRIBUTION OF OXYGEN-CONTAINING FUNCTIONAL GROUPS IN PITCH  
FROM A HIGH-TEMPERATURE COAL TAR

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INTRODUCTION

The phenolic hydroxyl content of coal tar pitch is mainly confined to the portion insoluble in light petroleum. In this portion there is approximately one phenolic group per molecule of pitch constituent - indicating that the phenolic hydroxyl, although small in percentage, is a significant (1) constituent. It has been shown (2) that, for a series of pitch fractions prepared from coke-oven, vertical-retort, and low-temperature tars, 40 to 68 per cent of the oxygen in the benzene-soluble, light-petroleum-insoluble fractions and 28 to 63 per cent of the oxygen in the pyridine-soluble, benzene-insoluble fractions is in the form of phenolic groups.

The present paper describes a systematic study of the oxygen-containing groups in a pitch from a high-temperature tar obtained by carbonizing a medium-volatile bituminous coal at 1000°C. in a technical-scale plant simulating conditions in a by-product coke-oven. An attempt has been made to account for all the oxygen, other than ethereal oxygen, in the pitch and to relate the concentration of the various functional groups to the molecular size of the pitch fraction.

EXPERIMENTAL

A. Preparation of Pitch and Pitch Fractions

A pitch of softening point 66°C. (K. and S.) was prepared by rapid distillation (70 grams per minute) of a 5-kilogram charge of tar in a metal still of the S.T.P.T.C.\* type - a method believed to yield a pitch similar to those produced industrially in pipe stills (3).

The pitch was separated into four fractions by solvent extractions:

- (i) "Crystalloids" - soluble in light petroleum (b.p. 60 to 80°C.).
- (ii) "Resinoids" - insoluble in light petroleum but soluble in benzene.
- (iii) "C<sub>2</sub>" - insoluble in benzene but soluble in pyridine.
- (iv) "C<sub>1</sub>" - insoluble in pyridine.

The C<sub>2</sub> fractions were further separated by fractional precipitation of a pyridine solution of the C<sub>2</sub> with water.

All separations and functional-group analyses were carried out in darkness and in an atmosphere of nitrogen.

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\* Standardization of Tar Products Tests Committee (Great Britain).

## B. Determination of Functional Groups

### 1. Phenolic Groups

I. Non-aqueous titration. - Mixtures of the sample (0.1 to 0.5 gram) with 2,6-xylenol (0.01 to 0.02 gram) were titrated potentiometrically in pyridine solution (or suspension) with 0.2N sodium aminoethoxide in ethylene diamine as described by Greenhow and Smith (4). By co-titration with xylenol it is possible to estimate phenolic groups not normally giving a sharp end point in the absence of this reagent, but in addition the method gives an estimate of the carboxyl, phenolic ester, phenolic lactone, and some quinone groups. Carbon dioxide and carboxylic acids give a separate inflexion in the titration curve (4), and may be allowed for; the inflexion is sharpened by the addition of benzoic acid to the sample (see 3, II below). Titrations were reproducible within 10 per cent.

II. Mesylation. - The sample (0.8 to 1 gram) in pyridine (50 ml.) was treated at 0 to 5°C. with freshly distilled methane sulphonyl chloride (7 ml.) for about 24 hours, the mixture poured into ice water (200 ml.) and acidified with 5N hydrochloric acid, the precipitate washed with 5N hydrochloric acid and, finally, with water, and dried in vacuo at 50°C. The hydroxyl content was measured from the increase in sulphur content of the sample; reproducibility was about four per cent. It was found that various pure compounds, including heterocyclic tertiary amines, quinones, esters, lactones, and carbazole derivatives, did not react with methane sulphonyl chloride under the conditions used. A low mesylation value was obtained with indole, probably by the addition of part of the reagent molecule to chains of indole polymer. Primary amines, secondary aliphatic amines, and alcohols react to give the expected mesyl derivatives.

III. Methylation. - Diazomethane in ether was used as the reagent, a 1:1 mixture of dry ether and benzene as the solvent for the pitch fraction, and methanol as the catalyst. The methylated product was separated into two fractions, one being insoluble and the other soluble in the reaction medium. Methoxyl determinations were carried out on the methylated sample before and after hydrolysis (with N hydrochloric acid) for measurement of the carboxylic acid content.

IV. Acetylation. - The technique used was that of Blom et al. (5) in which the sample is first treated with acetic anhydride in pyridine, the acetylated product is then hydrolysed with barium hydroxide, and finally the acetic acid is distilled from the acidified solution and titrated. The acetic acid distilled irregularly from hydrolysed acetylated crystalloids and resinoids, indicating that further hydrolysis, possibly of N-acetyl compounds, was taking place in the acid solution.

V. Methylation followed by acetylation. - Processes III and IV were used, in series.

VI. Acetylation followed by methylation. - Processes IV and III, in that order.

### 2. Carbonyl Groups

The method used was that of Blom et al. (5), in which hydroxylamine hydrochloride is the reagent. Oxime formation was measured in three ways, namely from (i) the increase in nitrogen content, (ii) the decrease in nitrogen content on hydrolysis of oxime, and (iii) determination of hydrolysable oxime as ammonia. Application of the method to pitch samples gave a reproducibility of about eight per cent.

### 3. Carboxylic Acids

These were determined by the hydrolysis of methylated samples (1, III above) and by two additional methods:

I. Decarboxylation. - A semi-micro procedure similar to that of Beroza (6) was used but with a larger sample (0.4 gram instead of 0.05 to 0.1 gram) because of the low carboxylic acid content of the pitch fractions. Reproducibility was about four per cent.

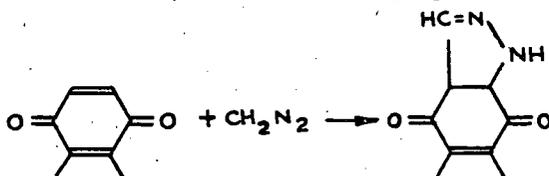
II. Non-aqueous titration. - A mixture of the sample (0.3 to 0.8 gram) with benzoic acid (0.015 to 0.025 gram) was titrated potentiometrically using the same solvent, titrant, and electrodes as in Method 1, I (above); the first major inflexion was taken as the end point. Reproducibility was about ten per cent.

#### 4. Ester Groups

The method employed by Knotnerus (7) for the determination of the saponification number of blown bitumens was adopted. Reproducibility was poor (about twenty per cent), probably because of the low solubility of the pitch fractions.

#### 5. Quinones

It is probable that much of the oxygen measured in the carbonyl determination is quinonoid. The increase in nitrogen content of samples following treatment with diazomethane could also be attributed to quinones - but only to 1,4-quinones of the types known to undergo addition with diazomethane to form pyrazoline rings (8, 9) - that is, "terminal ring" quinones:



A value for 1,4-quinones can therefore be calculated from the uptake of nitrogen.

#### C. Molecular Weights and Coking Values

Molecular weights were determined cryoscopically in phenanthrene, and coking values by the method of Charette and Girolami (10).

### RESULTS AND DISCUSSION

The solvent analysis of the pitch, the elementary analysis and coking values of the pitch and pitch fractions, and the molecular weights of the soluble fractions, are given in Table I. This shows that the percentage of oxygen tends to be higher in the less-soluble fractions of the pitch, and that decrease in solubility is accompanied by increase in molecular weight and coking value.

Table II summarizes the functional group analyses of the pitch fractions; values tabulated are the average of at least two determinations.

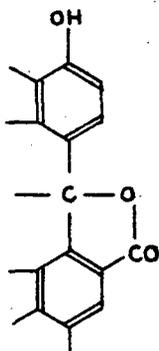
Close agreement for phenolic hydroxyl determined by non-aqueous titration and by mesylation was obtained for the crystalloids and the resinoids. The values for functional groups in the C<sub>1</sub> fraction are generally low (Table III), probably because of its insolubility. In this case the mesylation hydroxyl value is higher than the titration value and this may be due to the greater reactivity of the methane sulphonyl chloride or to the longer reaction time employed.

In comparison with the other techniques, methylation and acetylation gave lower values for phenolic hydroxyl.

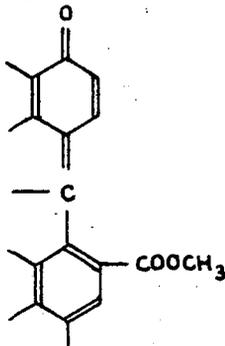
When methylated fractions were acetylated, higher overall hydroxyl values

were obtained than when either acetylation or methylation was used alone. On the other hand, when acetylated fractions were methylated, values were obtained similar to those with methylation alone, and infra-red examination of the methylated acetylated products revealed that all the acetyl groups had been eliminated. This elimination reaction was noted for pure compounds by Bredereck et al. (11). Results obtained by acetylation of methylated fractions suggest that methylation may make functional groups more accessible to acetic anhydride. Several types of hydroxyl groups appear to be present, probably of different acidities and/or steric disposition.

Carboxylic oxygen in the resinoids and  $C_2$  determined by hydrolysis of methylated fractions is higher than that measured by decarboxylation or non-aqueous titration, and is highest in the  $C_2$  fraction. High carboxyl and low hydroxyl (by methylation) values could be explained by lactones of the fluorescein type (12).



which, on treatment with diazomethane, give an ester



Such a reaction could account for the low phenolic (i.e. hydroxyl) values obtained with the  $C_2$  fraction.

Bearing in mind the relatively low accuracy of the decarboxylation and titration methods it is probable that the carboxylic acid contents of the resinoid and crystalloid fractions are negligible, and the methylation value for the resinoid fraction would again be due to the presence of lactones. The fact that there was little difference in the values given by these two methods for the carboxylic-acid content of the  $C_2$  fraction, indicates that these values are significant.

The resinoid and  $C_2$  fractions had the highest carbonyl contents. The three methods of measuring the extent of reaction with hydroxylamine gave similar results, indicating that nitrogen uptake was entirely in the form of hydrolysable oxime.

Calculation of 1,4-quinone oxygen from the nitrogen increase following methylation has given values lower than those for carbonyl oxygen (except with crystalloids), but of the same order. The results could be interpreted to mean

that much of the carbonyl is in the form of terminal-ring 1,4-quinones.

Diazomethane also forms pyrazolines with  $\alpha\beta$ -unsaturated ketones and aldehydes (8); but in the present investigation it is assumed that these are absent from high-temperature tar.

Ester groups appear to be absent from all fractions except the resinoid, which latter has an "ester-oxygen" content approximately equivalent to the content of carboxylic-acid oxygen measured by the hydrolysis of the methylated resinoids. This evidence supports the suggestion that methylation of a lactone had occurred.

Oxygen, as phenolic hydroxyl (by mesylation), carbonyl (by oxime formation), and carboxyl (by decarboxylation) is given as a percentage of the total oxygen (determined by the direct method) in Table III. It can be seen that for the resinoids the total functional-group oxygen is higher than, and for the crystalloids and  $C_1$  fraction lower than, the total oxygen; while for the  $C_2$  fraction the total functional-group oxygen is approximately the same as the total oxygen. The high value for functional-group oxygen in the resinoids could be explained, partly at least, by the possibility that mesylation will determine other groups in addition to phenolic ones. Non-aqueous titration - which gives the same value as mesylation - can determine certain terminal-ring, 1,4-quinones as "phenolic hydroxyl". The extent of such overlapping as this between the methods employed for functional-group analysis is difficult to estimate, and at present an approximate figure cannot be given for unreactive (i.e. ethereal) oxygen, although consideration of the results as a whole suggests that this should be low for the resinoids and the  $C_2$  fraction.

The  $C_2$  is the fusible fraction of highest molecular weight obtained by the solvent-extraction method used in this work, and it gives the highest yield of coke ( $C_1$ , being infusible, gives a char). Van Krevelen et al. (13) have shown that free carbon ( $C_1 + C_2$ ) of pitch is similar to a coking coal in its dilatometric properties, so that the  $C_2$  probably contains the more important coking constituents of pitch.

The present authors have separated the  $C_2$  into three parts by fractional precipitation of its pyridine solution with water (Table IV). As expected, the least soluble part had the highest molecular weight (832) and the most soluble the lowest (420). However, the coking values were similar for each part and the phenolic hydroxyl content was highest in the lowest molecular-weight fraction. Clearly, molecular size is not the only factor controlling either the insolubility of  $C_2$  in benzene or its high coking value. Results so far show that functional groups, of which phenolic hydroxyl is probably the most important, play a part.

#### CONCLUSIONS

- (1) The concentration of oxygen-containing functional groups is highest in the light-petroleum insoluble fractions and in particular in the  $C_2$ .
- (2) Phenolic hydroxyl, carbonyl, and carboxylic acid groups account for most of the oxygen in the pitch fractions examined.
- (3) Phenolic hydroxyl is the most important oxygen-containing functional group, whilst carbonyl oxygen and carboxylic-acid oxygen occur in approximately equal amounts except in the resinoid fraction, where the carbonyl oxygen is high (accounting for almost 50 per cent of the total) and the carboxylic-acid oxygen probably negligible.
- (4) The content of ethereal oxygen is probably low in the resinoids and the  $C_2$  fraction.
- (5) The "insolubility" and high coking value of the  $C_2$  fraction depend not only on

its high molecular weight but also on the presence of reactive centres, one of which is probably the phenolic hydroxyl group.

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#### REFERENCES

- (1) E.J. Greenhow and J.W. Smith, Fuel, Lond., 37, 354 (1958).
- (2) E.J. Greenhow and J.W. Smith, Aust. J. Appl. Sci., 2, 169 (1960).
- (3) D. McNeil and G.A. Vaughan, Instn. Gas Engrs, Lond., Publ. No.438, 5 (1953).
- (4) E.J. Greenhow and J.W. Smith, Analyst, 84, 457 (1959).
- (5) L. Blom, L. Edelhausen, and D.W. van Krevelen, Fuel, Lond., 36, 135 (1957).
- (6) M. Beroza, Anal. Chem., 25, 177 (1953).
- (7) J. Knotnerus, J. Inst. Pet., 42, 355 (1956).
- (8) C.D. Gutsche, Organic Reactions, VIII, 365 (1954).
- (9) M.L. Studebaker, E.W.D. Huffman, H.C. Wolfe, and L.C. Nabors, Ind. Engng Chem., 48, 162 (1956).
- (10) L.P. Charette and L. Girolami, Fuel, Lond., 37, 382 (1958).
- (11) H. Bredereck, R. Sieber, L. Kamphenkel, and R. Bamberger, Chem. Ber., 89, 1169 (1956).
- (12) O. Fischer and E. Hepp, Dtsch. Chem. Ges. Ber., 46, pt. 2, 1951 (1913).
- (13) D.W. van Krevelen, A. Schors, H. Bos, M.P. Groenewege, and R. Westrik, Fuel, Lond., 35, 241 (1956).

TABLE I. ANALYSIS AND PROPERTIES OF PITCH AND PITCH FRACTIONS

Pitch Fraction	% Total Pitch	Elementary Analysis						Mol. Wt.	Coking Value, %
		C	H	O*	N	S	Ash		
Crystalloids	38.5	92.0	5.6	1.7	1.1	0.4	230	10.8	
Resinoids	18.5	90.2	4.8	2.8	2.2	0.4	381	58.3	
C <sub>2</sub>	15.5	86.7	4.2	4.3	2.6	0.6	608	85.5	
C <sub>1</sub>	27.5	91.6	2.9	2.6	1.4	0.7	-	94.1	
Pitch	100	91.4	4.5	2.4	1.3	0.5	-	56.6	

\* Direct method.

TABLE II. FUNCTIONAL GROUP ANALYSES

Method of Analysis Fraction	Oxygen as Phenolic Hydroxyl, %								Oxygen as Carboxyl, %			Oxygen as Carbonyl, %	Oxygen as 1,4-Quinone, %	Oxygen as Esters, %
	Non- aqueous titrat- ion	Methyl- ation	Methyl- ation	Acetyl- ation	Methyl- ation followed by acetyl- ation	Methyl- ation followed by methyl- ation	Acetyl- ation followed by methyl- ation	Methyl- ation and hydro- lysis	Decarbox- ylation	Non- aqueous titrat- ion	Oxime form- ation	Nitrogen content of methyl- ated sample	Oxygen as Sapon- ification	
Crystalloids	0.90	0.95	0.36	0.54	0.75	0.46	< 0.1	0.19	< 0.1	0.25	0.41	nil		
Resinoids	1.9	1.9	0.83	0.63	1.27	0.52	0.58	< 0.1	< 0.1	1.34	1.00	0.43		
C <sub>2</sub>	2.0	2.5	0.57	1.2	1.51	0.59	1.47	0.93	1.1	0.93	0.86	nil		
C <sub>1</sub>	0.55	1.2	0.57	0.49	0.95	0.64	0.26	0.60	0.50	0.44	0.39	nil		
Pitch	-	2.1	0.39	0.96	-	-	0.25	0.23	-	0.53	0.35	-		

TABLE III. FUNCTIONAL-GROUP OXYGEN AS PERCENTAGE  
OF TOTAL OXYGEN

Fraction Functional Groups	Crystalloids	Resinoids	C <sub>2</sub>	C <sub>1</sub>
Phenolic hydroxyl (mesylation)	56	68	58	46
Carbonyl (oxime formation)	15	48	22	17
Carboxylic acid (decarboxylation)	11	3	22	23
Total	82	119	102	86

TABLE IV. PRECIPITATION PRODUCTS FROM C<sub>2</sub> FRACTION

Fractions	Yield, as % of C <sub>2</sub> Fraction	Colour	Mol. Wt.	Oxygen, as Phenolic Hydroxyl, %	Coking Value, %
C <sub>2</sub> /1	46.6	Black	830	1.3	89.7
C <sub>2</sub> /2	26.6	Dark brown	545	2.2	89.1
C <sub>2</sub> /3	26.8	Reddish- brown	420	2.9	86.2

## GAS-LIQUID CHROMATOGRAPHIC ANALYSIS OF AROMATIC HYDROCARBONS BOILING BETWEEN 202° AND 280° IN A LOW-TEMPERATURE COAL TAR

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### INTRODUCTION

In a previous publication<sup>1</sup> the Bureau of Mines reported the results of a detailed gas-liquid chromatographic analysis of aromatic hydrocarbons boiling up to 218° in a low-temperature bituminous coal tar. The present work extends this detailed characterization to include compounds boiling up to 280°, specifically, compounds in the range 202° to 280°.

Previously, only about 10 aromatic hydrocarbons boiling between 202° and 280°, including naphthalene and 5 alkylnaphthalenes, were found in low-temperature tars and in all instances by older techniques<sup>2-6</sup>. Quantitative results were essentially non-existent.

In the present work, employment of the eminently effective combination of gas-liquid chromatography and spectrophotometry enabled this laboratory to identify 48 compounds, including 9 mentioned in the previous publication. Of these identified compounds 20 are alkylnaphthalenes, including all isomeric dimethylnaphthalenes, except the 1,8-isomer. The rest of the compounds identified include methylated indans, tetralins, indenes and biphenyls, and some oxygenated aromatic hydrocarbons. Cyclohexylbenzene and 2a,3,4,5-tetrahydroacenaphthene, which had never been reported in any low-temperature tar, were also found. Quantitative determinations were made on nearly all compounds.

A correlation between logarithm of relative retention at 220° and boiling point for some alkylbenzenes and some alkylnaphthalenes was established; this made it possible to identify several additional constituents of the tar. This correlation is similar to the one for alkylbenzenes at 150°<sup>1</sup>.

### EXPERIMENTAL WORK AND RESULTS

#### 1. Preparation of aromatic concentrates from the coal tar for gas-liquid chromatography

The same neutral oil from a West Virginia bituminous coal tar that was used in the earlier part of this work was used for the present analysis. The neutral oil was distilled to the equivalent of 260° in a Podbielniak Hyper-Cal high-temperature automatic distillation apparatus at 50 mm., with the results shown in Table I of the previous publication. The residue left from this distillation was further fractionated at 10 mm. in a Fisher Unitized distillation apparatus with a 12 mm. I.D. column, using a reflux ratio of 20 to 1. The results of this distillation are given in Table I. Equivalent atmospheric boiling points were estimated from a standard nomograph.

The distillate fractions were each separated into saturates, unsaturates, and aromatics by means of displacement chromatography with silica gel, as previously described. The data on displacement chromatography are summarized in Table II.

TABLE I  
FRACTIONATION OF NEUTRAL OILS IN FISHER STILL

Charge:	8.35 wt.-% of the tar		
	338.0 g.		
Distillate:	131.4 g. = 38.9 %		
Residue:	201.8 g. = 59.7 %		
Loss and holdup:	4.8 g. = 1.4 %		
Fraction No.	Head temperature, °C., 10 mm.	Estimated b.p., °C., 760 mm.	Weight, g.
1	122 - 124	257 - 259	2.9
2	124 - 127	259 - 262	9.0
3	127 - 129	262 - 265	9.0
4	129 - 132	265 - 268	9.3
5	132 - 134	268 - 270	8.5
6	134 - 135	270 - 272	6.2
7	135 - 137	272 - 274	9.2
8	137 - 138	274 - 275	9.6
9	138 - 139	275 - 276	9.0
10	139 - 141	276 - 278	9.0
11	141 - 143	278 - 280	8.6
12	143 - 144	280 - 282	9.4
13	144 - 146	282 - 284	9.2
14	146 - 148	284 - 286	9.3
15	148 - 149	286 - 287	9.6
16	149	287	3.6
Total			131.4

TABLE II

## DISPLACEMENT CHROMATOGRAPHIC SEPARATION OF NEUTRAL OIL DISTILLATE FRACTIONS INTO CHEMICAL TYPES

Distillate fraction No. <sup>a</sup>	Weight of charge, g.	Column temperature, °C.	Saturates + some olefins			Aromatics + some olefins and some O, S compounds			Material retained on column, g.	Weight of aromatics identified by GLC, g.
			<sup>20</sup> n <sub>D</sub> range	Total weight, g.	Number of fractions	<sup>20</sup> n <sub>D</sub> range	Total weight, g.	Number of fractions		
7 + 8 <sup>b</sup>	21	70	1.4025-1.4894	9.98	22	1.4915-1.5658	9.03	11	1.99	5.828
9 <sup>b</sup>	4.29	70	1.4281-1.4705	1.77	8	1.4995-1.5867	1.94	7	0.58	1.329
10 + 11 <sup>b</sup>	14.93	room temp.	1.4383-1.4938	7.04	18	1.4985-1.5640	6.36	13	1.53	3.152
12 + 13 <sup>c</sup>	12.58	room temp.	1.4321-1.4900	5.00	14	1.4990-1.5790	5.87	13	1.71	3.089
14 <sup>c</sup>	11.16	room temp.	1.4285-1.4769	5.17	13	1.4991-1.5864	5.24	13	0.75	2.314
15 <sup>c</sup>	15.15	room temp.	1.4294-1.4839	6.80	17	1.4971-1.5947	7.31	18	1.04	5.419
16 <sup>c</sup>	13.90	room temp.	1.4400-1.4830	4.11	11	1.5027-1.6039	7.81	18	1.98	5.771
17 <sup>c</sup>	12.70	room temp.	1.4442-1.4843	2.96	9	1.5001-1.6047	6.97	15	2.77	4.322
18 <sup>c</sup>	10.61	room temp.	1.4478-1.5059	3.40	8	1.5331-1.6050	6.14	12	1.07	4.665
19 <sup>c</sup>	15.90	room temp.	1.4378-1.4971	6.05	13	1.5083-1.6005	7.13	13	2.72	4.647
20 <sup>c</sup>	12.20	70	1.4317-1.5050	5.12	13	1.5219-1.5951	5.06	11	2.02	3.672
21 <sup>c</sup>	16.36	70	1.4361-1.5079	6.02	14	1.5179-1.5968	9.11	16	1.23	5.989

(Table II, continued)

22 <sup>c</sup>	17.75	70	1.4386-1.5087	5.17	14	1.5218-1.5989	11.22	22	1.36	8.048
23 <sup>c</sup>	17.14	70	1.4462-1.4988	3.89	9	1.5283-1.5916	12.24	20	1.01	8.516
24 <sup>c</sup>	5.45	70	1.4480-1.5044	1.53	6	1.5449-1.5953	3.52	10	0.40	2.863
25 <sup>d</sup>	16.42	85	1.4375-1.4769	2.20	6	1.5115-1.5970	12.73	23	1.49	11.502
26 <sup>d</sup>	17.48	85	1.4395-1.4941	2.36	6	1.5228-1.5983	13.50	28	1.62	11.874
27 <sup>d</sup>	17.55	85	1.4390-1.5000	2.25	6	1.5195-1.6014	13.59	23	1.71	10.691
28 <sup>d</sup>	19.23	90	1.4349-1.4857	2.96	7	1.5100-1.6025	14.58	25	1.69	10.057
29 <sup>d</sup>	10.19	90	1.4375-1.4941	2.03	5	1.5251-1.6040	7.00	12	1.16	5.414
1* <sup>d</sup>	2.90	95	1.4698	0.40	1	1.5489-1.6015	2.30	6	0.20	1.436
2* <sup>d</sup>	7.88	95	1.4572-1.4743	0.93	2	1.5359-1.6027	5.98	11	0.97	4.991
3* <sup>d</sup>	5.96	95	1.4509-1.4888	1.42	3	1.5421-1.5998	3.76	7	0.78	2.931
4* <sup>d</sup>	7.66	95	1.4537-1.5048	2.01	4	1.5232-1.5978	4.84	8	0.81	2.870
5* <sup>d</sup>	8.33	95	1.4591-1.4916	1.13	3	1.5172-1.5960	6.17	11	1.03	3.739
6* <sup>d</sup>	6.00	95	1.4587-1.4895	1.40	3	1.5189-1.5903	3.93	6	0.67	2.865
7* <sup>d</sup>	5.99	95	1.4555-1.5136	1.64	4	1.5460-1.6009	3.88	8	0.47	2.773
8* <sup>d</sup>	8.74	95	1.4565-1.5171	1.66	4	1.5340-1.5982	6.07	12	1.01	3.622

a Asterisk (\*) designates fractions shown in Table I of this report; other fractions are shown in Table I of the previous report.

b Desorbent - butyl alcohol.

c Desorbent - isobutyl alcohol.

d Desorbent - cyclohexanol.

## II. Analysis of aromatic hydrocarbons by gas-liquid chromatography

Apparatus and operating conditions. A Perkin-Elmer model 154C Vapor Fractometer equipped with thermistor detectors was used. The response range of the recorder was from 0 to 2.5 mv, and the chart speed varied from 4 to 20 inches per hour, depending on the retention times of the components. The peak areas on the chromatogram were measured with a planimeter.

Two columns were used, each made from a 20-ft. x 1/4-in. O.D. copper tubing filled with approximately 75 g. of packing made of 25% Apiezon L grease on 30- to 60-mesh firebrick. One of the columns was used at 200°, which was the temperature chosen for the analysis of the fractions boiling between 202° and 233°. The other column was used at 220°, which was the temperature for the analysis of the fractions boiling between 233° and 275°. The samples varied in size from 5  $\mu$ l to 15  $\mu$ l and were injected into the column with a 50- $\mu$ l syringe. The carrier gas was helium, admitted to the column at a pressure of 30 lb./in.<sup>2</sup>, corresponding to a flow rate of 100 ml./min.; the outlet pressure was atmospheric. The potential for the detector was 8 V. Throughout the work the temperature stayed within  $\pm 0.1^\circ$  and the helium pressure and the voltage of the detector stayed constant.

The efficiency of the column was calculated by using the equation: No. of theoretical plates =  $16(x/y)^2$ , where  $y$  = length of peak baseline (as defined) and  $x$  = length from start of the run to middle of baseline section. Referring to 1,3,5-triethylbenzene and to 1-methylnaphthalene, the efficiency of the column at 200° was 2393 and 3948 theoretical plates, respectively, and for the column at 220° was 3364 and 4356.

General approach for identification. The retention times of 58 aromatic hydrocarbons boiling in the range of the neutral oil samples were obtained. Their calculated relative retentions (either time or volume) referred to 1,3,5-triethylbenzene at 200° and 220°, and their boiling points are shown in Table III. The aromatic fractions obtained by displacement chromatography were each examined by GLC under the same conditions as for the known compounds.

The approach for identification was principally the same as that described in the previous paper, except that ultraviolet spectrophotometry was included in addition to infrared. Components producing peaks were collected in the previously described manner. The ultraviolet spectra were obtained in cyclohexane solutions.

Generally, two methods were followed to identify the aromatic hydrocarbons. The first consisted of (a) preliminary identification of the unknown by comparing its retention time with those of known compounds, and (b) final confirmation of the identity by comparing the infrared spectrum of the collected material with that of the authentic specimen. In some instances, two components were found to have been eluted together. The infrared spectrum of the material producing a single peak served not only for qualitative identification but also for quantitative estimation of the components. The chromatograms for two different aromatic cuts shown in Figure 1 illustrate a good separation in (A) and a complete overlapping of some components in (B), which were subsequently identified and their ratios estimated by infrared spectrophotometry. Table IV shows the results of the identifications, the peak numbers in this table corresponding to the peak numbers in Figure 1.

The second method of identification involved the correlation curves of relative retention and boiling points, which were applied in those instances where retention times of authentic specimens were not available. These correlation curves are shown in Figure 2 and are discussed more fully in a later section. Boiling points of the components producing various peaks were obtained from their

TABLE III

BOILING POINTS, RELATIVE RETENTIONS, AND CALIBRATION FACTORS ( $f_c$ )  
OF SOME AROMATIC HYDROCARBONS

Compound	Boiling point		At 200°		At 220°	
	°C./760 mm.	Source	Relative retention <sup>a</sup>	$f_c$ <sup>b</sup>	Relative retention <sup>a</sup>	$f_c$ <sup>b</sup>
n-Propyl benzene	159.217	c	0.37	0.86	0.40	0.85
1-Methyl-2-n-propyl benzene	184.80	c	0.62	0.95	0.64	0.93
1,4-Diethyl benzene	183.752	c	0.58	0.93	0.61	0.93
1,3-Dimethyl-5-ethyl benzene	183.75	c	0.58	0.91	0.60	0.89
1,2-Dimethyl-4-ethyl benzene	189.75	c	0.67	0.94	0.70	0.92
1-Methyl-3,5-diethyl benzene	200.70	c	0.77	1.00	0.79	0.97
1,2,4,5-Tetramethyl benzene	196.80	c	0.82	0.98	0.84	0.98
1,2,3,5-Tetramethyl benzene	198.00	c	0.85	1.02	0.87	0.99
1,3,5-Triethyl benzene	216.2	c	1.00	1.00	1.00	1.00
Pentamethyl benzene	231.8	c	1.72	1.01	1.75	1.00
Hexamethyl benzene	263.8	d	3.58	1.01	3.47	1.01
Cyclohexyl benzene	240.13	e	2.09	1.03	2.05	1.02
1,2,3,4-Tetrahydronaphthalene	207.57	c	1.14	1.54	1.16	1.52
Indan	177.82	c	0.59	1.42	--	--
Naphthalene	217.96	c	1.35	1.02	1.37	1.03
2-Methylnaphthalene	241.14	f	2.12	1.04	2.10	1.02
1-Methylnaphthalene	244.78	f	2.32	1.01	2.28	1.02
2-Ethyl naphthalene	257.9	c	3.01	1.08	2.93	1.07
1-Ethyl naphthalene	258.67	c	3.04	1.05	2.96	1.05
2,7-Dimethylnaphthalene	262	c	3.21	1.07	3.13	1.05
2,6-Dimethylnaphthalene	261	f	3.28	1.03	3.17	1.04
1,7-Dimethylnaphthalene	262.9	e	3.41	1.03	3.29	1.03
1,6-Dimethylnaphthalene	265.5	e	3.54	1.04	3.43	1.02
1,3-Dimethylnaphthalene	265	c	--	--	3.43	--
2,3-Dimethylnaphthalene	268	f	3.80	1.05	3.68	1.03
1,5-Dimethylnaphthalene	270.1	e	3.99	1.03	3.83	1.03
1,2-Dimethylnaphthalene	271.1	g	4.10	--	3.93	--
1,3,7-Trimethylnaphthalene	281.7	e	--	--	4.88	1.09
2,3,6-Trimethylnaphthalene	288.1	g	--	--	5.51	1.09
2,3,5-Trimethylnaphthalene	289	e	--	--	5.66	1.07
2a,3,4,5-Tetrahydroace- naphthene	252	e	2.88	1.20	2.80	1.20
Acenaphthylene	270	d	--	--	4.05	--
Acenaphthene	277.2	f	--	--	4.53	1.12
Biphenyl	255.0	c	2.66	1.01	2.60	1.00
3-Methylbiphenyl	272.70	c	--	--	3.82	1.04
2-Methylbiphenyl	260	d	2.46	--	2.51	1.06
4-Methylbiphenyl	267	d	--	--	3.10	--
2-Methylindene	204.1	e	1.05	1.08	1.08	1.06
2-Ethyl indene	222.5	e	1.64	1.10	1.63	1.09
3-Ethyl indene	218.1	e	1.58	1.08	1.57	1.09
1,3-Dimethylindene	207.5	e	1.09	--	1.10	--
2,3-Dimethylindene	224.5	e	1.70	--	1.69	--
2,6-Dimethylindene	226.8	e	1.63	1.09	1.62	1.07
1-Methyl-3-ethylindene	64-5/1.3	e	1.62	--	1.60	--
3-Methyl-2-ethylindene	74-6/1.25	e	2.40	--	2.34	--
2,3,6-Trimethylindene	242.6	e	2.57	--	2.51	--
Benzofuran	171.38	f	0.52	0.99	0.55	1.02
Dibenzofuran	287	f	--	--	5.02	1.18

(Table III, continued)

Diphenyl ether	258.14	e	2.53	1.06	2.47	1.05
5-Methylindan	202.0	c	0.97 <sup>h</sup>	--	0.96 <sup>h</sup>	--
4-Methylindan	205.5	c	1.05 <sup>h</sup>	--	1.07 <sup>h</sup>	--
3-Methylindene	205	c	1.07 <sup>h</sup>	--	1.09 <sup>h</sup>	--
1,2,3,4-Tetramethylbenzene	205.04	c	1.01 <sup>h</sup>	--	1.07 <sup>h</sup>	--
1,6-Dimethylindan	210.9/740.0	i	1.09 <sup>h</sup>	--	1.07 <sup>h</sup>	--
4,7-Dimethylindan	227.6/745.5	j	1.67 <sup>h</sup>	--	1.64 <sup>h</sup>	--
2-Methyl-1,2,3,4-tetrahydro- naphthalene	220.2	k	1.38 <sup>h</sup>	--	1.35 <sup>h</sup>	--
6-Methyl-1,2,3,4-tetrahydro- naphthalene	229.03	c	1.75 <sup>h</sup>	--	1.72 <sup>h</sup>	--
1,4-Dimethylnaphthalene	268.5	c	--	--	3.70 <sup>h</sup>	--

a Dead volume corrected.

b Defined in eq. 1.

c API Research Project 44, Selected Values of Properties of Hydrocarbons and Related Compounds, Carnegie Institute of Technology, Pittsburgh, Pa.

d G. Egloff, Physical Constants of Hydrocarbons, Reinhold Publishing Corp., New York, 1957.

e Determined in this laboratory.

f From Coal Tar Research Assoc., "Coal Tar Data Book," Gomersal, near Leeds, England (1953).

g From Gesellschaft für Teerverwertung mbH, "GfT-Aromaten," Duisburg-Meiderich, Germany.

h The relative retentions of these compounds were determined from tar components identified by I. R.

i J. Entel, C. H. Ruof, and H. C. Howard, Anal. Chem. **25** (1953) 1303.

j J. Entel, Anal. Chem. **26** (1954) 612.

k A. S. Bailey and C. M. Staveley, J. Inst. Petroleum **42** (1956) 97.

TABLE IV

IDENTIFICATION OF COMPONENTS PRODUCING ELUTION PEAKS IN THE GLC OF TWO AROMATIC CUTS FROM DISTILLATE FRACTIONS 10 + 11 AND 26

Peak No.	Relative retention at 220°	Compound identified by I. R.	Relative retention of authentic specimen at 220°
1	1.98	Not identified	--
2	2.08	2-Methylnaphthalene	2.10
3	2.29	1-Methylnaphthalene	2.28
4	2.47	Diphenyl ether	2.47
5	2.56	Biphenyl	2.60
6	2.91	2-Ethyl naphthalene	2.93
7	3.18	2,7-Dimethylnaphthalene	3.13
		2,6-Dimethylnaphthalene	3.17
8	3.30	1,7-Dimethylnaphthalene	3.29
9	3.46	1,3-Dimethylnaphthalene	3.43
		1,6-Dimethylnaphthalene	3.43

D-8126

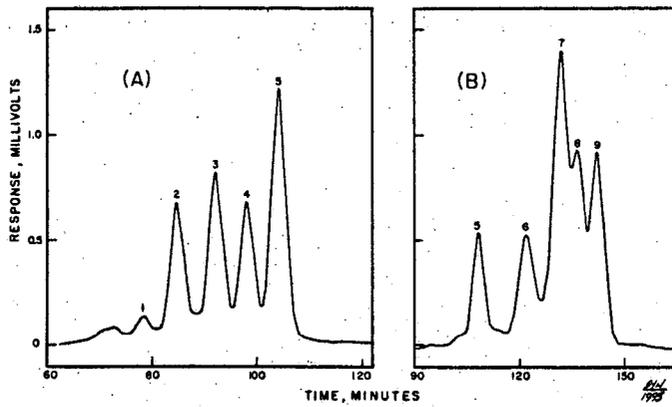


Fig. 1. Chromatograms of two aromatic cuts obtained from distillate fractions 10 + 11 (A) and 26 (B).

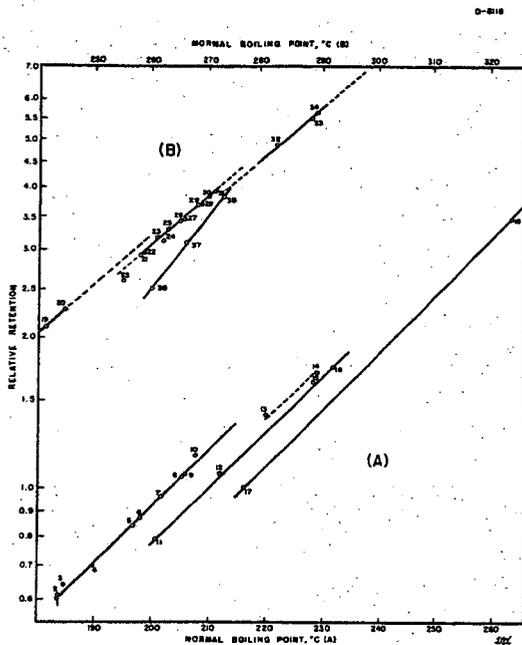


Fig. 2. Correlation between relative retentions and boiling points of some alkybenzenes (A) and alkylnaphthalenes (B) at 220° on Apiezon L grease.

Legend:

- |   |                               |
|---|-------------------------------|
| 1 1,3-Dimethyl-5-ethylbenzene             | 20 1-Methylnaphthalene        |
| 2 1,4-Diethylbenzene                      | 21 2-Ethylnaphthalene         |
| 3 1-Methyl-2-n-propylbenzene              | 22 1-Ethylnaphthalene         |
| 4 1,2-Dimethyl-4-ethylbenzene             | 23 2,6-Dimethylnaphthalene    |
| 5 1,2,4,5-Tetramethylbenzene              | 24 2,7-Dimethylnaphthalene    |
| 6 1,2,3,5-Tetramethylbenzene              | 25 1,7-Dimethylnaphthalene    |
| 7 5-Methylindan                           | 26 1,3-Dimethylnaphthalene    |
| 8 4-Methylindan                           | 27 1,6-Dimethylnaphthalene    |
| 9 1,2,3,4-Tetramethylbenzene              | 28 2,3-Dimethylnaphthalene    |
| 10 1,2,3,4-Tetrahydronaphthalene          | 29 1,4-Dimethylnaphthalene    |
| 11 1-Methyl-3,5-diethylbenzene            | 30 1,5-Dimethylnaphthalene    |
| 12 1,6-Dimethylindan                      | 31 1,2-Dimethylnaphthalene    |
| 13 2-Methyl-1,2,3,4-tetrahydronaphthalene | 32 1,3,7-Trimethylnaphthalene |
| 14 6-Methyl-1,2,3,4-tetrahydronaphthalene | 33 2,3,6-Trimethylnaphthalene |
| 15 4,7-Dimethylindan                      | 34 2,3,5-Trimethylnaphthalene |
| 16 Pentamethylbenzene                     | 35 Biphenyl                   |
| 17 1,3,5-Triethylbenzene                  | 36 2-Methylbiphenyl           |
| 18 Hexamethylbenzene                      | 37 4-Methylbiphenyl           |
| 19 2-Methylnaphthalene                    | 38 3-Methylbiphenyl           |

relative retention by these curves and were used as a preliminary means of identification. Since relative retention or boiling point could not be depended on entirely for identification, confirmation of identity depended on the comparison of the infrared or ultraviolet spectra of the collected samples with published spectra of the pure compounds. However, not all of the spectra of the probable constituents could be found in the literature; to substantiate the preliminary identification, spectral-structural correlations became necessary. Table V shows eight alkyl-naphthalenes identified by the second method. The details of these identifications are as follows:

(1) Constituent having a relative retention of 3.70: The boiling point of the constituent, obtained from its relative retention by the correlation curve for dimethylnaphthalenes, agreed very well with that of 1,4-dimethylnaphthalene. The identity of this naphthalene was confirmed by comparing the infrared spectrum of the constituent with that of 1,4-dimethylnaphthalene, published by the American Petroleum Institute (see Table VI).

(2) Constituents having relative retentions of 4.80 and 5.20: According to the correlation curve for trimethylnaphthalenes, the boiling points for these constituents were 281.5° and 285°, respectively. They are somewhat higher than the literature values for 1,3,6-, 1,2,6-, and 1,2,7-trimethylnaphthalene. However, the ultraviolet spectrum of the sample having a relative retention of 4.80 matched well with the literature spectrum of 1,3,6-trimethylnaphthalene. The material having a relative retention of 5.20 was found to have more than one constituent and was collected as two individual samples, one corresponding to the first half of the peak and the other the second half. By comparing the ultraviolet spectra of the two samples with the published spectra of 1,2,6- and 1,2,7-trimethylnaphthalene, the first sample was found to contain principally 1,2,6-, and the second to contain 1,2,7- as a major and 1,2,6- as a minor component.

(3) Constituents having a relative retention of 4.39: The boiling point obtained for this material from the trimethylnaphthalene correlation curve was 277.3°, a few degrees higher than any of the literature values for the four possible 1,6- and 1,7-methylethyl- and ethylmethylnaphthalenes. The identification of the material therefore depended mainly on spectral-structural correlations, as follows: An examination of the ultraviolet spectra of 1-methyl-, 1-ethyl-, 2-methyl-, and 2-ethylnaphthalene showed that the two 1-alkylnaphthalenes absorb at nearly identical maxima in the region of 300 m $\mu$  to 320 m $\mu$  but differ in absorptivities; the same is true for the two 2-alkylnaphthalenes. A similar situation was also observed in the 300 m $\mu$  to 330 m $\mu$  region for 1,4,5-trimethyl- and 1,4-dimethyl-5-ethylnaphthalene and for 1,3,5-trimethyl- and 1,3-dimethyl-5-ethylnaphthalene upon examining the ultraviolet spectral data of these compounds reported by Evans, Smith, and Straus<sup>8</sup>. This indicates that for absorption in the 300 m $\mu$  to 330 m $\mu$  region methyl groups and ethyl groups can be interchanged without significantly changing the position of the absorption peak; however, the absorptivities are usually altered. Therefore, naphthalene substituted with one methyl group and one ethyl group could be expected to show nearly identical absorption maxima in the 300 m $\mu$  to 330 m $\mu$  region as the naphthalenes substituted with two methyl groups in the same positions. The constituents had absorption bands at 307.8 m $\mu$ , 314.7 m $\mu$ , and 322 m $\mu$  which are also exhibited by 1,6- and 1,7-dimethylnaphthalene, both of which had already been accounted for in much lower boiling fractions. It therefore appeared likely that one or more of the four possible 1,6- or 1,7-methylethyl- or ethylmethylnaphthalenes were present. The infrared spectrum of the material was in agreement with this conclusion. According to Werner, Kennard, and Rayson<sup>9</sup>, the two strong bands shown in the sample spectrum at 783 cm.<sup>-1</sup> and 810 cm.<sup>-1</sup> could be due to 3H and 2H out-of-plane deformation vibrations of 1,6-disubstituted naphthalene, and the other two strong bands at 760 cm.<sup>-1</sup> and 835 cm.<sup>-1</sup> could be due to the same vibrations of 1,7-disubstituted naphthalene.

TABLE V

IDENTIFICATION OF EIGHT ALKYLNAPHTHALENES

Relative retention at 220°	Compound	Literature <sup>a</sup> b.p., °C. 760 mm.	B.P., °C. obtained from the correlation curve	Spectroscopic identification
3.70	1,4-Dimethylnaphthalene	268.5	268.4	Infrared
4.80	1,3,6-Trimethylnaphthalene	280	281.5	Ultraviolet
5.20	1,2,6-Trimethylnaphthalene	280	285	Ultraviolet
	1,2,7-Trimethylnaphthalene	278		Ultraviolet
4.39	1-Methyl-6-ethylnaphthalene, or 1-Ethyl-6-methylnaphthalene	273	277.3	Ultraviolet and infrared spectral-structural correlations
	1-Methyl-7-ethylnaphthalene, or 1-Ethyl-7-methylnaphthalene	270		
	2-Methyl-6-ethylnaphthalene	271		
	2-Methyl-7-ethylnaphthalene	270		
4.15	1-Methyl-6-ethylnaphthalene	270	275.2	Ultraviolet and infrared spectral-structural correlations
	1-Methyl-7-ethylnaphthalene	270		

<sup>a</sup> API Research Project 44, Selected Values of Properties of Hydrocarbons and Related Compounds, Carnegie Institute of Technology, Pittsburgh, Pa.

TABLE VI

ANALYSIS OF INDIVIDUAL AROMATIC HYDROCARBONS BOILING BETWEEN 202° AND 280°  
IN NEUTRAL OIL DISTILLATE FRACTIONS

Compounds identified	Fractions	Method of identification	Source of spectrum	Total weight, g.	Wt. % in neutral oil <sup>a</sup>
1,2,3,4-Tetramethylbenzene <sup>b</sup>	6,7,8,9	Rel. retention-b.p. correlation, I.R.	c	1.0681	0.153
1,2-Dimethyl-3-n-propylbenzene <sup>b</sup>	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.-structural correlation	-	0.2976	0.042
1,4-Dimethyl-2-n-propylbenzene <sup>b</sup>	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.-structural correlation	-	0.5874	0.084
1-Methyl-2,4-diethylbenzene <sup>b</sup>	6-13	Rel. retention-b.p. correlation, I.R.-structural correlation	-	0.9873	0.141
5-Methylindan <sup>b</sup>	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.	c	1.7566	0.251
4-Methylindan <sup>b,d</sup>	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.	c	1.7389	0.249
1,6-Dimethylindan	7-14	Rel. retention-b.p. correlation, I.R.	c	2.3746	0.340
4,7-Dimethylindan	7-16	Rel. retention-b.p. correlation, I.R.	c	1.3034	0.186
3-Methylindene <sup>b</sup>	5,6,7,8	I.R.	c	0.7141	0.102
3-Ethylindene	7-17	Rel. retention, I.R.	e	1.3126	0.188
2-Ethylindene	7-17	Rel. retention, I.R.	e	1.3032	0.186
2,3-Dimethylindene	7-17	Rel. retention, I.R.	e	1.7762	0.254
1,2,3,4-Tetrahydronaphthalene <sup>b,d</sup>	5,6,7,8	Rel. retention, I.R.	e	0.6170	0.088

(Table VI, continued)

2-Methyl-1,2,3,4-tetrahydro-naphthalene	7-15	I.R.	c	1.0426	0.149
6-Methyl-1,2,3,4-tetrahydro-naphthalene	12,13,14,15	I.R.	c	0.4958	0.071
Naphthalene <sup>b,d</sup>	6-15	Rel. retention, I.R.	e	6.3853	0.914
1-Methylnaphthalene <sup>d</sup>	14-24	Rel. retention, I.R.	e	12.0615	1.728
2-Methylnaphthalene <sup>d</sup>	12-24	Rel. retention, I.R.	e	16.1630	2.315
1-Ethylnaphthalene	20-29, 1* <sup>f</sup>	Rel. retention, I.R.	e	1.9777	0.283
2-Ethylnaphthalene	20-29, 1*	Rel. retention, I.R.	e	3.1184	0.456
2,7-Dimethylnaphthalene	21-29, 1*,2*	Rel. retention, I.R.	e	4.8187	0.690
1,7-Dimethylnaphthalene	23-29, 1*,2*	Rel. retention, I.R.	e	4.7915	0.686
2,6-Dimethylnaphthalene <sup>d</sup>	23-29, 1*,2*	Rel. retention, I.R.	e	4.1664	0.596
1,6-Dimethylnaphthalene <sup>d</sup>	25-29, 1*-5*	Rel. retention, I.R.	e	6.4648	0.926
1,3-Dimethylnaphthalene	25-29, 1*-5*	Rel. retention, I.R.	e	6.5617	0.940
2,3-Dimethylnaphthalene <sup>d</sup>	27,28,29, 1*-7*	Rel. retention, I.R.	e	3.8247	0.547
1,5-Dimethylnaphthalene	28,29, 1*-7*	Rel. retention, I.R.	e	3.6861	0.528
1,2-Dimethylnaphthalene	29, 1*-7*	Rel. retention, I.R.	e	3.5632	0.510
1,4-Dimethylnaphthalene	3*,4*	Rel. retention- b.p. correlation, I.R.	c	0.0979	0.014
2-Methyl-6-ethylnaphthalene } 2-Methyl-7-ethylnaphthalene }	4*-8*	Rel. retention- b.p. correlation, U.V. and I.R. structural correlations	-	3.9029	0.559
1-Methyl-7-ethylnaphthalene <sup>g</sup> and/or 1-Methyl-6-ethylnaphthalene <sup>g</sup>	4*-8*	Rel. retention- b.p. correlation, U.V. and I.R. structural correlations	-	3.2925	0.471
1,3,6-Trimethylnaphthalene	5*-7*	Rel. retention- b.p. correlation, U.V.	h	0.7338	0.105
1,3,7-Trimethylnaphthalene	5*-7*	Rel. retention, I.R.	e	0.452	0.064

(Table VI, continued)

1,2,6-Trimethylnaphthalene	6*-8*	Rel. retention- b.p. correlation, U.V.	h	0.8751	---
1,2,7-Trimethylnaphthalene			h		
Biphenyl <sup>d</sup>	18-29,1*	Rel. retention, I.R.	e	18.8235	2.696
4-Methylbiphenyl	28,29,1*,2*	Rel. retention, I.R.	e	0.7271	0.104
3-Methylbiphenyl	1*-7*	Rel. retention, I.R.	e	1.2431	0.178
Cyclohexyl benzene	12-15	Rel. retention, I.R.	e	0.2769	0.039
2a,3,4,5-Tetrahydroacenaphthene	20-26	Rel. retention, I.R.	e	1.1713	0.167
Acenaphthylene	4*-6*	Rel. retention, I.R.	e	0.6963	0.099
Acenaphthene <sup>d</sup>	2*-8*	Rel. retention, I.R.	e	2.336	---
Diphenyl ether	18-29,1*,2*	Rel. retention, I.R.	e	38.5897	5.528
2,3-Dimethylbenzofuran	14-16	I.R.-structural correlation	-	0.1778	0.025
Dimethylbenzofuran [I]	7-13	I.R.-structural correlation	-	1.7848	0.255
Dimethylbenzofuran [II]	9-15	I.R.-structural correlation	-	0.6451	0.092
Dibenzofuran	5*-8*	Rel. retention, I.R.	e	1.4718	---

a Total neutral oil distilling up to about 360°, representing 16.92 wt. % of the total tar.

b Identified in prior work by this laboratory<sup>1</sup>.

c American Petroleum Institute, Research Project 44, Infrared spectral data, Carnegie Institute of Technology, Pittsburgh, Pa.

d Previously identified by others<sup>2-6</sup>.

e This laboratory.

f Asterisk (\*) designates fractions shown in Table I of this report; other fractions are shown in Table I of the previous report<sup>1</sup>.

g The positions of the ethyl and methyl groups might be reversed.

h E. Heilbronner, U. Fröhlicher and P. A. Plattner, *Helv. Chim. Acta*, 32 (1949) 2479.

(4) Constituents having a relative retention of 4.15: This material appeared to consist of a mixture of 2-methyl-6-ethyl- and 2-methyl-7-ethylnaphthalene. The boiling point of the sample found by the trimethylnaphthalene curve was several degrees higher than the literature value for the two naphthalenes. However, the ultraviolet absorption maxima in the 300-330 m $\mu$  range for the constituent producing the first half of the peak were at 303 m $\mu$ , 310 m $\mu$ , 317 m $\mu$ , and 324.8 m $\mu$ , in close agreement with the much lower boiling 2,6-dimethylnaphthalene. The maxima shown by the second constituent were nearly identical to those for 2,7-dimethylnaphthalene at 307 m $\mu$ , 317 m $\mu$ , and 321 m $\mu$ . The presence of 2-methyl-6-ethyl- and 2-methyl-7-ethylnaphthalene was thus indicated. The infrared bands at 800 cm.<sup>-1</sup> to 900 cm.<sup>-1</sup> substantiated these identifications. The strong bands shown by the first constituent at 823 cm.<sup>-1</sup> and 874 cm.<sup>-1</sup> and those shown by the second constituent at 835 cm.<sup>-1</sup> and 876 cm.<sup>-1</sup> could be due, respectively, to 2H and 1H out-of-plane deformation vibrations of 2,6- and 2,7-disubstituted naphthalenes<sup>9</sup>.

In addition to these alkyl naphthalenes, three dialkylbenzofurans, of which one might be the 2,3-dimethyl-isomer, were tentatively identified by the characteristic infrared bands of benzofurans, observed by examining the spectra of benzofuran and all its monomethyl derivatives<sup>10</sup>. A strong band between 1,250 cm.<sup>-1</sup> and 1,280 cm.<sup>-1</sup> and one or two between 1,090 cm.<sup>-1</sup> and 1,160 cm.<sup>-1</sup> could be characteristic of benzofurans. According to Bellamy<sup>11</sup>, compounds containing the structure = C - O - may absorb near 1,250 cm.<sup>-1</sup> and in unsaturated cyclic compounds, with the structure = C - O - C =, a band may appear near 1,100 cm.<sup>-1</sup> or somewhat higher frequencies. Therefore, in the spectra of the benzofuran constituents, the bands between 1,250 cm.<sup>-1</sup> and 1,280 cm.<sup>-1</sup> and between 1,090 cm.<sup>-1</sup> and 1,160 cm.<sup>-1</sup> may be due to the furan structure in the molecule.

One benzofuran sample, having a relative retention of 1.28 at 200°, showed a strong band at 1,251 cm.<sup>-1</sup> as in 2-methylbenzofuran and another strong band at 1,092 cm.<sup>-1</sup> as in 3-methylbenzofuran. This sample also absorbed strongly at 742 cm.<sup>-1</sup>, similarly to 2-methyl- and 3-methylbenzofuran, both of which have a band at 746 cm.<sup>-1</sup> that is probably due to the 4H out-of-plane deformation vibration in the benzene ring. The boiling point of 2,3-dimethylbenzofuran from the literature<sup>12</sup> is approximately 220°, which falls in the boiling range of the distillate fractions containing this component. It is, therefore, very likely that this constituent is 2,3-dimethylbenzofuran. The other two samples showed the characteristic infrared bands of benzofurans in both regions. In addition, a few sharp bands also appeared between 1,000 cm.<sup>-1</sup> and 1,400 cm.<sup>-1</sup>. These were considered to be dimethylbenzofurans, all of the isomers of which boil well within the range 210° to 230°.

#### Quantitative estimation of aromatic hydrocarbons.

The internal standard method, which was described in the previous paper<sup>1</sup>, was employed for quantitative analysis of the samples, 1,2,3-triethylbenzene being selected as the standard. The equation used for the calculations is as follows:

$$f_C = A_S W_C / A_C W_S \dots \dots \dots (1)$$

where  $f_C$  is the calibration factor, as defined,  $A_S$  and  $A_C$  are the areas for the standard and component in the mixture, and  $W_C$  and  $W_S$  are the weight-percentages of the compound and the standard. The  $f_C$  values for a number of aromatic hydrocarbons were determined at 200° and 220° and are given in Table III. No significant difference was found between the values for each compound at these two temperatures. These values were used to determine the weight-percentages of the constituents in the fractions. For those compounds present in the tar for which authentic specimens were not available, the  $f_C$  values of their isomers or of structurally similar compounds were used. For example, an average  $f_C$  of 1.03 for six dimethylnaphthalenes was used to calculate the amounts of the 1,2- and 1,4-dimethyl isomers, an average of 1.08 for three trimethylnaphthalenes was used for other trimethyl and

methylethynaphthalenes, the  $f_C$  value of 0.99 for 1,2,3,5-tetramethylbenzene was used for 1,2,3,4-tetramethylbenzene, the value of 1.42 for indan was used for all indan derivatives, the value of 1.52 for tetralin was used for the two methyl-tetralins, and 1.05, an average of the values for 2-methyl- and 3-methylbiphenyl, was used for 4-methylbiphenyl.

The aromatic hydrocarbons boiling between 202° and 280° found in the low-temperature bituminous tar and their quantities are presented in Table VI. The values of weight-percentages in neutral oil of the three highest boiling components are not entered, since they are also expected to be present in the next higher boiling fraction.

## DISCUSSION

### Correlation between relative retentions and boiling points of alkylbenzenes and alkylnaphthalenes.

When the logarithms of relative retentions at 220° for alkylbenzenes and for alkylnaphthalenes, in either instance having an equal number of carbon atoms in the alkyl groups, were plotted against their boiling points, a straight line resulted. The relationship is similar to that established for a number of alkylbenzenes at 150°, as previously reported<sup>1</sup>.

Figure 2 (A) shows three parallel lines corresponding to alkylbenzenes having 4, 5, and 6 carbon atoms in the alkyl groups. Indans, which have a benzene nucleus with a 1,2-trimethylene-type alkylation, fall closely on the correlation curves for alkylbenzenes having the corresponding number of carbon atoms in alkyl groups. However, tetralin (point 10 in Fig. 2), which has a 1,2-tetramethylene-type alkylation, does not fit so closely to the line for  $C_{10}$ -alkylbenzenes, and its 2-methyl- and 6-methyl-derivatives (points 13 and 14) are well off the line for  $C_{11}$ -alkylbenzenes. However, a line drawn between points 13 and 14 is essentially parallel to the line for the  $C_{11}$ -alkylbenzenes. No clear-cut relationship can be established between the indans and the tetralins with this limited data for alkyltetralins.

Figure 2 (B) shows three parallel straight lines corresponding to alkylnaphthalenes having 1, 2, and 3 carbon atoms in the alkyl groups. A fourth line representing three monomethylbiphenyls (points 36, 37, and 38) is not parallel to the naphthalene lines.

A difference in slope can be observed among the three groups--benzenes, naphthalenes, and biphenyls. The slope of the benzenes is 0.0113, that of the naphthalenes is 0.0098, and that of the biphenyls is 0.0164.

## ACKNOWLEDGMENTS

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## REFERENCES

- 1 T.-C. L. CHANG and C. KARR, JR., Anal. Chim. Acta, 21 (1959) 474.
- 2 A. JÄGER and G. KATTWINKEL, Erdöl u. Kohle, 8 (1955) 629.
- 3 O. KRUBER, Oel u. Kohle, ver. Petroleum, 35 (1939) 770.
- 4 K. KURIHARA, J. Fuel Soc. (Japan), 7 (1928) 61 and 607.

- 5 G. T. MORGAN and A. E. J. FETTET, J. Soc. Dyers Colourists, 54 (1938) 17.
- 6 A. PARANT, Compt. rend. congr. ind. gaz. Paris, 65 (1948) 409.
- 7 D. H. DESTY, Vapor Phase Chromatography, Academic Press, Inc., New York, 1956, p. xiii.
- 8 R. F. EVANS, J. C. SMITH, and F. B. STRAUS, J. Inst. Petroleum, 40 (1954) 7.
- 9 R. L. WERNER, W. KENNARD, and D. RAYSON, Australian J. Chem., 8 (1955) 346.
- 10 SAMUEL P. SADTLER & SON, INC., "The Sadtler Standard Spectra," Philadelphia, Pa.
- 11 L. T. BELLAMY, The Infrared Spectra of Complex Molecules, John Wiley & Sons, Inc., New York, 1956, pp. 102-104.
- 12 M. BISAGNI, N. P. BUU-HOÏ, and R. ROYER, J. Chem. Soc., (1955) 3688.

## FIA ANALYSIS OF COAL TAR

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Several rapid and simple analytical procedures have been used for coal tar assay; likewise, many long and tedious methods have been worked out. The rapid, simple methods are generally criticized for not giving sufficient information while the long, tedious methods are unpopular because they are just that--long and tedious. The present system is offered as an analytical tool which is neither very tedious nor greatly time consuming but which gives considerable useful information.

The Fluorescent Indicator Adsorption (FIA) method was originally designed for use on light petroleum fractions of a fluid nature. Essentially it consists of displacement adsorption chromatography of hydrocarbon mixtures on a silica gel column, fluorescent indicators being used to detect the zones containing the various chemical types, namely, saturates, olefins, and aromatics.

### Adaptation of FIA to Coal Tar

Two major problems were encountered by the Bureau of Mines in adapting this analysis for use on coal tar. First, the tar is often too viscous to flow in a chromatographic column, and second, coal tar contains compounds other than hydrocarbons such as neutral oxygenates, tar acids, and tar bases.

First attempts by the Bureau to chromatograph samples of low-temperature tar were unsuccessful, as the waxes would solidify during fractionation and prevent the movement of the sample in the column. A steam-heated column was constructed, but the silica gel would not absorb at the elevated temperature, and no separation was possible. Attempts were made to remove the waxes by precipitating them from a cold acetone solution of the tar or by extracting them with petroleum ether. Neither system was satisfactory, as it was difficult to establish with any accuracy just how much wax was removed. The problem was finally solved by diluting the tar with a precisely measured amount of petroleum ether; this served to dissolve the waxes and allowed the tar to move freely down the column, and since the amount of petroleum ether added was known, this could be corrected for in the results.

For solution of the second problem, it was necessary to demonstrate that the FIA method could be used to separate nonhydrocarbon materials as well as hydrocarbons, because the nonhydrocarbons make up a large part of the tar. A synthetic mixture, composed of heptane, octene, benzene, acetophenone, and o-cresol, was made up for this demonstration. When this mixture was run using the standard FIA dyed-gel, the hydrocarbons separated in the usual manner; the acetophenone section then took up the pink dye which normally indicates the end of the chromatogram; the cresol section, a light tan color, followed.

Gross tar, distilled to its cracking temperature, separated on the silica gel column into the same number of zones, but the dark color of the neutral-oxygen and tar acid fractions made it impossible to detect visually the boundary between these two zones. When samples from these sections were examined by infrared spectra, however, bands characteristic of ketone and phenolic hydroxy groups were identified.

Attempts to determine tar bases by the FIA method have so far been unsuccessful.

At this stage of development, it became apparent that not all of the tar sample was being eluted. To correct this failure, changes were made in column design, and stronger displacing agents were employed. Eventually a satisfactory charging column was evolved, and pyridine was chosen as the most suitable displacing agent.

It was found that definition of the boundaries between the various groups was far better when gravity flow was used than when the separation was carried out under pressure. The charging column, therefore, was designed to facilitate the flow so that an analysis by this technique could be completed in a reasonable time. By shortening the charging sections and eliminating the usual capillary, highly satisfactory separations were realized in 6 to 8 hours.

Best results have been obtained from distilled tars. Gross, undistilled tar contains polymeric material and heavy pitch which often obscure the top level of the chromatogram. Tar fractions and whole tars distilled to any temperature up to the cracking point give excellent results. If distillation is impractical or undesirable, the tar can be separated from most of the pitch by dissolving in ether and filtering, or the sample can be washed through a silica gel column with low-boiling petroleum ether or heptane until the eluent is clear, then stripped of solvent.

This, then, is the assay system in its current stage of development. The charging tube consists of two sections, each 10 cm. long; the upper section is 12 mm. OD while the lower is 7 mm. OD. These tubes are joined in a smooth taper, and the lower end of the lower section is tapered to fit into 1/8-inch Tygon tubing that is used to attach the measuring tube. The measuring tube is 3 mm. OD and 120 cm. long and is drawn out to a capillary on the lower end. Davison 923 silica gel, which has been activated at 200° C. overnight, is then funneled into the column. Packing the column is most easily done by attaching a vibrator to a ring stand and clamping the column to this stand. The vibrator is run throughout the packing operation, both to aid filling and to insure uniform packing. When the column has filled to the middle of the 7-mm. section, a small amount of dyed gel is added, and then plain silica gel again to bring the level to about the middle of the upper section.

The sample is prepared by placing 2 ml. of petroleum ether into a 10-ml. graduate and adding tar to bring the level of the mixture to the 4 ml. mark. One to two ml. of pyridine are added and the sample is then well mixed. One ml. of this sample mixture is placed directly on the silica gel in the column, and as soon as the sample is completely adsorbed, an additional layer of 2 to 3 cm. of silica gel is placed on top of the column and packed down. Eluent is added and the chromatogram allowed to develop by gravity flow.

When the upper boundary of the sample is well into the measuring tube, the column is placed in a dark room, where it is illuminated with ultraviolet light and the various sections measured with a meter stick. Half of the total length is due to the added petroleum ether and therefore is subtracted from the length of the saturate section. What remains in this section represents the saturates from the tar. The remaining sections are measured, and the length of each section is proportional to the amount of that chemical type present in the tar.

#### Results from FIA Assay System

Sine this method is not fully developed, it has not been used extensively on specific assay problems; however, in the course of development, some interesting facts have been disclosed. Confirmation of considerable amounts of oxygen-containing material in the neutral oil is of interest. The FIA analysis of a typical neutral oil fraction from lignite tar follows:

FIA ANALYSIS OF A NEUTRAL OIL FRACTION

Boiling 301-304° C.

Saturates, vol. per cent	18.4
Olefins	7.1
Aromatics	53.3
Oxy-compounds	21.2

The maximum oxygen content of this neutral oil is 3 per cent; therefore, it would seem unreasonable to find that 21 per cent of the sample is oxygen-containing compounds. The mean molecular weight, however, is in the order of 200, and if each such molecule contained a single oxygen atom, the oxygen content would be 8 per cent. To bring the oxygen content to 3 per cent, 350-gram atoms of oxygen-free material must be assumed, for a total of 550-gram atoms. Of this, 36-weight per cent is oxygen-containing material. From this we can see that 21 per cent oxygen-containing neutral compounds in a sample containing 3 per cent oxygen is not at all unreasonable.

Several assays, including cuts from various temperature ranges as well as those distilled over the full boiling range, have been made on distilled fractions of gross tar. Further refinements are necessary before the method can be fully evaluated for this purpose, but there is little doubt that the FIA analysis can be used to differentiate between various tars and to give a good estimate of the chemical types they contain. As an example, the comparative analyses of tars obtained from a North Dakota and a Texas lignite follow.

FIA ASSAY OF TWO GROSS TARS

(Boiling 80-360°)

	North Dakota Tar	Texas Tar
Saturate, vol. per cent	15.1	16.7
Olefins	7.6	10.1
Aromatics	29.7	34.9
Oxy-compounds (neutral + acid)	48.4	38.4

Future Problems

Foremost among the remaining problems is that of distinguishing the boundary between neutral oxy-compounds and tar acids. The boundary is easily observed in very light-colored samples but is completely obscured in the dark color of most tars.

Another desirable development would be a more rapid analysis, particularly for control work. Any speedup would almost certainly result in loss of accuracy, although this loss could be minimized to a tolerable level in most cases. At present, the average run takes about 6 hours.

Eventually, if the system is to be completely general, means must be found to determine tar bases.

- (1) ASTM. Tentative Method of Test for Hydrocarbon Types in Liquid Petroleum Products (Fluorescent Indicator Adsorption (FIA) Method). ASTM D 1319-58T (1954); Revised 1955, 1956, 1958.
- (2) CRIDDLE, D. W., AND LETOURNEAU, R. L. Fluorescent Indicator Adsorption Method for Hydrocarbon-Type Analysis. Anal. Chem. 23, 1620-4 (1951).

APPLICATION OF HIGH VACUUM MICRO-DISTILLATION TO THE STUDY OF  
COAL-TAR AND PETROLEUM PITCHES

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INTRODUCTION

The binder pitches used in the manufacture of carbon electrodes are of coal-tar or petroleum origin and exhibit pronounced differences in their properties depending on their source and mode of production. Various means have been devised to detect these differences, but distillation has very seldom been used. Obviously there are many reasons for this lack of interest in distillation, but the main one is probably the thermal lability of this type of material or at least of some of its constituents. However, the difficulty associated with the thermal lability can be overcome by making use of high vacuum technique.

There are a number of molecular stills commercially available, but, in general they require the use of fairly large samples. In the investigation described herein this was a major handicap since the available samples were mostly experimental and of limited supply. Furthermore, we were not interested in collecting fractions and studying each fraction as the amount of work involved would have been prohibitive, especially in view of the fact that it was intended to test a fairly large number of samples; past experience in our own laboratory had clearly indicated that work based on only a few samples cannot be really informative as the conclusions drawn can be greatly influenced by the type of pitch used and the treatment the pitch has undergone. Our main interest was to find out whether distillation could yield significantly different data which might be useful in pitch evaluation. The micro-molecular still used by Sims<sup>(1)</sup> for the analytical distillation of organic mixtures appeared to offer the desired features; the technique was reasonably rapid and requires only milligram quantities of material. With such a still the amount of distillate at various temperatures is calculated from the measured contraction of a calibrated quartz helix.

EXPERIMENTAL

Still. - The apparatus (Figure 1) consists essentially of a pan suspended from a quartz helix in an evacuated Pyrex tube. The sample is heated by an internal heating coil and the contraction of the quartz helix due to the loss of weight of the sample in the course of distillation is measured by a sensitive-reading cathetometer.

The sample pan is made of aluminium. A disk of 5/8 in. diameter is stamped out of a sheet of aluminium foil by using a steel punch, and formed into a cylindrical pan of 3/8 in. diameter and 1/8 in. high wall in a specially designed mould. The aluminium pan has an area of 0.75 cm<sup>2</sup> and weighs approximately 10 mg.

The stirrup, which holds the pan, is cut from a sheet of stainless steel of approximately 0.0065 in. thickness. It is in the shape of a cross with arms 1 1/2 mm wide; the length of the 3 short arms is 6 mm, the length of the long arm, 33 mm. The ends of the arms are bent upwards in such a way that the pan can be placed between them. The end of the long arm is shaped into a hook to be inserted into the loop of the Pyrex filament which in turn is hung on the quartz helix (Figure 1). The weight of the stirrup is reduced to approximately 50 mg by immersion in hydrochloric acid.

The heating coil, 6 in. long and 1/2 in. in diameter, has a resistance of 14 ohms. It is made of 24 gauge Chromel "A" wire and is wound on three strip-mica spacers. The voltage is controlled by a variable transformer (Variac), with a range of 0-135 volts and a maximum output current of 7.5 amperes. The maximum temperature of 350°C inside the heating coil is obtained by operating at a Variac setting of 60 (60 volts).

\* Now with Aluminium Industrie A. G. Chippis, Switzerland.

Since the pan containing the sample is continuously moving upwards during a distillation, due to the loss of weight, it was important to know the temperature distribution inside the heating coil. The temperature, after the still had been evacuated, was raised to 350° C at a rate of approximately 6.6° C per minute by increasing the Variac by one scale division every minute; the temperature was measured by means of the chromel-alumel thermocouple on the central axis of the heating coil. The thermocouple was moved in steps of 1/2 in. and at each position the heating cycle was repeated and temperatures were recorded. The position of the thermocouple was measured by means of a scale printed on the wall of the still proper; the zero of the scale was level with the top of the heating coil. Figure 2 shows the axial temperature distribution of the heating coil.

The heating rate of approximately 6.6° C/minute was initially selected because of practical considerations. A higher heating rate was not desirable since gas evolution during distillation would be too fast. A slower heating rate (Variac setting increased by one scale division every second minute, which meant double distillation time) was tried, but did not change the results significantly; the shape of the elimination curve stayed the same except that the peak of the curve moved slightly towards a lower temperature.

By raising the Variac by one scale division every minute, the temperature, however, did not increase at a satisfactorily uniform rate; the heating rate was slightly higher at the beginning than at the end of distillation. A modified scale was prepared for the Variac and it was then possible to obtain a heating rate of 6.6° C/minute throughout the distillation.

Vacuum System. - The system was evacuated by a Duo-seal, two-stage vacuum pump. (Canadian Laboratory Supplies Limited, Catalogue No. A-72-703B). High vacuum was obtained by a Supervac OD-25 Oil Diffusion Pump, (Central Scientific Company, Catalogue No. 93330, No. 1), and was measured by a McLeod gauge. Apiezon grease "N" was used for all glass joints and stopcocks.

Measuring Device. - The relative position of the pan - and thus the weight loss of the sample during a distillation - was measured by a Wild cathetometer (H. Wild, Surveying Instruments Supply Company, Ltd., Heerbrugg, Switzerland). The cathetometer consists of a horizontal telescope with a magnification of 12x, mounted so as to slide upon an upright pillar with an attached glass staff. The telescope is adjusted in height by rack and pinion action until its crosshairs coincide with the lowest end of the quartz helix. The position of the telescope upon the vertical, graduated glass staff can then be read by means of a microscope. Direct reading to 0.1 mm and safe estimation to 0.01 mm can be made with this instrument.

Calibration of Quartz Helix. - Analytical balance weights, covering a range up to 100 mg, were placed in the sample pan and the extension of the quartz helix caused by each weight increase measured with the cathetometer. For each one milligram increment in load, the helix was lengthened by 1.1092 mm.

Contraction of the quartz helix in the course of a distillation was due to two causes: (a) reduction in load as a result of distillation and (b) heating of the quartz helix. The thermal contraction of the helix was measured over the entire temperature range from room temperature to 350° C; it was found to be roughly 0.01 mm per 6.6° C within the normal distance travelled by the pan during a distillation. Positive corrections were accordingly made to all cathetometer readings.

Sample Preparation. - Preliminary distillations had shown that at a temperature between 80 and 150° C, bubbles due to gas evolution started to form on the surface of the pitch. The bubbles gradually increased in size and finally collapsed, imparting a jerking motion to the pan so that it was impossible to take readings on the cathetometer. It was finally found that with a mixture of 30% pitch and 70% calcined petroleum coke no bubbling occurred and the readings on the cathetometer could be made without difficulty. A blank distillation run with coke alone showed that no trace of volatile was present in the coke.

Coke, calcined at 1400° C and ground to -35 +48 mesh, was mixed in a mortar with finely ground pitch (-20 mesh) in the ratio of 2:1. From this mixture, 166.5 mg (55.5 mg pitch) were weighed into the aluminium pan. This particular sample size was chosen because (a) the cathetometer readings could be multiplied directly by the factor 2 in order to obtain the percentage distilled, and (b) the pan remained within a zone of reasonably uniform temperature throughout the complete distillation cycle, as shown in Figure 2.

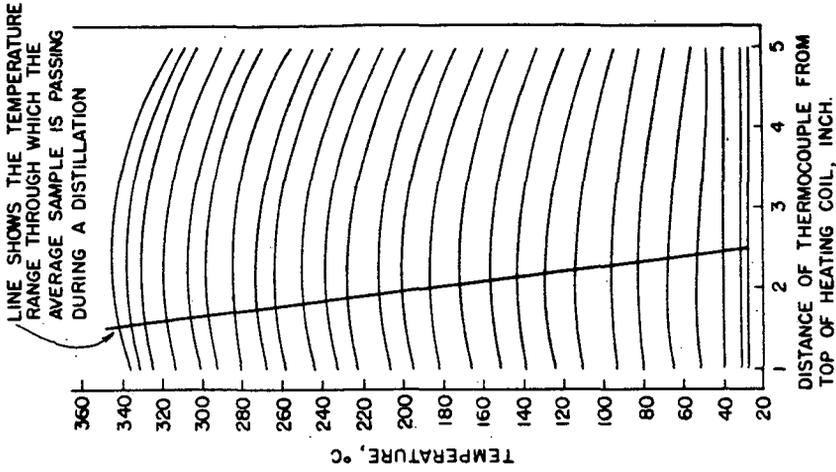


FIGURE 2

AXIAL TEMPERATURE DISTRIBUTION OF HEATING COIL.

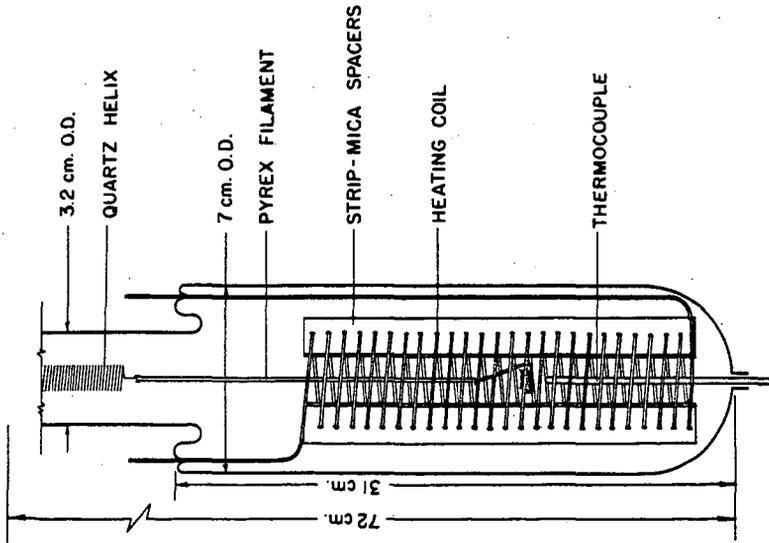


FIGURE 1

MICRO POT-TYPE STILL

Distillation Procedure. - After the pressure of the system has been reduced to  $10^{-5}$  mm Hg as read on the McLeod gauge, the sample was gradually heated up to 350° C. In the course of the distillation, the contraction of the helix was recorded at constant intervals of one minute. To prevent condensation on the still wall facing the cathetometer and thus interference with the telescope readings, a jet of air was played on the appropriate area of the wall.

### RESULTS

A series of 20 binders - 17 coal-tar pitches and 3 petroleum pitches - was tested. They are identified in Table 1 which also lists their respective melting point, coking value, atomic carbon-hydrogen ratio, and compressive strength of test electrodes prepared from a mixture of petroleum coke and binder pitch; this last property is considered as the best individual criterion of binder quality.

Distillation runs yielded more than 1000 readings, which it is impractical to reproduce. The data were plotted in two fashions, as elimination curves and as distillation curves. Elimination curves represent the amount of distillate in each fraction expressed as weight percentage of the initial sample weight, while distillation curves relate temperatures to cumulative distillate percentages.

For present purposes, a selection has been made of three pitches - two coal-tar and one petroleum pitches - that illustrate the general behaviour pattern and also the more or less extreme ranges encountered. Figure 3, shows elimination curves, Figure 4, cumulative distillation curves for the same three pitches.

TABLE 1

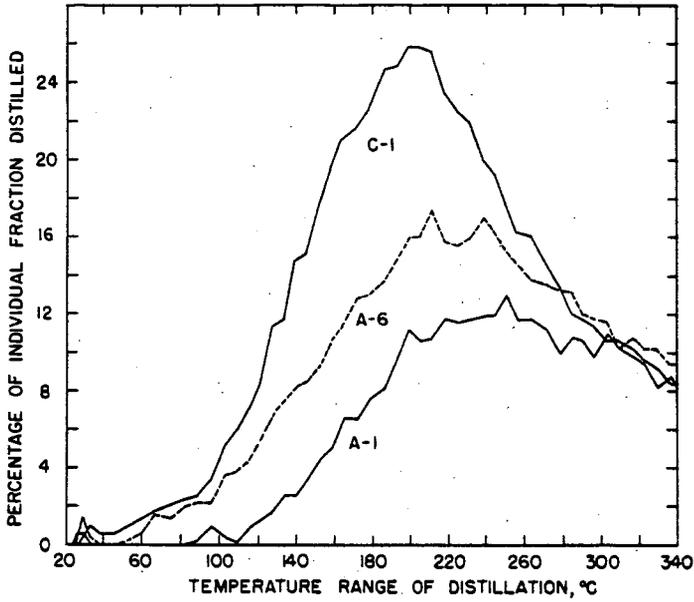
#### DESCRIPTION OF PITCH SAMPLES

Pitch Identification <sup>(a)</sup>	Melting Point <sup>(b)</sup> ° C	Coking Value <sup>(c)</sup> %	Carbon-Hydrogen Ratio (Atomic)	Compressive Strength of Test Electrodes (kg/cm <sup>2</sup> )
<u>Coal-Tar Pitches</u>				
A-1	137	64.8	1.86	444
A-2	145	69.5	1.88	440
A-3	101	57.9	1.79	354
A-4	106	57.8	1.75	352
A-5	67	51.1	1.77	340
A-6	97	55.6	1.76	336
A-7	68	45.0	1.64	289
A-8	66	41.5	1.61	273
B-1	89	54.4	1.67	381
B-2	94	58.5	1.84	348
B-3	89	56.6	1.83	341
B-4	95	56.9	1.76	339
B-5	90	51.7	1.76	320
B-6	89	51.4	1.71	305
B-7	89	53.5	1.59	295
B-8	95	49.5	1.62	252
C-1	65	32.9	1.49	181
<u>Petroleum Pitches</u>				
D-1	111	53.3	0.98	210
D-2	111	43.1	0.93	169
E-1	70	42.9	1.12	135

(a) A, B, C, D, E indicate different suppliers.

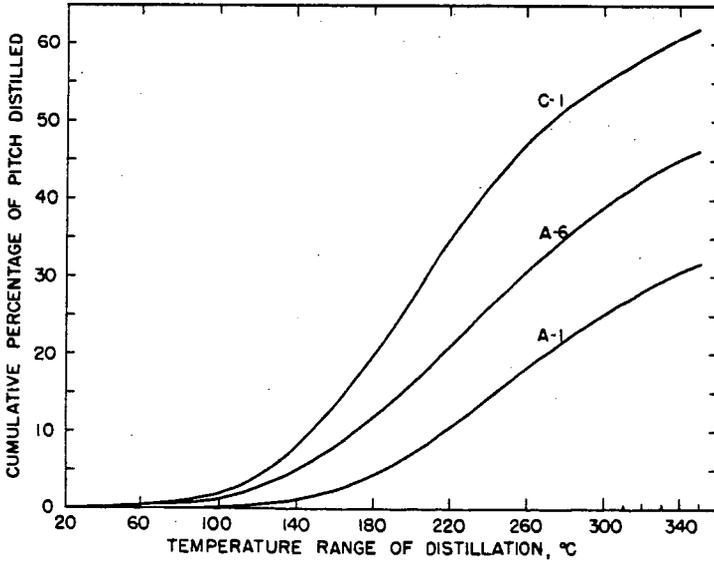
(b) Cube-in-air method was used for melting points greater than 80° C; below 80° C, cube-in-water.

(c) Method described in literature reference (2).



**FIGURE 3**

**ELIMINATION CURVES OF PITCH SAMPLES**



**FIGURE 4**

**CUMULATIVE DISTILLATION CURVES OF PITCH SAMPLES**

## DISCUSSION

From examination of the various curves, the three variables which appeared to be of some significance for pitch characterization were estimated to be (a) the slope of the relatively straight portion of the cumulative distillation curve, (b) the temperature at which the greatest percentage was distilled (elimination maximum) and (c) the cumulative percentage corresponding to the elimination maximum.

In general these three variables could have been obtained from the distillation curves, but in some cases the precision was inadequate. This difficulty was overcome by establishing the mathematical equation of each cumulative distillation curve and subsequently deriving the values shown in Table 2. As can be observed in Figure 4, the shape of the cumulative distillation curves is that of an elongated S; the "Gompertz" equation<sup>(3)</sup> was found to be satisfactory in defining such curves:

$$y = a \cdot b^{c^x} \quad \text{or}$$

$$\log y = \log a + c^x \log b$$

Inspection of Table 2 shows that low values of maximum slope ( $x_1$ ) and amount distilled at the elimination maximum ( $x_2$ ) tend to coincide with high values of compressive strength; this indicates some measure of individual relationships. Such a tendency does not exist for the elimination maximum ( $x_3$ ). Inspection alone, however, is inadequate to give a full appraisal of relationships and a better picture is supplied by statistical study.

The statistical procedure applied was the Multiple Correlation Technique<sup>(4)</sup> designed to assess the relationship between two or more variates. Complete statistical data are not reported herein; only those useful for the discussion of results are summarized in Table 3.

Statistically speaking the correlation coefficients given in Table 3 for maximum slope ( $R = 0.903$ ) and for % distilled ( $R = 0.766$ ) are highly significant but, from a practical viewpoint, the standard deviations about regression of compressive strength on either one of the two independent variables ( $\sigma = 36.7$  and  $54.7$  kg/cm<sup>2</sup> respectively) are rather high. In other words, although the maximum slope alone accounts for 81.4% ( $R^2$ ) of the variations in compressive strength, and % distilled alone, for 58.7%, the proportion of variations in compressive strength not accounted for is undeniably high. It was thought then that, taken together, variations in slope and % distilled, or even variations in all three independent variables might account for a much higher proportion of the variations in compressive strength. However, tests 3, 4 and 5 of Table 3 clearly indicate that this was not the case. In fact the correlation between compressive strength and slope alone (test 1) is as good as the correlation between compressive strength and any combinations of two or three independent variables.

From the above discussion, it can be concluded that high vacuum micro-distillation of pitch, as carried out during this investigation, represents another analytical tool which permits a certain differentiation between various pitches, but this differentiation is not considered satisfactory for prediction of pitch quality. However, it is believed that, because of its good reproducibility, it could be used advantageously as another means of controlling pitch uniformity.

## ACKNOWLEDGEMENTS

The authors acknowledge the help of the National Research Council (Ottawa, Canada) in constructing the still, and also express their appreciation to Aluminium Laboratories Limited for permission to publish.

## REFERENCES

- (1) Sims, R. P. A., Vacuum II, 245-256 (1952).
- (2) Charette, L. P., and Girolami, L., Fuel, XXXVII, 382-392 (1958).
- (3) Davis, Dave S., Empirical equations and nomography. First Edition, New York and London, McGraw-Hill Inc., 1943, p. 57.
- (4) Dwyer, Paul S., Recent development in correlation technique. J. A. M. Statistical Association, 37, 441-460 (1942).

**TABLE 2**  
**MAXIMUM SLOPE, PERCENTAGE DISTILLED AT ELIMINATION MAXIMUM AND**  
**ELIMINATION MAXIMUM OF PITCH SAMPLES**  
 (in order of decreasing compressive strength of test electrodes)

Pitch Identification	Compressive Strength kg/cm <sup>2</sup>	Maximum Slope (x <sub>1</sub> ) %/° C	Amount Distilled (x <sub>2</sub> ) %	Elimination Maximum (x <sub>3</sub> ) ° C
<u>Coal-Tar Pitches</u>				
A-1	444	.1848	15.2	243
A-2	440	.1824	15.4	259
E-1	381	.1998	19.4	191
A-3	354	.1993	19.2	207
A-4	352	.2170	20.4	235
B-2	348	.2192	20.8	220
B-3	341	.2348	20.6	217
A-5	340	.2626	21.4	192
B-4	339	.2294	24.8	236
A-6	336	.2421	21.2	218
B-5	320	.2035	21.5	216
B-6	305	.2270	23.2	225
B-7	295	.2486	22.4	217
A-7	289	.2956	22.8	182
A-8	273	.3135	26.0	199
B-8	252	.2269	20.0	200
C-1	181	.3706	25.8	194
<u>Petroleum Pitches</u>				
D-1	210	.3116	22.3	286
D-2	169	.3470	24.8	289
E-1	135	.3698	23.9	251

**TABLE 3**  
**CORRELATION BETWEEN COMPRESSIVE STRENGTH AND DISTILLATION DATA**

Test No.	Variables <sup>(a)</sup>	Correlation Data <sup>(b)</sup>		Standard Deviation <sup>(c)</sup> (kg/cm <sup>2</sup> )
		R	R <sup>2</sup>	
1	x <sub>1</sub>	0.903	0.814	36.7
2	x <sub>2</sub>	0.766	0.587	54.7
3	x <sub>1</sub> , x <sub>2</sub>	0.910	0.828	36.4
4	x <sub>1</sub> , x <sub>3</sub>	0.905	0.819	37.3
5	x <sub>1</sub> , x <sub>2</sub> , x <sub>3</sub>	0.916	0.838	36.3

(a) x<sub>1</sub> = maximum slope; x<sub>2</sub> = % distilled at elimination maximum;  
 x<sub>3</sub> = elimination maximum.

(b) R<sub>2</sub> = correlation coefficient  
 R x 100 = % of total variation in compressive strength accounted for by  
 the variations in the specified independent variables or combinations  
 of them.

(c) Standard deviation about regression of compressive strength on the  
 independent variables or combinations of them.

SOLVENT FRACTIONATION OF ELECTRODE BINDER PITCHES

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INTRODUCTION

Solvent fractionation has been used fairly extensively for studying composition and structure of pitches. Among the more recent papers published on the subject are those of Wood and Phillips, (1) Mallison, (2) Franck, (3) and Lissner and Schäfer. (4) However, most of the studies dealt with a small number of samples and rather elaborate fractionation techniques. Past experience in our own laboratory has indicated that there is danger in studying too few samples: the conclusions drawn can be greatly influenced by the types of pitch used or by the treatment the pitch has undergone. For these considerations, and also because the time involved even for simple fractionation is always fairly long, it was preferred to try a fractionation procedure which would be relatively simple in operation as well as in number of fractions produced, thus allowing the coverage of a large number of binders. A two-stage fractionation, which would permit isolation of the much-discussed carbon-I (C-I), appeared appropriate.

EXPERIMENTAL

Choice of Solvents

In order to select the most suitable fractionation agents, 14 solvents were examined. The procedure employed consisted in refluxing 1 gram of pitch in 100 ml of solvent for one hour, and determining the amount of the undissolved material collected on a fritted porcelain filtering crucible. In tests with high boiling point solvents such as quinoline and nitrobenzene, the sample was digested only (no refluxing) in the solvent at 80-90° C on a steam bath. The results of solubility tests on five coal-tar pitches ranging in melting point from 92 to 180° C are shown in Table 1.

TABLE 1  
SOLUBILITY OF PITCH IN SOLVENTS

Solvents	Percent Solubility					Average
	92° C Pitch	100° C Pitch	108° C Pitch	127° C Pitch	180° C Pitch	
Quinoline	71	93	90	82	71	81
Nitrobenzene	66	88	84	67	57	72
Pyridine	61	88	82	67	59	71
Chloroform	52	68	68	55	46	58
Toluene	53	70	68	53	44	58
Benzene	50	67	66	56	40	56
Carbon Tetrachloride	45	58	54	38	27	44
Acetone	44	56	50	31	28	42
Buryl Alcohol	33	40	39	27	19	32
n-Heptane	25	25	22	15	7	19
Isopropyl Alcohol	20	27	22	11	7	17
n-Hexane	19	17	15	9	6	13
Methyl Alcohol	16	19	15	7	4	12
Petroleum Ether	10	8	8	9	4	8

Of the solvents examined, quinoline and acetone were selected for various reasons. Quinoline appeared to be the solvent having the strongest dissolving power and, as such, would isolate the least soluble fraction usually referred to as carbon-1. Acetone was chosen because it appeared to provide a fair distribution of the pitch quinoline-soluble portion into two fractions; furthermore, acetone, because of its high volatility, can be driven off easily at low temperature.

#### Fractionation Procedure

A sample size of 20 grams was found adequate in most cases to provide fractions in sufficient quantity to permit their analysis.

Hard binders were ground to pass a 65 mesh sieve. Soft binders were slightly heated for easier manipulation.

#### Acetone-Soluble Fraction

Since it was inconvenient to carry out the extraction in one operation on account of the considerable quantity of acetone, equivalent to the proportion employed in the solubility tests, successive extractions were carried out to complete the separation of the acetone-soluble fraction. With 20 grams of starting binder material, three extractions, with 500 ml of acetone each, were generally sufficient. Between extractions, the acetone solution was filtered off, the residue washed with acetone and dried. During the first, and occasionally also during the second extraction, part of the pitch softened and formed agglomerates; consequently it was necessary to grind the residue between extractions. Soxhlet extraction was attempted on a few pitches, but the agglomeration was even worse. The filtration was carried out on a specially made aluminium filter support with a detachable top light enough to be weighed on an analytical balance. A combination of a double layer of glass-fiber filter paper and one analytical filter paper disk was used as filtering medium.

To recover the acetone-soluble portion from the filtrates and washings, the bulk of the acetone was removed by careful distillation. Occasionally, the solution showed tendency to bump, even when "Boileezer" stones were added; it was therefore preferable to remove the acetone simply by slow evaporation. In either case, the concentrated solution was finally transferred to a tared vessel and the remaining acetone removed by evaporation in a vacuum oven.

#### Quinoline-Insoluble Fraction

The residue from the acetone extraction was ground to a fine powder in a glass mortar and digested with quinoline on a steam bath while stirring. In the preliminary work, a constant amount of quinoline was used for all pitches. However, it was observed that the filtration rate varied, depending on the pitch type, from fast to zero; the filtration was especially difficult with heat-treated or cut-back pitches. This difficulty was overcome, and fast filtration obtained, by using a quantity of quinoline proportional to the expected percentage of the intermediate fraction (quinoline-soluble, acetone-insoluble); this percentage was calculated by deducting from the known acetone-insoluble content, the amount of quinoline-insoluble determined by an analytical standard procedure on a small sample.

For filtration, the same type of filtering set-up as specified for the acetone-soluble fraction was used. The quinoline-insoluble residue was washed with quinoline and acetone, dried and weighed.

#### Quinoline-Soluble, Acetone-Insoluble Fraction

The recovery of this intermediate fraction from the filtered quinoline solution presented some difficulty. It was found impossible to get rid completely of the quinoline by distillation at atmospheric pressure or even under vacuum without excessive heating of the residue. A procedure was finally worked out whereby the bulk of the quinoline was first removed by gentle distillation at atmospheric pressure, followed by evaporation in an open dish on a steam bath until a suitable concentration was attained. The concentrated solution was then poured slowly while stirring into acetone; the extent to which the quinoline solution was concentrated prior to precipitation, and the volume of acetone used were proportional to the amount of solute. A dense, almost crystalline precipitate formed which was easily filtered. After filtration, it was ground to a fine powder, re-extracted with acetone, re-filtered and dried. After this treatment, there was no trace of quinoline odour and it was assumed that the solvent was completely removed. Because of practical difficulties, no attempt was made to recover the very small amount of solute which remained in the filtrate.

A flow diagram illustrating the complete fractionation technique is given in Figure 1.

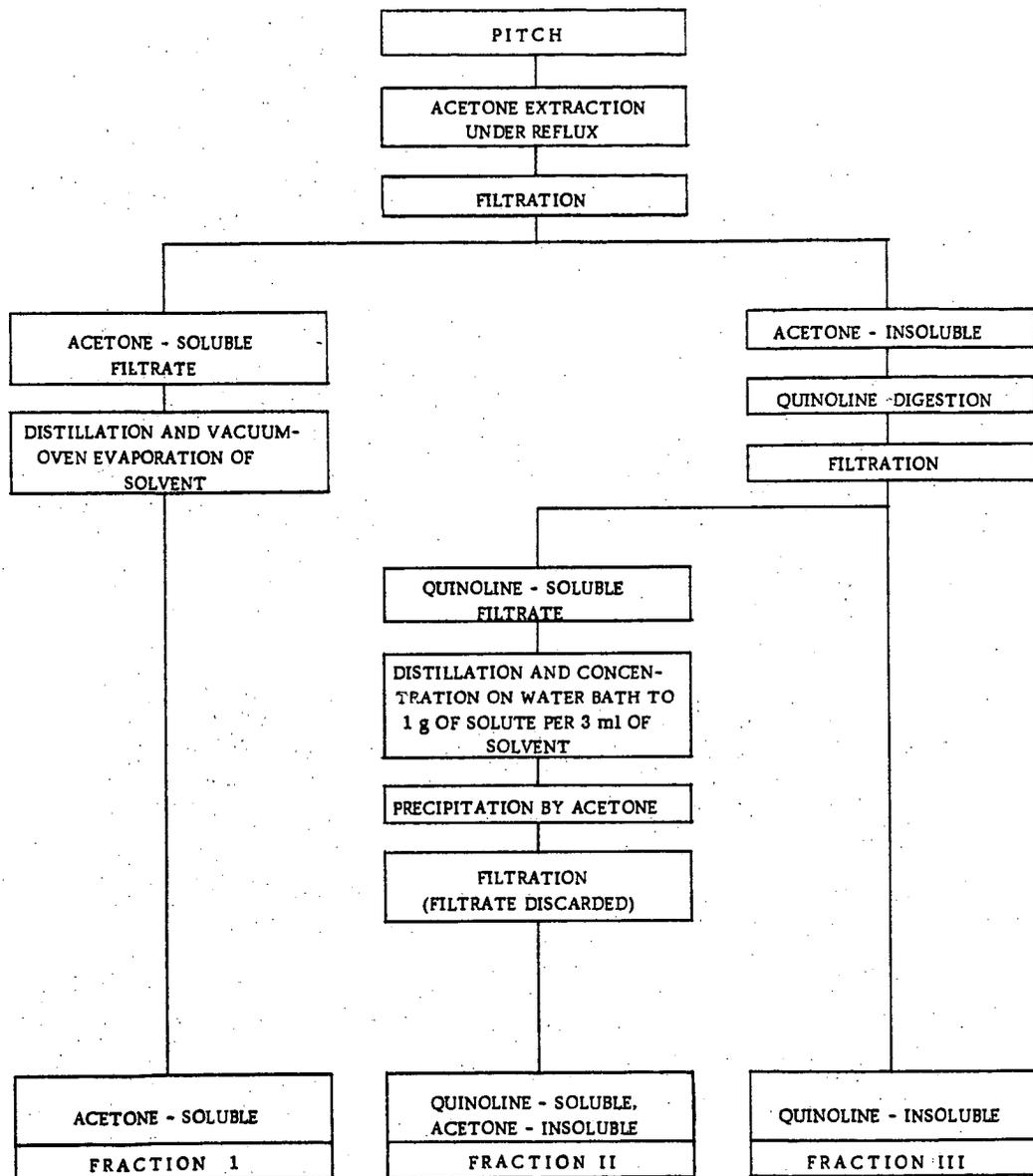


FIGURE 1

FRACTIONATION SCHEME

## RESULTS

The samples of binder pitch selected for this investigation represented different types of pitch, different producers and different levels of quality. They are listed in Table 2 which also contains some of their properties.

In all, 26 samples were fractionated: 14 straight-distilled pitches; three heat-treated pitches; six cut-back pitches, i. e. pitches which had been produced by blending heat-treated pitches with some light materials such as oil or tar; one chemically-treated pitch prepared from straight-distilled pitch by digesting with 2% sulphur; and finally two petroleum pitches. Twelve additional regular production petroleum pitches, all from the same source, were also fractionated, but only one is reported since identical observations were made on all. Consequently, it should be borne in mind that conclusions drawn and observations made on regular production petroleum pitches are based effectively on a fairly large number of samples and not only on sample J-1.

Fractionation results and some characteristics of pitch fractions are presented in Table 3.

## DISCUSSION

### Acetone-Soluble Fraction

The acetone-soluble fraction is a dark brown, almost black material which at room temperature has a consistency ranging from that of tar or very heavy grease to that of solid pitch. Thus, there is a noticeable difference in viscosity for fractions obtained from different pitches, as shown by the equiviscous temperatures given in Table 3. The coking value of the fraction is low, but also covers a fairly wide range; in general, it is lower for cut-back binders than for straight-distilled pitches of equivalent softening point. It is also of some interest to note that the coking value of the acetone-soluble fraction for regular production petroleum pitches, exemplified by sample J-1, is higher than for any of the coal-tar pitches, although the carbon-hydrogen ratio is significantly lower.

Only the acetone-soluble fraction was found suitable for viscosity determination. As shown in Figure 2, there is a definite trend for the temperature coefficient of whole pitches to decrease with larger differences between the equiviscous temperature at 15 poises of the whole pitch and that of the acetone-soluble. The only real exception is the experimental petroleum sample J-2; difficulty experienced with this pitch in preparing mix for test electrodes might be explained at least in part by this deviation, which is the result of the very low equiviscous temperature of the acetone-soluble as compared to the high equiviscous temperature of the whole pitch. On the basis of present knowledge, it can be hypothesized that this petroleum pitch was produced by severe cracking of a petroleum crude and dilution of the residuum with light material to obtain the desired melting point.

The relationship between coking value of the acetone-soluble fraction and its equiviscous temperature, shown in Figure 3, illustrates some interesting facts. The acetone-soluble fractions of four of the six cut-back pitches are characterized by low coking value - approximately 15% - and low equiviscous temperature - approximately 52° C. Considering the melting point level of these pitches, it can be reasonably assumed from this relationship that they were produced by diluting high softening point binders presumably with very light materials such as "oils"; this is a process by which binders of low quality can be expected to result. Straight-distilled pitch C-2 also contains an acetone-soluble fraction exhibiting low coking value and low equiviscous temperature, and yet is not a cut-back pitch; in this instance, it should be remembered that the softening point of C-2 is very low compared to those of cut-back pitches mentioned above and consequently, there is no discontinuity between the acetone-soluble characteristics and those of the whole pitch. Samples A-4 and C-7 are also cut-back pitches, but the material used for diluting was tar, which explains the higher figure for coking value and equiviscous temperature of their acetone-soluble.

### Quinoline-Soluble, Acetone-Insoluble Fraction

The quinoline-soluble, acetone-insoluble fraction consists of a black-brown brittle substance which can be pulverized easily. Upon heating, it does not melt although it shows some tendency to fuse. Its carbon-hydrogen ratio is somewhat higher than that of the whole binder, and does not show much variation; there is, however, a noticeable difference between the fractions from binders of coal-tar and petroleum origin, the latter having a lower carbon-hydrogen ratio. The same applies to the coking value; it is lower for petroleum pitches, with the exception of the experimental one, than for binders of coal-tar origin.

TABLE 2

DESCRIPTION OF PITCH SAMPLES

Sample Identification <sup>(a)</sup>	Compressive Strength of Test Electrodes kg/cm <sup>2</sup>	Melting Point °C	Coking Value %	C-I (Quinoline-Insoluble) %	Atomic Carbon-Hydrogen Ratio	Density g/cc	Viscosity Data <sup>(b)</sup>		
							EVT <sub>15</sub>	EVT <sub>1015</sub>	Temperature Coefficient poises/°C
<u>COAL-TAR STRAIGHT-DISTILLED PITCHES</u>									
A-1	430	111	61.6	14.0	1.97	1.35	162	123	25.6
B-1	382	109	59.8	15.7	1.91	1.36	165	124	24.4
C-1	365	95	57.7	16.7	1.93	1.35	149	108	24.4
D-1	361	108	59.4	23.1	1.84	1.36	170	126	22.7
E-1	360	107	59.4	13.7	1.85	1.34	158	118	25.0
F-1	354	108	58.2	9.9	1.72	1.33	166	127	25.6
C-2	354	50	44.5	13.4	1.76	1.28	86	54	31.2
C-3	351	112	56.2	6.5	1.80	1.32	172	131	24.4
A-2	347	95	55.5	3.4	1.74	1.32	149	114	28.6
G-1	320	100	53.1	7.4	1.68	1.30	150	110	25.0
G-2	320	88	53.5	10.0	1.82	1.32	141	102	25.6
H-1	296	69	44.1	6.8	1.66	1.24	111	78	30.3
C-4	274	93	51.4	5.8	1.73	1.33	147	110	27.0
I-1	257	93	49.7	4.9	1.62	1.31	147	111	27.8
<u>COAL-TAR HEAT-TREATED PITCHES</u>									
C-5	444	138	65.6	14.2	1.86	1.33	207	158	20.4
A-3	410	129	67.3	21.3	1.92	1.35	204	152	19.2
C-6	339	102	56.8	11.5	1.78	1.32	162	119	23.2
<u>COAL-TAR CUT-BACK PITCHES</u>									
A-4	376	102	56.0	14.2	1.67	1.32	162	121	24.4
C-7	354	105	57.2	9.8	1.79	1.32	166	125	24.4
I-2	313	104	55.7	14.2	1.68	1.32	170	123	21.3
I-3	309	104	53.9	18.9	1.69	1.33	158	115	23.2
I-4	275	102	56.5	17.9	1.70	1.32	166	115	19.6
A-5	165	107	60.9	28.9	1.80	1.34	175	117	17.2
<u>COAL-TAR CHEMICALLY-TREATED PITCH</u>									
A-6	246	100	49.6	4.7	1.59	1.30	153	115	26.3
<u>PETROLEUM PITCHES</u>									
J-1 regular production	300	109	55.6	19.0	1.46	1.28	166	127	25.6
J-2 experimental	-	132	56.7	14.6	1.49	1.30	209	155	18.5

(a) Letters indicate different suppliers.

(b) EVT refers to equiviscous temperature i. e. the temperature at which a pitch has a specified viscosity. EVT<sub>15</sub> and EVT<sub>1015</sub> correspond to viscosities of 15 and 1015 poises respectively.

Temperature coefficient of viscosity is obtained from the following expression:  $1000/(EVT_{15} - EVT_{1015})$ .

Note: Analytical data were obtained by Aluminium Laboratories Limited internal methods.

TABLE 3

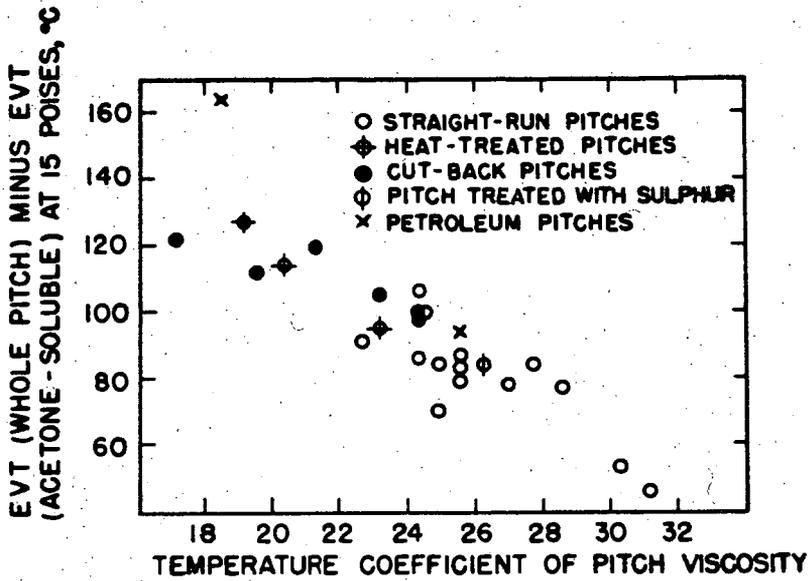
FRACTIONATION RESULTS AND CHARACTERISTICS OF FRACTIONS.

Sample Identification	% Fraction			% Coking Value			Atomic C/H			Density, g/cc			EVT <sub>15</sub> , °C
	I	II	III	I	II	III	I	II	III	I	II	III	
<u>COAL-TAR STRAIGHT-DISTILLED PITCHES</u>													
A-1	44.1	42.8	13.1	26.8	88.4	98.8	1.60	2.03	4.26	1.24	1.37	1.62	72
B-1	46.0	39.1	14.9	20.5	90.4	98.9	1.54	2.04	4.55	1.20	1.43	1.63	66
C-1	47.1	37.3	15.6	20.4	88.8	97.9	1.58	2.01	4.03	1.23	1.37	1.60	63
D-1	48.4	29.5	22.1	22.8	89.2	97.9	1.41	1.91	4.26	-	1.34	1.62	79
E-1	47.4	39.2	13.4	22.2	89.4	99.1	1.56	1.96	4.48	1.23	1.39	1.63	74
F-1	51.9	38.4	9.7	24.8	87.5	97.0	1.49	1.94	4.52	1.23	1.39	1.65	79
C-2	61.0	25.7	13.3	16.4	87.3	97.6	1.50	2.01	4.27	1.21	1.38	1.63	40
C-3	49.9	44.1	6.0	22.2	91.2	96.6	1.50	2.06	4.18	1.22	1.39	1.63	66
A-2	56.2	40.5	3.3	21.7	91.0	97.7	1.54	2.04	4.20	1.22	-	-	72
G-1	57.4	35.6	7.0	23.5	91.1	97.0	1.45	1.95	3.77	1.23	1.37	1.59	80
G-2	54.2	36.8	9.0	19.7	90.7	98.6	1.50	2.00	4.05	1.23	-	-	62
H-1	67.2	26.8	6.0	19.0	88.8	99.1	1.44	1.90	3.73	1.21	-	-	58
C-4	57.7	37.1	5.2	20.3	90.5	97.3	1.51	2.03	3.77	1.23	1.40	1.61	69
I-1	60.9	34.0	5.1	20.0	90.9	97.1	1.42	1.98	3.40	1.21	1.38	1.55	63
<u>COAL-TAR HEAT-TREATED PITCHES</u>													
C-5	42.9	44.8	12.3	26.6	91.7	96.0	1.56	2.05	2.96	1.26	1.33	1.51	93
A-3	37.1	43.5	19.4	19.1	92.8	96.4	1.58	2.15	3.19	1.23	1.39	1.52	77
C-6	51.5	38.2	10.3	20.3	93.2	98.7	1.50	2.07	2.95	1.21	1.39	1.50	67
<u>COAL-TAR CUT-BACK PITCHES</u>													
A-4	52.8	34.6	12.6	21.9	91.3	96.9	1.43	1.97	2.52	1.21	1.37	1.44	63
C-7	51.6	40.0	8.4	19.3	92.0	96.4	1.54	2.13	3.30	1.22	1.29	1.55	68
I-2	49.9	36.5	13.6	14.9	93.1	97.4	1.40	1.95	2.62	1.20	1.26	1.46	51
I-3	52.6	29.9	17.5	16.1	93.4	98.0	1.45	1.93	2.48	1.19	1.26	1.44	53
I-4	50.3	33.5	16.2	16.3	92.0	98.3	1.42	2.00	2.55	1.20	1.22	1.28	54
A-5	44.5	27.7	27.8	14.4	94.3	97.9	1.49	2.12	2.54	1.22	1.37	1.45	53
<u>COAL-TAR CHEMICALLY-TREATED PITCH</u>													
A-6	59.4	36.8	3.8	19.9	88.0	94.5	1.47	1.88	3.25	1.20	-	-	69
<u>PETROLEUM PITCHES</u>													
J-1	53.9	25.7	18.4	27.4	83.4	96.1	1.20	1.58	3.01	-	1.35	1.51	72
J-2	47.3	39.0	13.7	18.1	92.0	97.0	1.16	1.78	2.46	1.14	1.31	1.51	45

I = Acetone-Soluble.

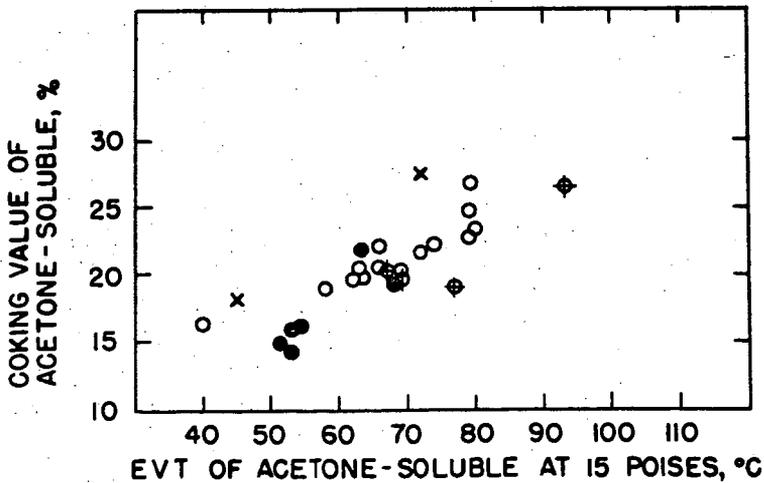
II = Quinoline-Soluble, Acetone-Insoluble.

III = Quinoline-Insoluble.



**FIGURE 2**

RELATIONSHIP OF VISCOSITY DATA OF WHOLE PITCH AND ACETONE-SOLUBLE FRACTION



**FIGURE 3**

RELATIONSHIP OF VISCOSITY DATA TO COKING VALUE OF ACETONE-SOLUBLE

### Quinoline-Insoluble Fraction

The quinoline-insoluble fraction is a black, very fine powder. Upon heating it does not show any sign of melting or fusing; it remains practically unchanged in appearance even when heated to 500°C. Its coking value is very high (over 95%), and shows no significant variation for the different pitches. These characteristics would suggest an almost inert material if it were not for its carbon-hydrogen ratio which varies considerably; this constitutes an interesting property which permits significant comparisons between the various pitches. For instance, the carbon-hydrogen ratio of the quinoline-insoluble of all straight-distilled pitches except one are above, or close to, 4.0; the low carbon-hydrogen of the exception (I-1) might well reflect a significant variation in the production and possibly processing of the tar; at the time this sample was produced, pitches from the same source were not considered satisfactory for carbon electrode manufacture in actual plant operation. On the other hand, for straight-distilled pitches which have been subjected to some thermal treatment such as samples C-5, A-3, and C-6, the carbon-hydrogen of the quinoline-insoluble shows a large decrease. This is probably the result of transformation of part of the quinoline-soluble, acetone-insoluble fraction into a type of quinoline-insoluble having a lower carbon-hydrogen ratio than the normal quinoline-insoluble of straight-distilled pitches. The same applies to cut-back binders prepared from heat-treated, high-melting pitches; thus the variation in carbon-hydrogen of the quinoline-insoluble can be very useful in differentiating types of pitches. It can also be observed from Table 3 that density of quinoline-insoluble fraction, is higher for straight-distilled pitches than for treated or cut-back pitches, and follows well carbon-hydrogen ratio with one exception, No. I-4; no explanation can be offered for this apparently abnormal result. This relationship between density and carbon-hydrogen ratio is much better defined for the quinoline-insoluble fraction than for the other two fractions or the whole binder.

Evidence of the presence of different types of quinoline-insoluble particles was found from microscopic examination of quinoline-insoluble fractions from different types of pitches. It was observed that the quinoline-insoluble of straight-distilled pitches consists of very fine particles, of the order of one micron, while in heat-treated and cut-back pitches the insoluble is a mixture of very fine particles and of particles of ten microns and larger; the shape of the particles is also different.

### Relationship to Pitch Quality

Although it is logical to assume that fraction characteristics must have some bearing on pitch quality, no significant relationship could be established between any single characteristic and compressive strength of test electrodes which was taken as quality criterion in the investigation described herein. The only fraction which showed some promise was the quinoline-insoluble.

Examination of compressive strength and per cent quinoline-insoluble for straight-distilled pitches (see Tables 2 and 3) indicates a definite trend for higher compressive strengths to be associated with higher quinoline-insoluble contents. However, this does not hold if we examine the different types of pitch together. For instance, cut-back pitch A-5 has the highest quinoline-insoluble of all pitches and yet its corresponding compressive strength is by far the lowest. This is not altogether unexpected, since it can be easily visualized that there must be a limit to the amount of quinoline-insoluble which can be tolerated in a binder. However, this limit seems to vary for different types of pitches; for instance, straight-distilled pitch D-1 contains only a few per cent less quinoline-insoluble than cut-back pitch A-5 and yet its compressive strength is much higher. This might be explained by the large difference in carbon-hydrogen ratio of their respective quinoline-insoluble fraction, 4.3 as compared to 2.5.

It can also be visualized that there exists an optimum percentage for the quinoline-insoluble fraction. Out of mere curiosity compressive strength versus per cent quinoline-insoluble was plotted for approximately 175 pitch samples of different types and from different sources. The curve showed a maximum for compressive strength at approximately 14% quinoline-insoluble; this is roughly the quinoline-insoluble content of most of the best straight-distilled pitches shown in Table 3.

From all these observations made on the quinoline-insoluble fraction, it can be said with a reasonable degree of confidence that this fraction is of some importance in the performance of a pitch as binder. As mentioned earlier, its concentration alone is of little use if pitches of different types are considered. However, by a suitable combination of the amount of the quinoline-insoluble fraction and its carbon-hydrogen ratio and by assuming an optimum percentage - let us say 14% - it might be possible to arrive at a factor which, along with other characteristics of pitch or pitch fractions such as viscosity and coking value, might prove valuable for pitch characterization.

#### ACKNOWLEDGEMENTS

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#### LITERATURE REFERENCES

- (1) Wood, L. J., and Phillips, G., J. Appl. Chem. 5, 326 (1955).
- (2) Mallison, H., Bitumen, Asphalte, Teere, Peche, 7, 265 (1956).
- (3) Franck, M. G., Brennstoffchemie, 36, 12 (1955).
- (4) Lissner, A., and Schäfer, H. G., J. Prakt. Chemie, 1, 230 (1955).

THE RELATIONSHIP BETWEEN THE CONSISTENCY OF THE GREEN ELECTRODE MIX  
AND THE PROPERTIES OF TEST ELECTRODES

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Introduction

In the panel discussion that followed the symposium on "Tars, Pitches and Asphalts" at the 1959 spring meeting of the American Chemical Society in Boston, members of the panel emphasized that more attention should be given to the measurement and study of the rheological properties of green electrode mixes.

Because of widespread interest in this subject, a preliminary research program was initiated at the Applied Research Laboratory of the United States Steel Corporation to investigate the relationship between the consistency of the green mix and the crushing strength and volume electrical resistivity of specimen electrodes. Consistency has been defined as that property of a body that tends to resist deformation.<sup>1)\*</sup> In this paper, consistency is defined more specifically as the torque required to shear the green mix at a constant rate and temperature.

A careful search of the Chemical Abstract indexes covering a 53-year period from 1907 to 1960 revealed that no information has been published on the relationship between the consistency of the green mix and the properties of test electrodes. Only one reference<sup>2)</sup> was found that described an instrument for quantitatively measuring the consistency of green electrode mixes. This instrument, Russian-built, is simply a cone penetrometer that has been modified to measure the pressure (limiting shear stress) required to drive a standard cone, under constant force, into the test mixture to a full stop. Although this instrument has many desirable features, such as simplicity of design and operation, it was not precise or sensitive enough for use in the present investigation. Subsequently, a technical brochure<sup>3)</sup> indicated that another instrument, the Brabender Plastograph, had the desirable characteristics, and was used in the ensuing investigation.

This paper describes the evaluation of rheological properties of green mixes prepared from two coal-tar pitch binders and the properties of the test electrodes made from them. It is hoped that this information will provide a better understanding of the relationship between the rheology of the green mix and electrode performance.

Experimental

For this preliminary study two electrode binders and a calcined petroleum coke were used. The more common properties of the binders are shown in Table I. Both binders were produced in full-scale equipment from the same feed stock. Binder A, a pitch of demonstrated utility, was produced by continuous vacuum-flash distillation. Binder B was specially processed to have essentially the same softening point as Binder A, but a viscosity and a  $\beta$ -resin content significantly higher.

With the exception of the viscosity, standard test methods common to the aluminum and carbon industries were used to measure the properties of the binders. The absolute viscosity of the binders was determined by a Brookfield Synchro-Lectric Viscometer equipped with a 12-inch spindle extension. A special device for heating

\* See References.

the air in contact with the pitch and the spindle was used with this instrument. A schematic drawing of the assembled apparatus is shown in Figure 1. The air heater was used to reduce the unwanted drag or torque exerted on the rotating spindle by the "skin" of pitch that has a tendency to form on the surface of the test sample when it is exposed to air at room temperature.

Selected properties of the petroleum coke, used by the Laboratory as a standard, are shown in Table II. The coke was calcined at 1300 C by the supplier and then graded at the Laboratory into the six fractions shown in the table. Because the fractions were sized relative to the dimensions of our laboratory-scale electrode-baking apparatus, they are smaller than the fractions used commercially.

Since the experimental procedures are somewhat involved, the major steps are briefly outlined below. A more detailed discussion of the various procedures will follow.

1. A series of green mixes containing from 31 per cent to 38 per cent binder was prepared in a Brabender Plastograph.
2. The consistency of each mix was measured in the Plastograph as the mix was being prepared.
3. Each batch of green mix was then baked in accordance with a standard Laboratory procedure to yield small test electrodes.
4. The electrodes were tested for crushing strength and volume electrical resistivity.

The Brabender Plastograph, used to prepare the green mixes and measure their consistencies, is shown in Figure 2. The instrument was purchased from C. W. Brabender Instruments Inc., South Hackensack, New Jersey. The sigma blades in the mixing head (1) are driven by a dynamometer (2), which is suspended between floating bearings (3). The torque produced by the blades as they turn in the material at a constant rate of shear is transmitted to the dynamometer. The dynamometer translates the torque through a series of balance levers (4) to a direct-reading balance (5), which is calibrated to indicate the torque in meter-gram units. A strip chart (6) provides a continuous record of the consistency in terms of meter-gram units. Excessive movement of the lever system is dampened by an oil dash pot (7).

The mixing head has a working capacity of 650 milliliters. It is heated by recirculating hot oil from a constant-temperature bath (8) through a jacket that surrounds the mixing head. A special insulated lid (9), not supplied by the manufacturer of the instrument, minimizes the loss of heat from the head and was indispensable as an aid in maintaining the mix at a uniform temperature. Through a small opening in the lid, 5/8 inch in diameter, coke additions can be made without removing the lid.

As mentioned above, green mixes containing from 31 per cent to 38 per cent binder were prepared and their consistencies measured. The composition of a typical batch of green mix is shown in Table III. In this batch, 462 grams of the various coke fractions were blended, as described below, with 238.0 grams (34 weight per cent) of Binder A to yield 700 grams of mix. In all the mixes, the total amount of the two components was held constant at 700 grams.

In the preparation of a typical mix, the calculated amount of molten binder, at a temperature of about 155 C, is added to the preheated mixing head. After the binder has mixed for exactly 7 minutes, the preheated (to 155 C) 10- to 30-mesh coke

fraction is added through the opening in the insulated lid. The remaining fractions are then added in the order of decreasing size at 5-minute intervals. The addition of these fractions is illustrated in Figure 3. Mixing is continued at 155 C for 30 minutes after the addition of the last (minus 325-mesh) coke fraction. The torque reading, in meter-grams, at the end of this mixing period is recorded as the consistency of the mix.

The change in consistency that occurs as the various coke fractions are added to the binder is illustrated by the typical consistency curves that are reproduced in Figure 4. Reading from right to left, the steps in the curve represent the increase in consistency that occurs as the six coke fractions are added to the binder at 5-minute intervals. The position of the left extremity of the curve defines the consistency of the mix. The sensitivity of the instrument to the change in consistency brought about by the addition of the various coke fractions is clearly indicated. The second curve in this figure was included to demonstrate the excellent repeatability of the instrument over the entire consistency range.

After measuring the consistency, the green mixes were packed into perforated graphite molds, Figure 5, and baked to a temperature of 1000 C in 24 hours. The baked electrodes were then tested for crushing strength and electrical resistivity. The procedure for preparing, baking, and testing specimen electrodes was described in a paper<sup>4</sup>) presented at the Spring 1959 meeting of this Division.

#### Results and Discussion

To make clear the relationship between the consistency of the various green mixes and the properties of the test electrodes, the experimental data were plotted in bar-chart form. The relationship between the consistency and crushing strength for both binders is illustrated in Figure 6. The black bars represent the consistency of the mix at various levels of binder concentration, and the white bars show the crushing strength of specimen electrodes prepared from green mixes containing various percentages of binder. The number at the top of each bar represents the percentage of binder in the mix. From this chart, it is evident that an excellent correlation exists between the consistency of the green mix and the crushing strength of the test electrodes. It is extremely interesting to observe that, as the percentage of binder increases within the limits shown, the consistency and crushing-strength values for each binder pass through a maximum simultaneously. This relationship suggests that the consistency of a green mix can be measured to determine the optimum percentage of binder to use in the preparation of an electrode with maximum crushing strength. For Binder A, for example, a maximum consistency value was obtained at a binder concentration of 34 per cent. This mix in turn produced an electrode with the highest strength. Therefore, the optimum percentage of binder is 34 per cent.

This chart also shows that Binder B, which had been processed to have a higher viscosity than A, yielded mixes with consistencies significantly higher than those of Binder A. In a like manner, Binder B produced electrodes with crushing strengths somewhat higher than those of Binder A. It is also interesting to note that the percentage of binder required to obtain electrodes with maximum strength was about the same for each binder. The fact that a stronger electrode can be obtained with the specially treated binder (Binder B) seems to indicate that the special treatment was indeed very beneficial.

Figure 7 shows the relationship between the consistency of the mix and the electrical resistivity of the electrodes. It is evident that a good correlation also exists between these parameters. For each binder, as the consistency values pass through a maximum the resistivity values pass through a minimum. This relationship

suggests that the consistency of the mix can also be employed to determine the optimum percentage of binder to use in preparing an electrode with minimum electrical resistivity. Binder B produced electrodes with resistivities somewhat lower than those of Binder A. Once again, the beneficial effect of the special treatment was demonstrated.

#### Summary

The Applied Research Laboratory has studied the relationship between the consistency of the green electrode mix and selected properties of test electrodes. The results of this preliminary investigation suggest that (1) the consistency of the green mix can be used to determine the optimum concentration of binder required to produce electrodes of the highest quality, (2) the Brabender Plastograph, with slight but important modifications, is a suitable instrument for measuring the consistency of green mixes, and (3) for the same concentration of binder in the green mix, an appropriately treated binder will yield better electrodes than an untreated binder. This investigation is being continued to further verify and extend these findings. It is anticipated that the results of this more extensive study will be presented at a future meeting of this Division.

#### Literature References

1. "Standard Definitions of Terms Relating to Rheological Properties of Matter," ASTM Standards 1942, I, 941.
2. A. S. Fialkov and I. G. Davidovitch, "The Use of a Conical Plastometer for Controlling the Quality of Mixtures of Carbon Compositions," Zavodskaya Laboratoriya (USSR), 9, 261 to 263 (1957).
3. Technical Brochure, Brabender Plastograph, C. W. Brabender Instruments Incorporated, South Hackensack, New Jersey.
4. H. L. Jones, Jr., A. W. Simon, and M. H. Wilt, "A Laboratory Evaluation of Pitch Binders Using Compressive Strength of Test Electrodes," Journal of Chemical and Engineering Data, 5, No. 1, 84 to 87 (1960).

Table I  
PROPERTIES OF BINDERS

	<u>BINDER A</u>	<u>BINDER B</u>
SOFTENING POINT, CUBE-IN-AIR, C	102.3	105.5
BETA RESINS (BI-QI), wt %	11.9	19.2
SPECIFIC GRAVITY (60 F/60 F)	1.32	1.32
VISCOSITY, CENTIPOISES		
at 140 C	4600	7610
at 150 C	1630	3200
at 160 C	810	1340
IRON, wt %	0.020	0.018
ATOMIC CARBON/HYDROGEN RATIO	1.78	1.77
BENZENE INSOLUBLES, wt %	21.9	28.6
QUINOLINE INSOLUBLES, wt %	10.0	9.4
COKE VALUE, CONRADSON, wt %	55.2	55.4
DISTILLATION, wt %		
to 270 C	0.0	0.0
270 to 300 C	0.2	0.2
300 to 360 C	1.7	2.6
360 to 400 C	10.1	10.1
SULFUR, wt %	0.62	0.59

Table II  
PROPERTIES OF CALCINED PETROLEUM COKE

APPARENT DENSITY, GM/CM <sup>3</sup>	0.898
CARBON, wt%	97.61
HYDROGEN, wt%	0.24
ASH, wt %	0.35
SULFUR, wt%	1.27
SIEVE ANALYSIS, wt %	
-10 +30 MESH	20
-30 +50 MESH	16
-50 +100 MESH	19
-100 +200 MESH	13
-200 +325 MESH	10
-325 ON PAN	22

Table III  
COMPOSITION OF A TYPICAL BATCH OF GREEN MIX

	WEIGHT IN GRAMS	WEIGHT PER CENT OF MIX
BINDER A	238.0	34.0
COKE FRACTIONS		
-10 +30 MESH	92.4	13.2
-30 +50 MESH	73.9	10.6
-50 +100 MESH	87.8	12.5
-100 +200 MESH	60.1	8.6
-200 +325 MESH	46.2	6.6
-325 ON PAN	101.6	14.5
TOTAL	700.0	100.0

Note: Coke fractions are added to the binder  
in the order of decreasing particle size.

### APPARATUS FOR VISCOSITY DETERMINATIONS

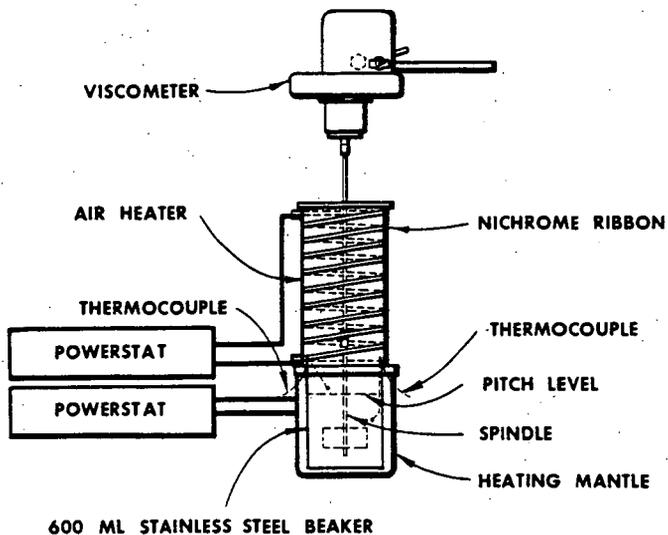


Figure 1. APPARATUS FOR VISCOSITY DETERMINATIONS

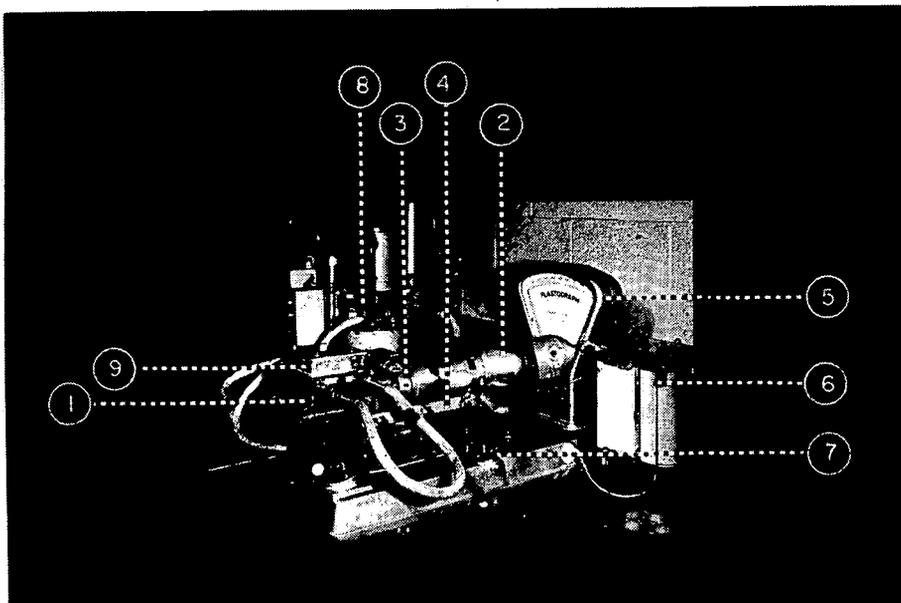


Figure 2. BRABENDER PLASTOGRAPH

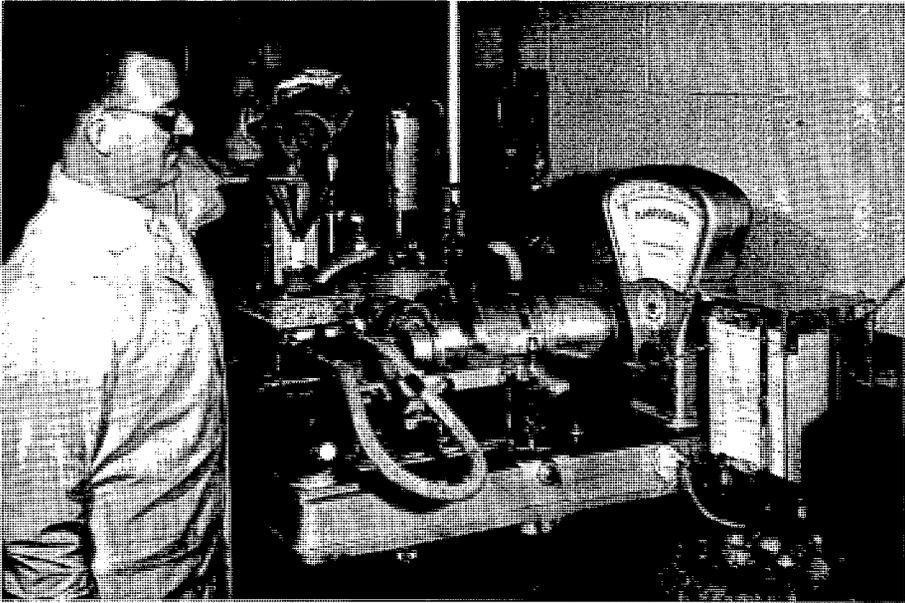


Figure 3. ADDING PETROLEUM COKE FRACTIONS

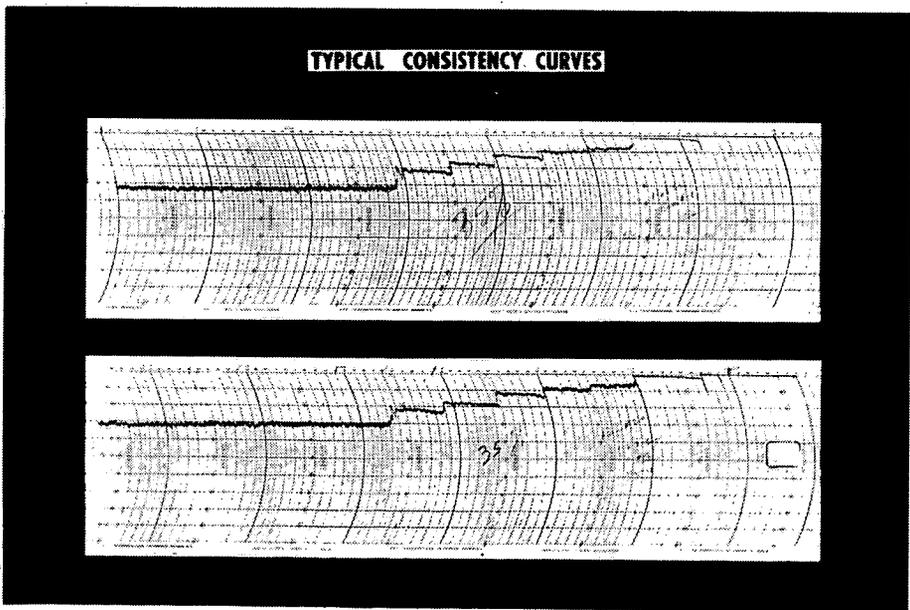


Figure 4. TYPICAL CONSISTENCY CURVES



Figure 5. PACKING THE GREEN MIX

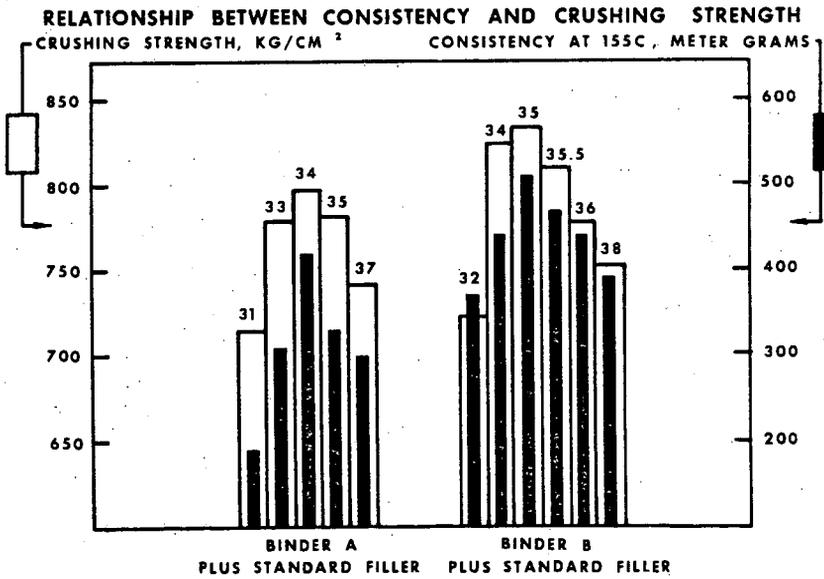


Figure 6. RELATIONSHIP BETWEEN CONSISTENCY AND CRUSHING STRENGTH

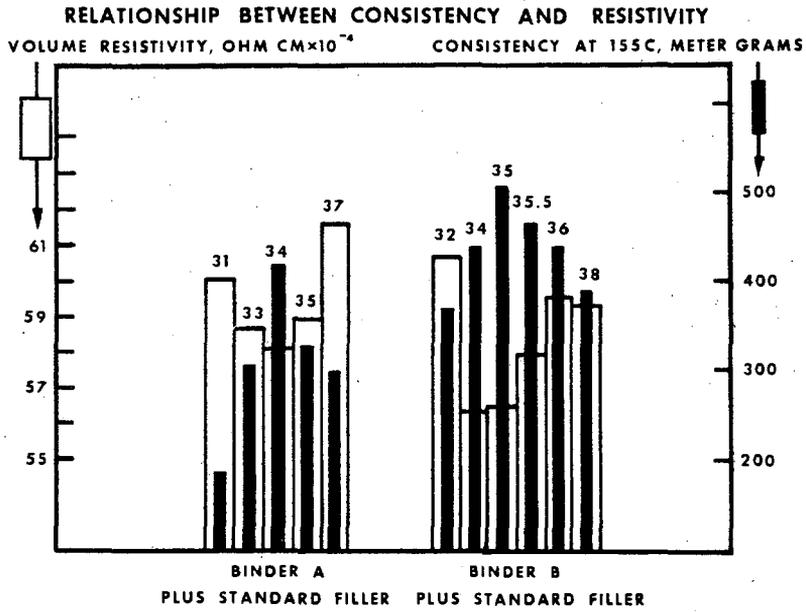


Figure 7. RELATIONSHIP BETWEEN CONSISTENCY AND RESISTIVITY

## THE RELATIONSHIP OF PITCH PROPERTIES TO ANODE PROPERTIES

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### Introduction

The aim of this report is to provide help in appraising a pitch for suitability as binder in the anodes of the alumina reduction plants. The information was gained from testing over 148 pitches from 21 producers. Commercially available and experimental petroleum oil, gas, asphalt, regular and low-temperature coal tar pitches were included.

An indication of the suitability of a pitch as binder is obtained by using as an index the properties of baked electrodes made in the laboratory with the test pitch. The electrodes are prepared using controlled conditions designed to maintain all variables as constant as possible other than the pitch being appraised. The laboratory techniques used produce electrode specimens that have the same level of values for the properties of apparent density, electrical resistivity, total porosity and crushing strength as those produced in the plant from the same materials.

This report (1) is based on the application of this technique to laboratory specimens of Soderberg composition. It furnishes some comparisons of the resulting properties to those of the anodes in the plants. (2) It gives the correlation found between the properties of the laboratory specimens and the analysis of the binder pitch. (3) It furnishes the percentage influence found for the measured pitch properties on variations in the properties of the laboratory-prepared carbon. (4) It provides equations which can be used to predict these properties of the laboratory specimens from the analysis of the binder pitch. Only the common determinations of softening point, coking value, components insoluble in benzene and quinoline, specific gravity and distillate fractions are required. The difference between the predicted and the measured physical properties are generally within the precision of the methods for measuring the properties. These equations can be used as guides by laboratories without facilities for preparing carbon anode specimens, by people with limited experience in evaluating pitches, and by pitch manufacturers in developing binder pitches.

### Experimental Results

#### Comparison of Properties of Laboratory Specimens with Those of Plant Anodes

Table I provides a comparison of the properties of baked carbon of Soderberg composition made of the same materials in the laboratory and in the reduction plant. This one comparison given as an example has been confirmed many times. This agreement between these properties of laboratory specimens and baked plant anodes greatly shortens the time required for a pitch appraisal in terms of these properties-- from soon after the arrival of the pitch sample in the laboratory, contrasted with six weeks or more after using the trial pitch in the Soderberg plant.

#### Correlation Between Pitch Properties and Properties of Laboratory Specimens.

Having established a technique for duplicating plant anode properties in the laboratory, it was used to determine the correlation between these properties and the properties of the pitch. During the period of 1941-1954, a plant laboratory found the following relationships. With few exceptions, as the softening point, coking value, benzene insoluble, quinoline insoluble, and specific gravity of the pitch increased, the values for anode properties of apparent density and crushing strength

also increased. This was accompanied by a decrease in electrical resistivity and total porosity. These findings differed in two respects from the experience reported by some laboratories during this period. The difference between the amount of benzene and quinoline insoluble components, commonly designated as "beta resins", was not found to have a pronounced correlation with these anode properties. Of special interest was the finding that the half of the specimens which had the highest apparent density and crushing strength and the lowest electrical resistivity and total porosity were made with pitches which had more than 10% of components insoluble in quinoline. At that time some had recommended that purchase specifications should restrict the quinoline insoluble content to a maximum of 10%.

Findings of the plant laboratory for a series of 28 coal tar, petroleum, and experimental pitches, submitted by nine pitch producers, are given in Figure 1. The properties of the anode specimens are arranged in order of increasing apparent density. The properties of the pitch from which each anode was made are listed directly underneath. Instead of drawing the best straight line through the plotted data points, they were connected to adjacent points to show that most of the properties of pitches which were measured are inherently interrelated and strongly affect the properties of the anodes.

This approach to the evaluation of pitches was continued by the Research Laboratory when it began operating in 1955. During a period of four years, 114 additional pitches were tested. This series also included commercial and experimental petroleum oil, gas, asphalt, regular and low-temperature coal tar pitches from domestic and foreign producers. The relationships between properties of pitches and anode specimens made with them found by the plant laboratory were confirmed. There was no indication that changes in pitch manufacturing operations nor in sources of supply changed the general relationship of the properties of pitches to laboratory specimens during the 19-year period. To determine to what extent the peaks and depressions in the plotted relationship of pitches and anodes were due to plotting different pitch types, sources of tars, and processes, separate graphs were made for pitches of one type. Figure 2 makes the comparison for nine coal tar pitches from a single vendor during a two-year period. Figure 3 shows the relationship for 12 pitches of petroleum origin. In general, the interrelation of pitch properties and their effect on the laboratory specimens was found to apply to all types of these pitches.

#### Another Comparison of Laboratory and Plant Experience.

Figure 2 shows a pronounced relationship of the softening point of high-temperature coal tar pitches to anode properties. Additional confirmation that laboratory experiences are translatable into plant experience is furnished in Figure 4. It contains data for plant paste made with three pitches having different softening points. Figure 4 indicates the reproducibility of sample testing and constant quality of plant paste over a three-month period, and the sensitivity of the test method to detect changes in paste induced by changes in the binder. Material used in this series was obtained from routine sampling of plant paste for quality control. It shows how changing from a binder with a softening point of 90°C to one with 110°C resulted in improvement in these properties, to the extent of shifting the range for apparent density from 1.51-1.59 to 1.55-1.65 gms./cu.cm., electrical resistivity from 58-65 to 52-61 ohms/m./sq.mm. and crushing strength from 6,200-7,500 to 6,800-9,000 lbs./sq.in.

#### Percentage Influence of Measured Pitch Properties on Variations in Properties of Baked Laboratory Specimens.

A multiple correlation was made to determine quantitatively the effect of each of these properties of the binder on those of the baked carbon. Data was processed from 455 specimens representing 51 pitches of all types tested over a two-year period. This series of pitches produced laboratory specimens with a range in properties of

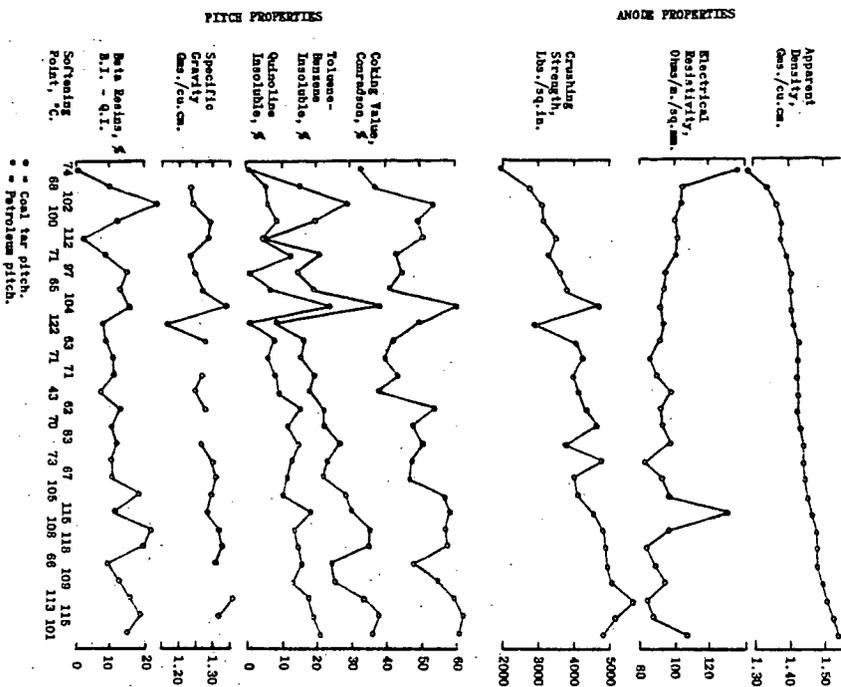


FIGURE 1. CORRELATION OF THE PROPERTIES OF LABORATORY SOFTENING SPECIMENS WITH BINDER PROPERTIES. BACKGROUND EXPERIMENT 1941-1954.

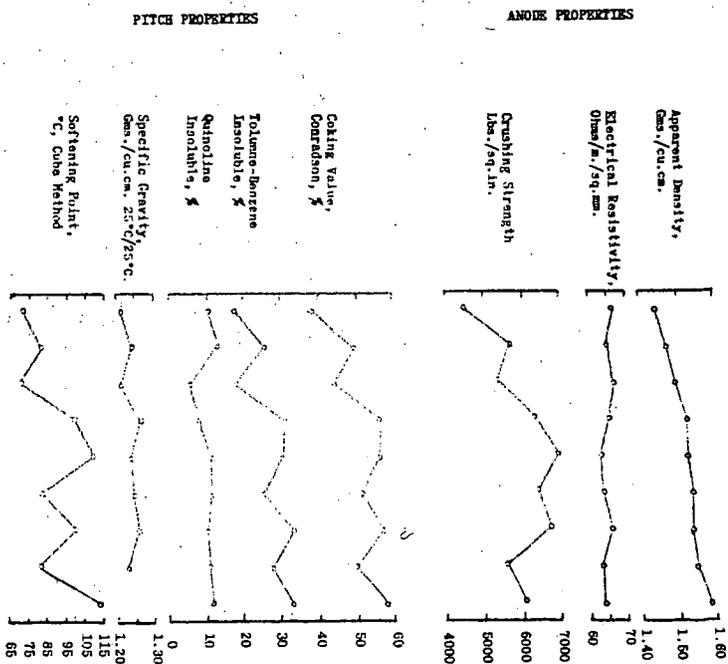


FIGURE 2. CORRELATION OF THE PROPERTIES OF LABORATORY SPECIMENS WITH BINDER PROPERTIES. HIGH TEMPERATURE COAL TAR PITCHES FROM ONE PRODUCTION OVER TEN-YEAR PERIOD.

ANODE PROPERTIES

PITCH PROPERTIES

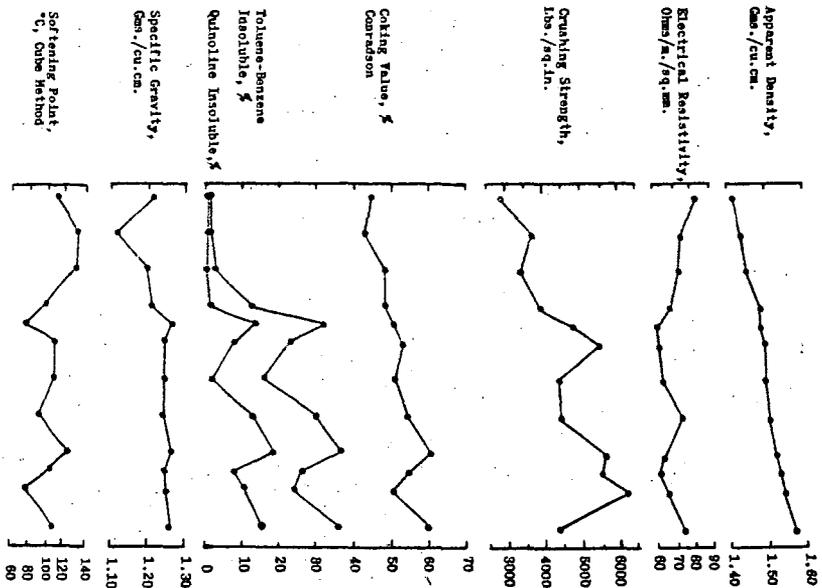


FIGURE 3. CORRELATION OF THE PROPERTIES OF LABORATORY SOFTENING SPECIMENS WITH BINDER PROPERTIES, ASPHALT, OIL, AND GAS PITCHES FROM SIX PRODUCERS.

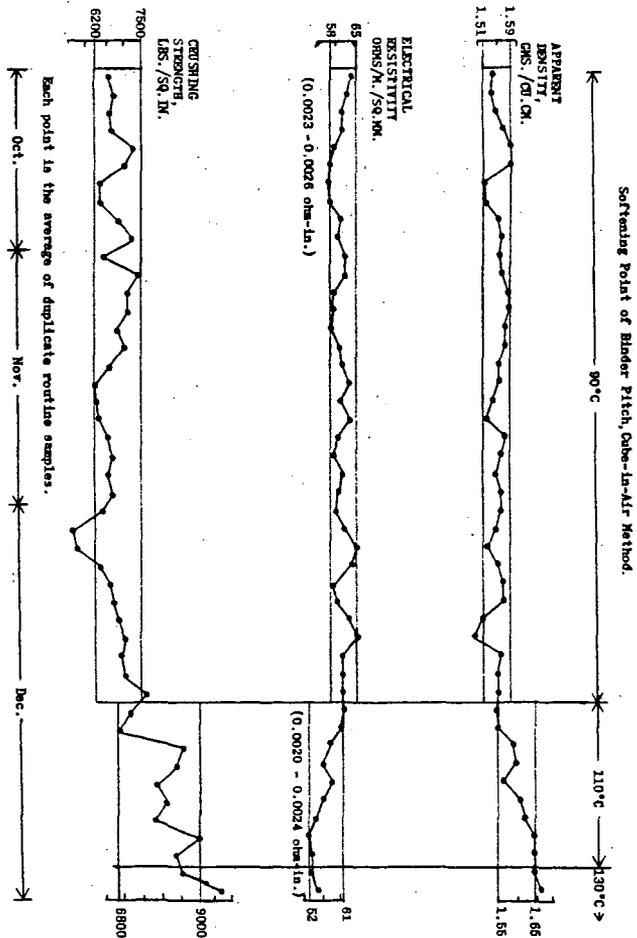


FIGURE 4. APPLICATION OF TESTS TO PLANT PASTE BASED IN LABORATORY SHOWS REPRODUCIBILITY, SENSITIVITY, AND RELATIONSHIP TO SOFTENING POINT.

1.34 to 1.60 gms./cu.cm. apparent density, 53.3 to 80.9 ohms/m./sq.mm. electrical resistivity, and 2,450 to 7,100 lbs./sq.in. crushing strength. The percentage influence of the measured pitch properties on variations in properties of baked carbon with the constant aggregate, mixing and baking conditions is given in Table II. The multiple correlation coefficients revealed that 83.7% of the variation in apparent density, 64.8% of the variation in electrical resistivity, and 79.6% of the variation in compression strength of baked carbon under these testing conditions are accounted for by variations in the six properties measured.

The correlation of the atomic carbon to hydrogen ratio of the whole pitch to these properties of the laboratory specimens was also made. It was found that its correlation did not significantly improve the predictability of the properties over that obtained with the multiple correlation equations for the six more common determinations.

TABLE I.  
COMPARISON OF PROPERTIES OF BAKED ANODES OF SODERBERG COMPOSITION MADE OF THE SAME MATERIALS BY THE LABORATORY AND BY A REDUCTION PLANT

Anode Preparation	Apparent Density Gms./cu.cm.	Electrical Resistivity, Ohms/m./sq.mm.	Compression Strength, Lbs./sq.in.
Samples Cored from	1.56	58.8	6,400
Anodes in a Reduction Plant	1.52	54.7	5,900
	1.55	107.0*	**
	1.55	54.2	**
	1.52	54.5	6,800
	<u>1.54</u>	<u>53.0</u>	<u>7,100</u>
Average	1.54	55.0	6,550
Paste Made in Plant, Baked in Laboratory	1.55	54.4	6,400
	1.52	53.0	7,100
	<u>1.55</u>	<u>54.8</u>	<u>6,200</u>
Average	1.54	54.1	6,600
Paste Made and Baked in Laboratory	1.54	54.6	6,900
	<u>1.54</u>	<u>54.6</u>	<u>6,900</u>
Average	1.54	54.6	6,900

\* This high resistivity value indicates that the area sampled in the continuous anode had not completed baking. It was not included in the average.

\*\* These samples were used for other tests and could not be crushed.

Equations for Predicting Properties of Resulting Anode Specimens from the Analysis of the Pitch.

Equations were established by Research personnel which permit the prediction of carbon properties made with the standard mixing and baking conditions. These equations and the methods used for the determination of the six properties of pitch are given in Table III.

The experimentally determined values for apparent density, electrical resistivity and crushing strength for the specimens used to obtain the equations are compared with the values predicted with the equations in Figures 5, 6 and 7, respectively.

Experimental Apparent Density, Gms./cu.cm.

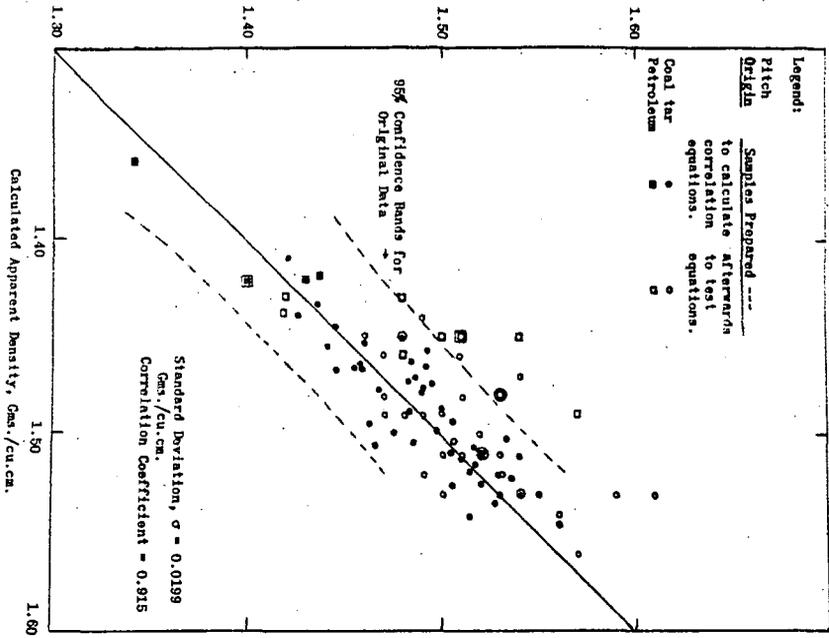


FIGURE 5. THE CORRELATION OF APPARENT DENSITY WITH VALUES CALCULATED USING THE MULTIPLE CORRELATION EQUATION.

Experimental Electrical Resistivity, Ohms/m./sq.mm.

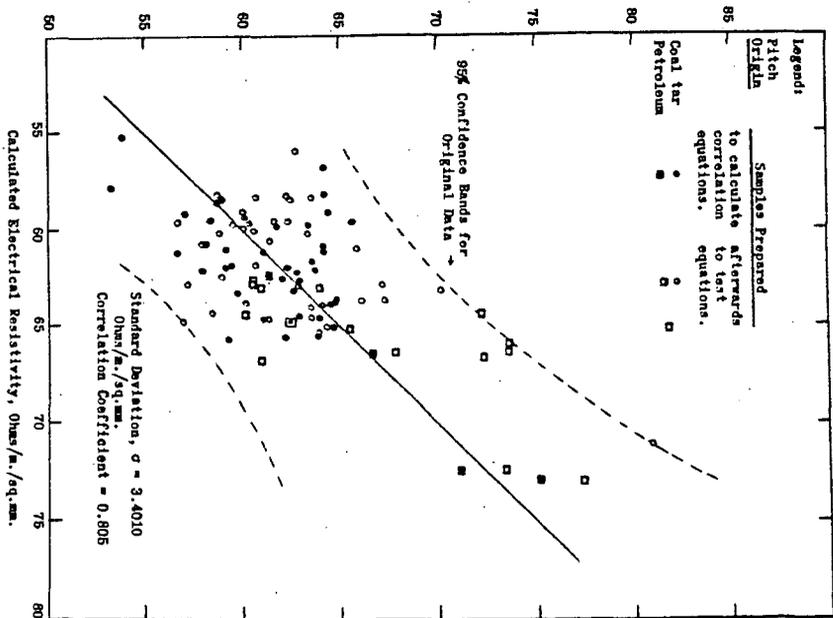


FIGURE 6. THE CORRELATION OF ELECTRICAL RESISTIVITY WITH VALUES CALCULATED USING THE MULTIPLE CORRELATION EQUATION.

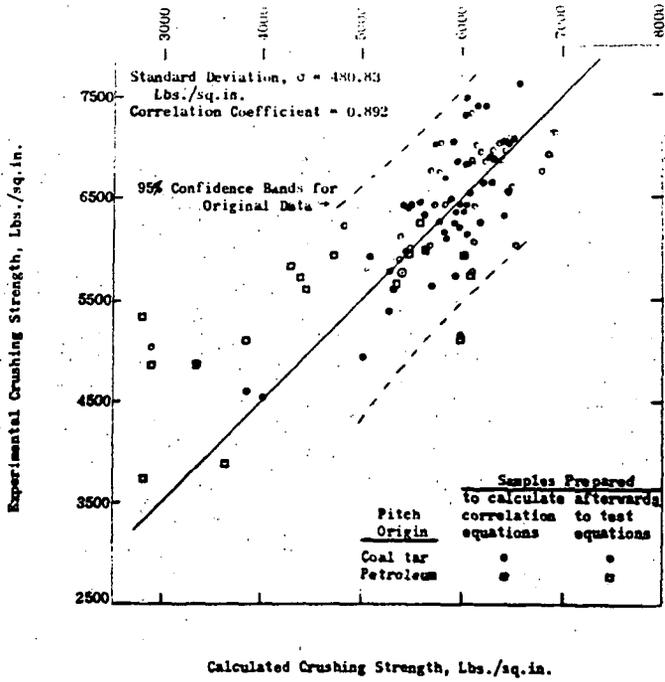


FIGURE 7. THE CORRELATION OF CRUSHING STRENGTH WITH VALUES CALCULATED USING THE MULTIPLE CORRELATION EQUATION.

The standard deviations for these measurements of apparent density, electrical resistivity and crushing strength of the specimens made with the standard conditions and commercial and experimental petroleum, oil, gas, asphalt, and regular and low-temperature coal tar pitches were 0.0199 gms./cu.cm., 3.4 ohms./m./sq.mm. and 480.8 lbs./sq.in., respectively. Correlation coefficients of 0.915, 0.805, and 0.892 were found between the predicted and experimental values for apparent density, electrical resistivity, and crushing strength, respectively. These correlation coefficients would have been 1.0 if these equations had been able to account for all the variations in the quality of the carbon.

These equations were applied to 51 additional pitches of all types. These predicted values are plotted against the experimentally determined properties on the same Figures 5, 6 and 7 to test the validity of the equations. In general, the predictions for all types of pitches were within the precision of the test methods for measuring the carbon at the 95% confidence level. The 95% confidence bands drawn on these figures were calculated only for the original 51 pitches used to develop the equations.

These equations are claimed to apply only to the type of coke, aggregate formulation, mixing and baking conditions used in this study. However, there are reasons to believe that they may be adjusted for other cokes and conditions by changing the last constant term of the equations to balance the influence of these factors on carbon properties.

TABLE II.

THE PERCENTAGE INFLUENCE OF MEASURED PITCH PROPERTIES ON VARIATIONS IN PROPERTIES OF BAKED CARBON WITH A CONSTANT AGGREGATE, MIXING AND BAKING CONDITIONS

Pitch Property	Apparent Density	Electrical Resistivity	Compression Strength
Softening Point, °C	21.43	2.98	8.28
Benzene Insoluble, %	0.59	0.39	0.16
Quinoline Insoluble, %	1.17	4.73	0.72
Coking Value, %	5.44	1.56	1.11
Conradson			
Specific Gravity, gms./cu. cm.	22.93	19.89	68.62
Distillation, % by wgt.			
270°C	7.45	9.78	0.56
271-300°C	5.44	4.41	0.08
301-360°C	6.44	7.06	0.0
361-400°C	6.36	6.80	0.0
Total	6.36	7.19	0.0
Total Percent of Variation Accounted For	83.7	64.8	79.6

Conclusions

Techniques for testing binder pitches provide very good comparisons between the properties of laboratory anode specimens and plant anodes.

Generally the apparent density and crushing strength of anodes increase, and the electrical resistivity decreases, as the softening point, coking

value, benzene and quinoline insoluble components, and specific gravity of the pitch binder increase.

Based on the multiple correlation coefficients, it was found that 83.7% of the variations in apparent density, 64.8% of the variations in electrical resistivity, and 79.6% of the variations in compressive strength of laboratory prepared and baked carbon are accounted for in the properties of softening point, coking value, benzene and quinoline insoluble components, specific gravity and distillation through 400°C.

In general, the equations presented permit predicting the apparent density, electrical resistivity, and crushing strength of laboratory anode specimens from analyses of all type pitches within the precision of the test methods for measuring the properties of the carbon.

These equations may serve as guides for laboratories without facilities for making and testing carbon anodes. They can be used by people with limited experience in appraising pitches.

TABLE III.

EQUATIONS FOR PREDICTING RESULTING PROPERTIES OF SPECIMENS OF  
SODERBERG COMPOSITION FROM THE CHEMICAL ANALYSIS OF THE  
PITCH

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APPARENT DENSITY (gms./cu.cm.)	= 0.00127a + 0.00048b + 0.00121c - 0.00167d + 0.60303e - 0.16131f - 0.15269g - 0.16023h - 0.16144i + 0.15997j + 0.6684
ELECTRICAL RESISTIVITY (ohms/m./sq.mm.)	= - 0.0538a - 0.0607b + 0.3906c - 0.1309d - 77.3591e + 11.1588f + 6.8737g + 9.2822h + 9.1307i - 9.2760j + 173.277
CRUSHING STRENGTH (lbs./sq.in.)	= 8.69a - 3.93b + 14.05c - 10.75d + 17,404e - 229.06f + 85.46g - 4.61h + 36.47i - 9.47j - 16,956.95

- a = softening point, °C, cube-in-air, Barrett's method D-7.  
b = benzene insoluble, %, Barrett's method B-7.  
c = quinoline insoluble, % Barrett's method B-21.  
d = coking value, %, Conradson, 3 g. sample, A.S.T.M. D-189-46.  
e = specific gravity, g./cu.cm., 25°C, Barrett's method D-4.  
f = distillation fraction 0-270°C, Barrett's method C-9.  
g = distillation fraction 271-300°C.  
h = distillation fraction 301-360°C.  
i = distillation fraction 361-400°C.  
j = Total distillate, 0-400°C.
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