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Studies in Tasmanite Shale Oil

By

R. F. CANE, M.SC., A.A.C.I.

Chemist, National Oil Pty. Ltd., Sydney

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INTRODUCTION

Although the chemical composition of petroleum has received much attention in recent years, there is a surprising lack of information from the systematic study of any one shale oil, with perhaps the exception of the work of Kogerman (1931) in Estonia, Hellsing (1921) in Sweden, and Horie (1935) in Japan, together with the various articles which have been published on the Scottish shales. However, practically no work has been published on the chemistry of Tasmanite oil and very little more on any Australian mineral oil.

The oil-producing substance of Tasmanite, seen under the microscope, consists of roundish discs that can be just discerned by the naked eye, although, as Singh (1932) has pointed out, during fossilization these spore cases have been distorted and ruptured. The general concensus of opinion is that they are innumerable sporangia which are allied to Lycopodaceous macrospores. This spore case material is the true kerogen of Tasmanite, and, in common with all shales, its pyrolysis takes place in two stages. A primary decomposition occurs, causing the kerogen to change into a gummy semi-solid bitumen of highly unsaturated nature; this bitumen is unstable at the temperature of the retort, and immediately decomposes into compounds of greater stability and saturation.

The oil taken for this research was produced by a gentle and approximate isothermal distillation of the shale, the temperature never rising above 400°C. There is little or no hydrogen sulphide produced during this pyrolysis, whereas in commercial retorting large quantities of this gas are produced. Assuming that the production of hydrogen sulphide is the result of the secondary decomposition mentioned above, the type of oil chosen for this research should give valuable information on the chemical structure of Tasmanite kerogen.

Research on shale oil presents a more difficult problem than might at first be expected; this is caused by the relatively high percentages of sulphur and nitrogen making the preparation of pure hydrocarbon mixtures very difficult indeed. Another contributing factor is the high olefine content of the oil, which causes the formation of large quantities of tarry matter when the oil is treated with sulphuric acid, in a manner which is applicable to flow oils containing a much smaller amount of this hydrocarbon type.

The crude oil possessed the following properties:—

Specific Gravity @ 15°C.	= 0·8540
Refractive Index @ 15°C.	= 1·4684
Water	= 0·34%
Tar Acids	= 4·5%
Tar Bases	= 3·2%
Sulphur	= 2·22%
Nitrogen	= 0·34%
Mercaptan Sulphur	= 0·30%
Diolefines	= 5·7%
Olefines + Aromatics	= 56·1%
Free Sulphur	not present
Hydrogen Sulphide	not present
Acetylenes	present, but not determined
Organic Peroxides	present, but not determined

The above values of the specific gravity and the refractive index; and all proceeding ones in this paper were determined in the following manner:—

The Specific Gravity was measured by means of the Westphal balance standardized against distilled water. If any small correction was thought necessary, the amount of the correction was obtained from the data published by Beale (1937).

The Refractive Index was found using an Abbé refractometer, and the temperature corrections were based on the Eykmann equation and the results of Kurtz and Ward (1936). Except where the temperature is given, both of these constants have been corrected to 20°C. All volumes are volume per cent, and all temperatures are given in degrees Centigrade and are not corrected for the emergent stem.

Distillation

The oil was fractionated in an iron drum of five gallons capacity, with an upright fractionating column at the top. This column was lagged with asbestos tape, between two layers of which was wound a helix of nichrome resistance wire, to a point 10 cm. from the top and to 23 cm. from the bottom, and by this means the column was warmed in the later stages, in order to produce a more even distillation. Inside the column, as a packing agent, were hung six one-yard lengths of brass chain. Towards the end of the distillation it was found impossible to get over the last fractions on account of the heat losses at the sides of the drum, and for this reason the last litre or so were distilled in a small apparatus of the normal laboratory type. Seventeen litres of the oil were distilled, with the results shown in the first four columns of Table I. The colour of the fractions varied progressively from colourless, in the first three fractions, through pale and dark yellow to nearly black in the last fractions.

Washing of the Fractions to Determine the Tar Acids and Tar Bases

100 ml. of each fraction were taken and poured into a stoppered separatory funnel, and an equal volume of 10 per cent aqueous sodium hydroxide added, then strongly agitated and the two layers allowed to separate out, the bottom layer run off, and the procedure repeated until the volume of the residual oil remained constant after two consecutive washings. The decrease in volume of the oil was taken as the percentage of *tar acids*. The above treatment was repeated substituting 10 per cent sulphuric acid for the caustic solution, and in this manner the amount of *tar bases* was determined. This treatment was

followed by a light sodium carbonate treat in order to remove traces of acid, then by a water wash, and finally the fractions were dehydrated over calcium chloride. The results of these treatments are shown in the Table I.

The Isolation of m-Cresol in the Tar Acids

The caustic washings from seven litres of the oil were united and the crude phenols liberated by dilute hydrochloric acid. They were redissolved in 4N caustic soda and the phenols—free from napthenic acids—liberated by means of carbon dioxide. The reddish oily liquid was fractionated using a Young and Thomas column.

Fraction No.	Boiling Range.	Density.	Refractive Index.
1	183-204	0·9811	1·5346
2	204-207	1·0119	1·5330
3	207-217	1·0138	1·5321
4	217-226	1·0216	1·5287
5	226-233	1·0285	1·5253
6	Residues.		

The first and second fractions were united and distilled three times and divided into the following cuts:—

Cut No.	Boiling Range.	Density.	Refractive Index.
I.	200-203	1·021	1·5201
II.	203-208	1·018	1·5220
III.	208-214	1·011	1·5284

All three fractions were water-white when freshly distilled, but developed a reddish tinge after a few days. They possessed the characteristic cresol odour, and were practically sulphur free (all thiocresols possess a boiling point lower than 200°C).

Isolation of m-Cresol from Cut I

This fraction was treated with mercuric chloride in order to remove traces of sulphur compounds, washed with water, and purified by ether extraction. The purified extract was again distilled, when the major portion distilled over at 204° ± 0·4. This was put aside and its characteristics found; density = 1·027 and refractive index = 1·5527, and on distillation with zinc dust it yielded toluene.

Schotten Baumann reaction with benzoyl chloride produced a benzoate of melting point 53·1°; this corresponds fairly closely with m-tolyl benzoate of m.p. = 54° (Behal & Choay, 1894), and gave no depression of melting point when mixed with the latter substance. Another portion was nitrated according to the method of Rashig (1900) and the trinitro derivative isolated; this was light yellow in colour and melted at 104·7°; the melting point of 2:4:6-trinitro-m-cresol = 106°.

According to Darzens (1931), anhydrous sodium acetate forms with m-cresol a complex $5.CH_3COONa.2CH_3C_6H_4OH$, which, on decomposition with water, yields m-cresol in a high degree of purity. This reaction, so the author maintains, is specific to m-cresol. A similar procedure was applied to the purified m-cresol from Tasmanite, with positive results. The m-cresol isolated had a melting point of 10·5° and refractive index of 1·5343 at 20°C, agreeing very closely with the data published by Darzens. All attempts to detect the ortho- and para-isomers were unsuccessful.

The Olefine Content

The determination of the correct olefine content is a matter of great difficulty in an oil such as this. Owing to the colour of the middle and last fractions, methods such as that of Mulliken and Wakeman (1935), involving the use of bromine, could not be used, as even the middle fractions had sufficient yellow colour to mask completely the very similar colour of the bromine. Moreover Thomas, Bloch, and Hoestra (1938) suggest that bromine absorption does not give correct values for the unsaturation when diolefines are present, which is undoubtedly the case in this oil. The use of the Francis bromide-bromate solution (Francis, 1926) was tried in the lower fractions without concordant results, probably due to the presence of cyclic olefines, which, according to Cortese (1929) give anomalous results.

After trying several reagents it was decided to employ sulphuric acid without the addition of boric acid as suggested by Kattwinkle (1927), as this has been shown incorrect by Tropsch and others (1929). It was fully realized that this method possessed many inherent disadvantages, such as the formation of polymerization products, attack on other substances, also the constitution of the saturated hydrocarbons is not necessarily the same before and after the sulphuric acid treatment, as new paraffins and napthenes may be formed under the influence of the acid (Brochet, 1893).

Optimum Acid Strength for Olefine Determination

In order to gain some idea of the action of different strengths of sulphuric acid on the oil, a representative fraction was treated with gradually increasing strength sulphuric acid, in the manner suggested by Fisher and Eisner (1937). The results of this are shown below:

Acid Strength.	Residual Volume.	Refractive Index.
%	ml.	
....	100	1·4812
70	93·0	1·4778
75	88·0	1·4785
80	82·5	1·4796
82·5	80·5	1·4800
85	76·6	1·4820
88	60·5	1·4795
90	58·0	1·4765
96	51·0	1·4583
100	44·5	1·4364
105	39·5	1·4385

From these figures it can be seen that there is incipient attack on the aromatics when the acid strength has reached 88 per cent and that complete removal of aromatics and the commencement of attack on the paraffin-naphthene mixture starts with the 100 per cent acid.

50 ml. of the acid and base-free oil were placed in a stoppered separatory funnel and treated with an equal volume of 85 per cent sulphuric acid for ten minutes with external cooling, the acid layer separated off, and the treatment continued until the volume of the residual oil was constant. The results are given in Table I.

The residual oils were water-white, had practically no odour, and did not decolourize a weak solution of potassium permanganate.

The presence of Diolefines

The presence of appreciable amounts of diolefines in the oil was indicated by the intense yellow colour in some fractions. A certain fraction, in which the presence of diolefines was strongly suspected, was placed in a flask with 20 per cent of its weight of maleic anhydride and kept at a temperature of 100°C. for four hours under reflux. At the end of this period the residual oil was decanted off and the crystals washed free from oil; these crystals were soluble in alcohol and melted at 145°. To prove that ring formation had actually taken place, 1·5 gm. of the maleic anhydride compound was heated with 2 gm. of resorcinol and 1 gm. of zinc chloride for several hours. The product of this reaction was an intense red solid, soluble in alcohol, and had a characteristic colour change from acid to alkaline solution. The formation of this coloured substance (to be assumed of the phthalein type) could only arise from a cyclic structure, necessitating ring closure between the maleic anhydride and the diolefine with the formation of an acid similar to terephthalic acid and the subsequent formation of the anhydride.

The Presence of Terpene-like Olefines

A series of investigations were carried out in order to determine whether terpenes or substances allied to them were present in the oil. It is not intended to give a detailed description of the work done in this direction, but to state briefly that no conclusive evidence for their presence was obtained, although certain lines of research produced promising results, notably halogenation, followed by treatment with mercuric acetate.

THE SULPHUR COMPOUNDS

Sulphur is always present in shale, and, in general, a similarity exists between the sulphur compounds in shale oil and those in petroleum, but it is found that aromatic compounds predominate in the oil from shale in contrast to the usual aliphatic nature of the sulphur compounds in petroleum.

An examination of the more important sulphur compounds occurring in shale oil will serve to show that they are essentially thiophenic in nature and for this reason investigations on the sulphur bodies in shale oil are usually more difficult than the corresponding work on petroleum. This is more easily realized when the unsaturated nature of the former is taken into account.

On an allied oil Morgan and Soule (1923) write, ' There is no concentration of sulphuric acid capable of removing such sulphur compounds without attacking the unsaturates which predominate in the neutral oil. These unsaturated compounds, moreover, interfere with the usual qualitative thiophene identifications, by reacting with the sulphuric acid of the indophenin test and with the nitric acid of the thalline test to give reddish brown shades which mask the colour reactions, even in the presence of added thiophene.'

The presence of sulphur compounds in an oil which is to be used for power purposes has been one of the great disadvantages against the employment of shale oil in this connexion, for not only does the sulphuric acid formed during its combustion have a corrosive effect on the cylinders of the engine, but recently Kruser and Schade (1933) have shown that such compounds can act as accelerators in gum formation.

Challenger (1926) and Schleiber (1915, 1916) have performed important investigations into the nature of the sulphur compounds occurring in shale oil; both of the above investigators have shown that these bodies are mainly derivatives of thiophene, and have succeeded in isolating thiophene itself and certain of the lower alkyl homologues.

EXPERIMENTAL

Mercaptans

Mercaptan sulphur was estimated by a modification of the method proposed by Bond (1933). The results are given in the first table.

The Thiophenes

Five litres of crude Tasmanite gasoline were given a light acid and alkali wash and then distilled with the following results:—

Fraction.	Temperature Range.	Volume mls.	Density @ 18°.	Refractive Index.	Sulphur % by Wt.
1	-50	9·6	0·6934	1·3834	0·20
2	50-70	87	0·7037	1·3972	0·53
3	70-90	457	0·7484	1·4088	1·18
4	90-110	491	0·7641	1·4207	1·51
5	110-130	538	0·7884	1·4364	1·97
6	130-150	593	0·7928	1·4389	2·31
7	150-160	163	0·8049	1·4469	3·06
8	160-170	161	0·8112	1·4496	3·58
9	170-180	115	0·8225	1·4558	3·24
10	180-190	91	0·8377	1·4590	3·22
11	190-200	58	0·8400	1·4654	3·02
12	Residues.				

Fractions 3 and 4 were united and subjected to more exact fractionation, thus:—

Fraction.	Temperature Range.	Density.	Refractive Index.	Sulphur % by Wt.
3a	70-75	0·7179	1·4003	1·02
3b	75-80	0·7295	1·4073	1·18
3c	80-85	0·7585	1·4232	1·48
3d	85-90	0·7667	1·4180	1·54
4a	90-95	0·7548	1·4205	1·48
4b	95-100	0·7585	1·4300	1·49

The Presence of Thiophene in Fractions 3c + 3d

A representative portion of these two fractions was again distilled and cut at 2° intervals. The 83°-85° cut was treated with mercuric chloride in the following manner:—Alcohol was added to the fraction until the solution contained 80 per cent alcohol, and to it was added twice the amount of mercuric chloride required to form the mercurichloride (assuming that all the sulphur was contained in the thiophene), and five times the quantity of sodium acetate necessary to combine with the liberated hydrochloric acid. It was allowed to stand for two days with frequent shaking, and at the end of this period the precipitate was filtered off. A portion of this precipitate after purification gave, on analysis:—

Chloride ... ...   11·8% found; 11·1 calculated

Sulphur ... ...   9·7% found; 10·0 calculated

The melting point of the compound was rather indefinite near 179°, and at 183° it commenced to blacken. The melting point of thiophene mercurichloride is reported by Steinkopf to be 183°. Another portion of the precipitate on distillation with 6N hydrochloric acid decomposed to produce a liquid which reacted positively to the usual thiophene colorimetric tests.

The Methyl-Thiophenes

Fractions 4*b* and 5 were united and distilled three times.

Fraction No.	Temperature Range.	Density.	Refractive. Index.	Sulphur % by Wt.
MT (i)	105-109	0·7642	1·4246	2·43
MT (ii)	109-117	0·7759	1·4345	2·98
MT (iii)	117-126	0·7808	1·4348	2·27

Lot MT (ii) was fractionated twice, and the final temperature limits taken at 111° to 115°. The volume of this fraction was 67 ml., and it contained 2·99 per cent sulphur. 60 ml. of this were dissolved in a litre and a half of alcohol and agitated with one litre of aqueous sodium acetate (33 per cent) and four litres of saturated aqueous mercuric acetate. After two and a half hours a dirty yellow precipitate formed; this was removed, and further precipitation allowed to take place. At the end of one day the combined precipitates were extracted with boiling alcohol and the solute crystallized and purified. The crystals melted between 202° and 204°. Steinkopf (1914) states that the melting point of 2-methylthiophene-5-mercurichloride is 204° with previous sintering, while the corresponding figure for the 3-methyl isomer is quoted at 138°. The methyl-thiophene-mercurichloride was decomposed with hydrochloric acid as before, and a portion of the liberated methylthiophene converted into its tribromo derivative. On recrystallization a sharp melting point was obtained at 85·6°. The melting point of tribromomethylthiophene is recorded in the literature at temperatures varying between 87° and 94° but most reliable sources place it at 86°. The melting point of the other isomer is 35°, while Gatterman (1885) states that a mixture of the two isomers cannot be separated by crystallization and melts at 74°. In order to complete the identification a small portion of the purified compound was oxidized to the corresponding acid with potassium permanganate. The melting point of this acid (126°) clearly corresponded to 2-thiophenecarboxylic acid.

Examination of Fraction 6 for Dimethylthiophenes

Fraction 6 was distilled several times and finally cut into two lots:—

6 (*a*) 130°-135° Density, 0·7854; Refractive Index, 1·4390.

6 (*b*) 135°-143° Density, 0·8012; Refractive Index, 1·4468.

No thiophene derivatives could be found in the first lot. The other lot, 6 (*b*), gave very peculiar results. 60 ml. were treated with mercuric acetate as before, and, within a half hour, a large amount of white granular precipitate was formed. The mixture was allowed to stand for thirty hours with frequent shaking, after which the precipitated mercury compounds were filtered off. An examination of the filtrate showed that the whole of the fraction had been converted into the mercury compound. The precipitate was washed with petroleum ether, after

which it was distilled with 6N hydrochloric acid, whereupon 57 ml. of a sweet aromatic oil were recovered. The oil burnt with a very smoky flame, and possessed the following properties:—

Density ... ...   0·8107
Refractive Index ... ...   1·4471
Sulphur ... ...   3·0 per cent

It reacted negatively to the usual thiophene tests. On distillation the whole of the distillate came over between 136° and 140°, which immediately precludes other sulphur containing substances, such as thioethers, thiols, thiophanes, &c., none of which have been reported to boil within these limits. In the case of 2:3-dimethylthiophene-mercurichloride, there is a direct covalent link between the mercury and carbon atoms, in contrast to the addition compounds formed when mercury salts act on other sulphur compounds, such as mercaptans. This latter type is split up on treatment with caustic alkalis with the formation of the oxide of the metal. It was proved in the present case that the compound under consideration was essentially aromatic in nature. However, at this juncture it seems inadvisable to assume that dimethylthiophenes are absent, nevertheless it appears that another type of sulphur compound is present in such large quantities that the usual methods used in the isolation of thiophene homologues are not applicable. It is hoped to continue this phase of the research in the future.

These investigations were carried out in the Department of Chemistry in the University of Tasmania during the tenure of a Commonwealth Government Research Scholarship (1938 and 1939).

SUMMARY

Tasmanite shale on gentle pyrolysis produces an unsaturated oil with a relatively high aromatic content. The oil was fractionated and the physical properties of the different fractions found, after which the fractions were washed with sodium hydroxide solution and dilute sulphuric acid, in order to determine the tar acids and tar bases. The isolation of m-cresol from the tar acids is described. The degree of unsaturation, as determined by 85 per cent sulphuric acid, varied between 40 per cent and 47 per cent, including as much as 11 per cent diolefines. It is probable that terpenes, or substances closely allied to them, occur in the oil, although their presence was not confirmed. Tasmanite shale oil contains large quantities of sulphur, the major portion of which is contained in heterocyclic molecules. The cyclic sulphur bodies in the lower fractions were thiophenic in nature and the presence of thiophene and methyl thiophene was confirmed.

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TABLE I.

Fraction.	Temperature Range.	Volume ml.	Specific Gravity @ 20°.	Refractive Index @ 20°.	Tar Acids.	Tar Bases.	After Removal of Acids and Bases.			Mercaptan Sulphur.
							Specific Gravity.	Refractive Index.	Olefines Per cent.	
A	36-60	60	0·6799	1·3857	0·0	0·5	0·6800	1·3858	40	0·000
B	60-70	414	0·6958	1·4038	0·0	0·5	0·6959	1·4039	40	0·029
C	70-80	162	0·7199	1·4046	0·0	1·0	0·7200	1·4048	46	0·044
D	90-100	227	0·7200	1·4060	0·0	1·1	0·7195	1·4063	47	0·074
E	100-110	125	0·7237	1·4097	0·0	1·0	0·7230	1·4098	46	0·105
F	110-120	256	0·7425	1·4130	0·0	1·1	0·7415	1·4130	45	0·082
G	120-130	261	0·7531	1·4205	0·0	1·1	0·7528	1·4200	44	0·115
H	130-140	497	0·7630	1·4242	0·1	1·4	0·7649	1·4254	45	0·126
I	140-150	544	0·7665	1·4284	0·3	1·6	0·7665	1·4286	45	0·164
J	150-160	529	0·7785	1·4329	0·4	2·0	0·7806	1·4330	44	0·232
K	160-170	956	0·7934	1·4418	0·5	2·4	0·7897	1·4380	42	0·273
L	170-180	841	0·8062	1·4468	1·5	2·5	0·8004	1·4419	40	0·282
M	180-200	910	0·8148	1·4523	2·0	2·5	0·8154	1·4494	40	0·226
N	200-220	2022	0·8298	1·4607	3·0	2·7	0·8277	1·4567	41	0·390
O	220-240	1920	0·8461	1·4657	3·5	3·5	0·8396	1·4612	40	0·507
P	240-260	1873	0·8713	1·4805	3·5	4·0	0·8668	1·4758	40	0·224
Q	260-280	822	0·8779	1·4848	4·5	4·0	0·8763	1·4832	40	0·392
R	280-300	864	0·8803	1·4932	5·0	4·5	0·8764	1·4906	41	0·421
S	300-320	778	0·8978	1·4992	5·0	4·5	0·9858	1·4974	41	0·438
T	320-340	843	0·9161	1·5077	5·5	4·5	0·8999	1·5056	40	0·515
U	340-360	705	0·9328	1·5183	5·5	4·0	0·9311	1·5170	40	0·344
V	360-	175	0·9514	1·5227	5·8	4·0	0·9500	1·5213	40	0·445