STUDIES IN THE HIGHER
COAL TAR BASES.

by

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INTRODUCTION.

The work to be described in this thesis takes the form of an investigation of the nitrogenous bases which can be extracted by sulphuric acid from the Naphthalene Oil and the Benzol Absorbing Oil fractions of coal tar, after the tar oils have been freed from phenols by extraction with caustic soda.

The chief objects of the investigation were:

1) To obtain a weight/temperature of distillation balance for both fractions of bases, thus showing the relative abundances of the more common fractions, and possibly indicating where any previously unidentified bases were liable to occur.

2) To make a closer study of the fractions boiling between 180° and 235°, and over 265°C/760 mm.Hg, as these two fractions have not been exhaustively studied in the past, and, where possible, to isolate and identify pure bases.

The nitrogenous bases which can be extracted by sulphuric acid from coal tar or coal tar oils consist mainly of pyridine, quinoline, isoquinoline, and their homologues, together with small quantities of pyrrole, aniline, toluidines, xylidines, acridine and naphthylamines.

According to present industrial practice the only/
the only bases which are extensively utilised are pyridine and its lower homologues, the commercially available products being :

Pure Pyridine - This is obtained by a close fractionation of the lower tar bases and is used as an intermediate in the production of "sulpha" drugs (sulphapyridine), dyestuffs, vulcanisation accelerators and waterproofing compounds, and as a solvent and catalyst.

"90-140° or 90-160° Bases" - These are obtained by crude fractionation of the lower tar bases and are used as denaturants, solvents, levelers in leather dyeing, insecticides, and also in the production of pattern effects on cotton and rayon, and in lubricating oil refining.

"90-180° Bases" - These are obtained by crude fractionation of tar bases and are used as solvents, in anthracene purification, and as restrainers in metal pickling baths.

In addition to these main industrial products the following are produced in smaller quantities :

Picolines - These have been produced in small quantities from time to time, but recently, owing to the great demand for nicotinic acid as an accessory dietary factor, an interest has been aroused in β-picoline, and considerable quantities have been produced for oxidation to nicotinic acid.

Lutidines/
Lutidines & Collidines - These have only been produced in semi-commercial and experimental quantities.

It is difficult to ascertain the sources of the above products owing to the differences in works practice throughout the country, especially with respect to the temperature ranges of the oil cuts taken, but it would appear that they are produced for the most part from the lower boiling tar oils, and according to present works practice the bases are seldom removed from the Naphthalene Oil and Benzol Absorbing Oil fractions.

The total United Kingdom production of "pyridine bases" amounted to 166,000 gallons in 1948 and to 167,000 gallons in 1949 (Min. of Fuel & Power), and there are indications that more could be used if it were available. If this is the case, it is possible that the Naphthalene Oil fraction might provide a useful auxiliary source.

Very little work has been carried out on the utilisation of the tar bases boiling above 180°C, such as are obtained from the Benzol Absorbing Oil fraction, although quinoline and isoquinoline have been isolated in semi-commercial and experimental quantities, and during the recent war the xylidines were separated for use as aviation fuel additives. It was considered, therefore, that some quantitative estimate/
estimate of the constitution of the Benzol Absorbing oil base fraction would be of considerable value.

The Origin of Nitrogen in Coal.

It is generally agreed that the nitrogen present in coals has come from plant or animal proteins, or both, which were laid down in earlier eras of the earth. The plants which were concerned with coal formation are now, with few exceptions, extinct, but it is reasonable to assume that their chemical composition did not vary substantially from those of our present day.

The plant proteins, which contain 15 - 19% nitrogen, are easily attacked by enzymes and converted into amino acids which, being water soluble, would possibly be partially washed or might be attacked by micro-organisms and converted into ammonia, elementary nitrogen and simpler nitrogen-free organic compounds. However, part of these amino-acids could react with aldehyde or hydroxyl groups of carbohydrates, thus :-

\[
\begin{align*}
R-C-O + H_2N-CH_2-C=O & \rightarrow R-C=NH-CH_2-C=O + H_2O \quad (i) \\
R-CH_2-OH + H-N-CH_2-C=O & \rightarrow R-CH_2-O=C-C=N + O=C-CH_2 \quad \text{OH} \\
\end{align*}
\]

Such reactions can lead to the formation of complex condensation products (i) with high molecular weights/
weights and colloidal properties (so-called melanoids), or to heterocyclic compounds (ii). Maillard (110) showed that the heating of these melanoids resulted in their decomposition with the production of heterocyclic nitrogen compounds. It is possible by this mechanism to account for the fact that in an accumulation of plant organisms and their transformation products (e.g. a peat bed), the nitrogen content does not decrease with progress in 'turfication', but sometimes increases.

This does not, however, account for the fact that the nitrogen present in coal is 10 - 30 times greater than that in present day wood. Some substance high in nitrogen must have been present in the material from which the coal was formed, and this substance was obviously protein. Terres (111) was able to prepare artificial brown coals, containing 4.16\% nitrogen, by pressure-heating peat sludge made by fermentation of peat moss which contained 1.73\% nitrogen. The increase in nitrogen content was due to the protein substances added by micro-organisms. Terres believed that brown coal is the final product resulting from the coalification of starting material consisting entirely of plant substance. However, when he fermented and artificially coalified proteinous material, he obtained a heavy distillable oil resembling crude petroleum which contained about 5\% nitrogen, and a non-volatile bitumen containing over/
over 6% nitrogen. Terres claimed that the sludge formed from protein putrefaction is the essential material from which coal bitumens are formed, and that for the formation of bituminous coals it is necessary to have protein material present along with lignin, cellulose, waxes and resins, which come from plant substance. This view explains the fact that bituminous coals generally contain more nitrogen than brown coals.

Animal remains, doubtless mixed with large amounts of plant remains, can also furnish proteins which may be responsible for the major part of nitrogen in coals. This has been put forward as an explanation of the large variations of nitrogen content within the same seam of coal. It has been shown that the protein of animal organisms vanishes completely under normal decomposition owing to the absence of carbohydrates, but provided that there were sufficient plant remains, the nitrogen could be retained in some such manner as that postulated by Maillard.

Possible additional sources of nitrogen in coal are - plant alkaloids, chlorophyll and other porphorins, chitin etc.

It can be seen that as yet there is no clearly defined view as to the origin of nitrogen in coal. It is sufficient, however, for the major part of this work to state that the nitrogen is combined in/
in coal as complex organic material which on carbonisation yields more simple organic bases which distil over in the tar. It is possible that by further elucidation of the composition of the base mixture derived from coal tar a more clear idea may be obtained as to the constitution of this complex organic material.
LITERATURE SURVEY ON THE BASES DERIVED FROM
COAL TAR AND OTHER RELATED SOURCES.

Dry distillation of nitrogen-containing materials, such as the vegetable alkaloids and animal oils, led to the first recognition of volatile organic basic substances. The "odorin" which was separated from bone oil by Unverdorben in 1827 (1) was not then characterised much beyond its obvious property of possessing a foul odour. In 1846 Anderson (2), in studying naphtha from coal tar, isolated a base by sulphuric acid extraction, neutralising with ammonia and subsequent distillation, which he considered similar to "odorin". A characterisation of the properties of this base caused Anderson to believe that it was a pure compound. He called it picoline and it is very likely that this material was a crude grade of α-picoline. This was the first reported instance of a systematic study of the pyridine molecule.

Concurrently with his discovery of phenol in coal tar, Runge (3), in 1834, also found three bases, one of which he called "leukol". In 1842 Gerhardt (4) obtained "chinolein" by caustic potash distillation of quinine and strychnine. Hofmann (5) showed that "leukol" and "chinolein" were identical. The name quinoline or chinoline was gradually adopted for this compound thereafter, although leucoline still continued to appear in the earlier literature.

It was/
It was not until 1885 that a reasonably pure grade of pyridine was isolated from coal tar by Williams (6). He obtained the compound by fractional distillation of the crude bases, removal of aniline with nitric acid, and fractional crystallisation of the platinum salts of the resultant bases. The fraction boiling at 116°C was considered to be pyridine. This boiling point approximates the best value given today.

Since this time a considerable amount of work has been carried out on the nitrogenous bases derived from coal tar, and much light has been cast upon the constitution of the crude base mixture. It has been shown that the main constituents of this mixture are tertiary bases of the pyridine, quinoline, and isoquinoline types, and it is with the isolation and identification of these types of compounds that this investigation is mainly concerned.

The following is a list of the homologues of pyridine, quinoline and isoquinoline which have been reported as coal tar constituents: -


Quinoline; 2-, 3-, 4-, 5-, 6-, 7- and 8-methylquinolines/
8-methylquinoline; 2:8-dimethylquinoline; 5:8-dimethylquinoline (Some doubt has been cast on the authenticity of this claim. See Appendix I.); 2:4:6-trimethylquinoline.

Isoquinoline; 1-, 3-, 6-, and 5 or 7-methylisoquinoline; 1:3-dimethylisoquinoline.

The following primary aromatic amines have also been isolated from coal tar:— Aniline; o-, m-, and p-toluidines; 2:3, 2:4-, 2:5- and 3:5-xylidines; α- and β-naphthylamines.

In addition, certain homologues of indole, carbazole and acridine have been isolated, and also three benzcarbazoles, phenanthridine and phenanthridone, but none of these types of compounds are liable to be met with in this investigation.

The physical constants of all the homologues of pyridine, quinoline and isoquinoline mentioned above are listed in Appendix I, together with the melting points of three derivatives of each, and references to their isolations from coal tar and other natural sources. It was not necessary to list the primary bases in this way, as no attempt has been made to isolate primary bases during this investigation.

Shale Oil Bases.

The general character of the nitrogenous bases/
bases extracted by sulphuric acid from shale oil is very similar to that of the bases obtained from coal tar.

In the pyridine series, all the homologues which have been isolated from coal tar have also been isolated from shale oil. In addition, Eguchi, in a very thorough examination of the nitrogenous bases derived from Fushun bituminous shale (9), has isolated 2:3:4:6-tetramethylpyridine, 2:6-dimethyl-4-ethylpyridine, 2:3-dimethyl-6-ethylpyridine and pyridane. Benzie & Milne, in a study of the Scottish shale oil bases (24), also isolated 2:3:4:6-tetramethylpyridine and, in addition, isolated a solid base which has now been proved to be 2:3:5:6-tetramethylpyridine.

In the higher boiling ranges the presence of quinolines and isoquinolines has been shown, but very little work has been carried out on these ranges.

In an investigation of the bases obtained from the "Sapropel" of the Karisino Lake region (U.S.S.R.), which may be considered as an intermediate between shale and petroleum, Lanin & Pozhil'tsova (107) isolated the following compounds: 3-Methylpyridine, 2-butylpyridine, 2:4- and 2:6-dimethylpyridines, 2:4-diethylpyridine, 2-methyl-6-ethylpyridine, 2-methyl-4-ethylpyridine, 4-methyl-3-ethylpyridine, 2:7-dimethyl-5-ethylpyridine and 2:4:6-trimethylpyridine.

Petroleum
Petroleum Oil Bases.

The literature dealing with the nitrogenous bases derived from petroleum is quite extensive, and it would therefore be outside the scope of this summary to attempt a complete survey.

Crude undistilled petroleum contains complex nitrogen compounds which cannot be extracted with acids, but can be concentrated by solvent extraction. These compounds have not been studied to any great extent, but according to Pott et al. (108) they may either consist of pyrrole, indole or carbazole types of compounds, or may be more complex and contain combined sulphur and oxygen.

During normal refining slight cracking takes place and these complex materials are partially broken down to form nitrogenous bases, the extent to which this break-down occurs being increased with rise in temperature of distillation.

Bailey and his co-workers have conducted an extensive series of researches on the bases obtained from Californian Petroleum distillates during the period 1928-1942 (published in the Journal of the American Chemical Society). These researches are of interest because of the novel methods of separation used, as well as for the isolation and identification of the following alkylquinolines;
alkylquinolines: 2:3-, 2:4- and 2:8-Dimethylquinolines; 2:3:8- and 2:4:6-trimethylquinolines; 2:3:4:8-tetramethylquinoline; 2-methyl-8-ethylquinoline; 2:3-dimethyl-8-ethylquinoline; 2:4-dimethyl-8-ethylquinoline; 2:3:4-trimethyl-8-ethylquinoline; 2:3-dimethyl-4:8-diethylquinoline; 2:3-dimethyl-8-n-propylquinoline; 2:4-dimethyl-8-n-propylquinoline; 2:3:8-trimethyl-4-ethylquinoline; 2:3:4-trimethyl-8-n-propylquinoline; 2:3:4-trimethyl-8-isopropylquinoline; 2:3-dimethyl-4-ethyl-8-n-propylquinoline; 2:4-dimethyl-8-sec-butylquinoline; 2:3- and 2:4-dimethylbenzo(h)quinoline.

A few non-aromatic bases have also been isolated from straight-run petroleum, but the elucidation of the structure of these bases has presented considerable difficulty.

Bailey and Bratton examined the bases derived from cracked petroleum and isolated the following compounds: 2-, and 4-methylpyridines; 2:4-, 2:5-, 2:6- and 3:5-dimethylpyridines; 2:4:6-trimethylpyridine; quinoline; 2-methylquinoline. These, they believed, accounted for the total amount of bases present.

Hackmann and Wibaut (25), on the other hand, examined the bases from a Californian Oil, cracked at 500°C. and 30 atmospheres pressure, and presumably of different origin to that used by Bailey/
Bailey, and obtained, in addition to all the compounds found by Bailey, the following: 3-methylpyridine; the remainder of the possible dimethylpyridines; 2:3:6-trimethylpyridine; 4-ethylpyridine; 2:4-, 2:5- and 2:6-methylethylpyridines; 2-ethyl-4-methylpyridine; 3-, 4-, 7- and 8-methylquinolines; 2:8-dimethylquinoline; isoquinoline; 1- and 3-methylisoquinolines. Several unidentified bases were also obtained.

The very noticeable differences in results obtained in these two investigations may, however, be explained by differences in the origin of the starting material and in cracking conditions.

From a study of the results obtained from these investigations on the bases derived from coal tar, shale oil and cracked and straight-run petroleum, certain notable points stand out.

1) The general character of the bases obtained in all cases is similar (i.e. they consist mainly of pyridine, quinoline and isoquinoline homologues), with the exception that aromatic primary amines appear to be more abundant in coal tar than in either shale oil or petroleum.

2) The individual components increase in complexity in the order - coal tar, cracked petroleum, shale oil, sapropel tar, straight-run petroleum.
petroleum. This fact indicates that the composition of the basic material derived from these natural sources depends more on the temperature attained in the processing of the starting material than on any other single factor, including even the origin of the starting material.

3) In the quinoline ranges the poly-substituted quinolines which have been isolated from any of these sources have all been substituted in the 2-position, with the exception of a claim made by Ganguli and Guha to the isolation of 5:8-dimethyl-quinoline about which there is some doubt (See note in Appendix I.). This phenomenon could be explained either by some peculiarity in the constitution of the complex organic material from which the bases are derived, or by the possibility that the poly-substituted quinolines which are substituted in the 2-position are more stable to heat.
ORIGIN OF THE STARTING MATERIAL.

The coal tar oil fractions, from which the bases were extracted for this investigation, were obtained by fractional distillation of vertical retort tar derived mainly from Granton Gas Works. The distillation was carried out in a continuous pipe still of the Wilton type which is described below, and the conditions were those of normal working.

Wilton Patent Pipe Still

At the Falkirk Works of Messrs. Scottish Tar Distillers Ltd. there are two sizes of Wilton Plants, one of which has a throughput of 150 tons/day and the other 75 tons/day. These do not, however, differ in fundamentals, and the sketch shown in Figure 1 applies to both sizes, as does the following description:

The crude tar, which is usually pre-heated to some extent, is pumped in at the point A in Fig. 1 and thence through the vapour-tar heat exchangers, (B) in which the temperature is raised to 50-60°C, to the waste-heat setting (C), which utilises waste from the main furnace to raise the temperature of the tar to 110°C.

The hot tar then travels to the primary flash chamber (D) where the water and light oil are flashed off, their vapours being led in at about the middle/
middle of the fractionating column.

The remaining liquid runs over into the mixing vessel (F) and is thence pumped to the coils of the main furnace (G) which may be heated with either liquid or solid fuel. The tar attains a temperature of 270-370°C in this furnace and then travels to the secondary flash chamber (E) where the volatile oils are flashed off leaving a pitch whose nature depends on the temperature to which the tar has been raised.

The hot pitch runs over into the mixing vessel where it mixes with the tar from D (in the ratio of about 1:7), and some volatile oils from the tar are vaporised. These vapours, along with the vapours from the secondary flash chamber, are led in at the foot of the fractionating column. The pitch/tar mixture is circulated through the main furnace again.

The pitch level in the mixing chamber is indicated by a mechanical float and pointer mechanism, and is controlled by a relay system to the control panel and thence to a motorised valve on the pitch off-take on the secondary flash chamber.

All three chambers in the distilling column are kept hot by means of steam which is superheated in the furnace and which passes through "pokers" in the chambers.

The input of tar is dependant on the size of the plant. In the 150 ton/day plant the pitch/tar mixture/
pitch/tar mixture passes through the circulating pump (H) at about 9,200 gals/hour.

The fractionating column has 35 crocodile bubble-cap and down-pipe trays. The over-heads from the column are passed through the vapour/tar heat exchangers, condensed, the water separated and part of the separated crude benzol returned to the column as reflux, in sufficient quantity to keep the column-head temperature at about 84°C.

The fractions are drawn off continuously from the five sidestreams on the side of the column, condensed and run to storage. Each side-stream can be drawn from three adjacent sections of the column as desired. The boiling range of any cut may be varied by collecting from a different section, or by varying the take-off rate at the cock.

**Naphthalene Oil**

The Naphthalene Oil from which the bases were derived for this investigation was obtained in a yield of 20 gallons/ton of the crude tar of 5% water content. On analysis it showed the following characteristics:–

- Specific Gravity of the oil 0.960
- Phenols present............ 5.0%
- Bases present............. 2.0%
- Water present............. trace

Distillation Test/
Distillation Test:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>190°C</td>
<td>3%</td>
</tr>
<tr>
<td>200°C</td>
<td>10%</td>
</tr>
<tr>
<td>210°C</td>
<td>30%</td>
</tr>
<tr>
<td>220°C</td>
<td>43%</td>
</tr>
<tr>
<td>230°C</td>
<td>65%</td>
</tr>
<tr>
<td>240°C</td>
<td>78%</td>
</tr>
<tr>
<td>250°C</td>
<td>83%</td>
</tr>
<tr>
<td>260°C</td>
<td>87%</td>
</tr>
<tr>
<td>270°C</td>
<td>91%</td>
</tr>
<tr>
<td>280°C</td>
<td>94%</td>
</tr>
<tr>
<td>290°C</td>
<td>95%</td>
</tr>
<tr>
<td>290°C</td>
<td>95%</td>
</tr>
<tr>
<td>290°C</td>
<td>95%</td>
</tr>
<tr>
<td>300°C</td>
<td>90%</td>
</tr>
<tr>
<td>304°C</td>
<td>95%</td>
</tr>
</tbody>
</table>

Benzol Absorbing Oil

The Benzol Absorbing Oil from which the bases were derived for this investigation was obtained in a yield of 18 gals/ton of the crude tar of 5% water content. On analysis it showed the following characteristics:

- Specific Gravity of the oil: 0.990
- Phenols present: trace
- Bases present: 2.4%
- Water present: trace

Distillation Test:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>230°C</td>
<td>6%</td>
</tr>
<tr>
<td>240°C</td>
<td>10%</td>
</tr>
<tr>
<td>250°C</td>
<td>20%</td>
</tr>
<tr>
<td>260°C</td>
<td>32%</td>
</tr>
<tr>
<td>270°C</td>
<td>43%</td>
</tr>
<tr>
<td>280°C</td>
<td>66%</td>
</tr>
<tr>
<td>290°C</td>
<td>78%</td>
</tr>
<tr>
<td>300°C</td>
<td>90%</td>
</tr>
<tr>
<td>304°C</td>
<td>95%</td>
</tr>
</tbody>
</table>

Both fractions of tar oils were separately freed from phenols by extraction with 10% caustic soda in a packed tower. The bases were then extracted from each of the phenol-free oils by stirring.
stirring the oils with 30% sulphuric acid in a lead-lined conical washer. The mixture was then run down into settling pans where a considerable amount of dirt and sludge separated. The aqueous "pyridine acid" was separated from the oil and pumped to a lead-lined beaker where the bases were liberated by means of soda ash. The free bases were then separated and dried over solid caustic soda.

Naphthalene Oil Bases.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity of oil washed for bases</td>
<td>3000galls</td>
</tr>
<tr>
<td>Strength of sulphuric acid used</td>
<td>30%</td>
</tr>
<tr>
<td>Quantity of sulphuric acid used</td>
<td>100galls</td>
</tr>
<tr>
<td>Yield of crude bases.........</td>
<td>1.8% on oil</td>
</tr>
<tr>
<td>Specific Gravity of crude bases</td>
<td>1.024 (5% water)</td>
</tr>
</tbody>
</table>

Distillation test on dry bases:

- Drop @ 136°C; 4% @ 140°C;
- 15% @ 160°C; 23% @ 170°C;
- 35% @ 180°C; 45% @ 190°C;
- 53% @ 200°C; 58% @ 210°C;
- 63% @ 220°C; 66% @ 230°C;
- 70% @ 240°C; 80% @ 250°C;
- 87% @ 260°C; 90% @ 270°C.

Benzol Absorbing Oil Bases.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity of oil washed for bases</td>
<td>5,500galls</td>
</tr>
<tr>
<td>Strength of sulphuric used......</td>
<td>30%</td>
</tr>
<tr>
<td>Quantity of sulphuric acid used</td>
<td>150galls</td>
</tr>
<tr>
<td>Yield of crude bases.........</td>
<td>2.0% on oil</td>
</tr>
<tr>
<td>Specific Gravity of crude bases</td>
<td>1.078 (5% water)</td>
</tr>
</tbody>
</table>

Distillation test/
Distillation test on dry bases:

<table>
<thead>
<tr>
<th>Drop</th>
<th>%</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.5</td>
<td>140</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>180</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>200</td>
</tr>
<tr>
<td>15</td>
<td>21</td>
<td>220</td>
</tr>
<tr>
<td>32</td>
<td>50</td>
<td>240</td>
</tr>
<tr>
<td>70</td>
<td>80</td>
<td>260</td>
</tr>
<tr>
<td>84</td>
<td>87</td>
<td>280</td>
</tr>
</tbody>
</table>

- 90% @ 250°C; 80% @ 270°C; 70% @ 300°C.
a) **Fractional Distillation.**

In the study of complex organic liquid mixtures fractional distillation has for many years proved of great importance. Until recent years, however, the methods used have been crude, and efficient laboratory-scale fractionation as known today has been developed mainly within the past two decades. Tribute for this advance is due in the main to the petroleum industry.

A number of excellent reviews of the literature dealing with distillation have been published from time to time, of which those of Ward (112) and Fay (113) are particularly useful. The bibliography of Stage and Schultze (114) covers the years 1920-1944, while that of Rose and Rose (115) covers the years 1941-1945 and includes abstracts of all papers on distillation. Developments during the years 1946-1948 have also been reviewed by Rose (116). The extensive literature on the design and testing of fractionating columns has been summarised by Underwood (117).

It would be imprecise in a work of this nature to attempt to summarise the literature on laboratory type fractionating equipment. The following, however, is a brief description of the main types of columns which find a use in the laboratory/
laboratory.

Unpacked Columns: Provided that the column is of small enough diameter, a fair degree of fractionation can be obtained from an unpacked column. High efficiencies, however, are obtained only when the boil-up rate and throughput are very low.

Bubble-cap Columns: Although this type of column is of the greatest industrial importance, their use in the laboratory is limited by the difficulty of manufacture, high liquid hold-up and high pressure drop. The "pear" type of column, which has been in use in laboratories for many years, is very similar to the bubble-cap column but is of little practical value.

Packed Columns: This type of column has found the most wide-spread use in the laboratory and many different packing materials have been used.

Prior to 1936, the most common random packings used in laboratory stills were glass and metal beads (118), "Lessing Rings" of metal or ceramic materials (119), metal eyelets, carding teeth (120) and jack chain (121). The fractionating efficiency of these packings was low, being only equivalent to about four theoretical plates per foot of height.

Notable increases in efficiency were obtained by Fenske (122) using single turn wire or glass helices, by Stedman (123) who used a regular packing in the form of conical wire gauzes, and by Leckey/
Leckey and Ewell (124) who produced a spiral packing made from wire gauze. These last two types of packing, however, possess the disadvantage of difficulty of fabrication.

A much greater advance in the efficiency of laboratory type fractionating columns was made by Dixon (125) who used a random packing of gauze rings. This packing consisted of small open-ended cylinders of wire gauze, and the column was operated in such a manner that a thin film of liquid was maintained over the entire surface of the cylinders. This film was produced by flooding the packing before commencing distillation. The packing showed a high fractionating efficiency, a performance of 84 theoretical plates per foot of height having been obtained by Dixon with some columns. It had also a low hold-up per theoretical plate, a low pressure drop and was easily fabricated.

It was shown by Dixon that the efficiency of gauze ring packed columns was dependant on the following factors:

1. Degree of wetting of the packing.
2. Boil-up rate during flooding. It was found that the best results were obtained by flooding at the same boil-up rate as that required during the fractionation itself.
3. Vapour velocity. It was shown that, provided a correct flooding treatment had been given, the efficiency/
the efficiency of the packing was approximately proportional to the reciprocal of the vapour velocity over the packing over a wide range.

4. Ring dimensions. It was shown that the efficiency decreased with increasing ring size and was roughly proportional to the area of gauze surface in a given column.

5. Gauze mesh. It was shown that a coarser mesh than 60x60 gave poor efficiency, and it appeared that this was due to the inability to support a film.

6. Column height and diameter. It was shown that the performance of a column was proportional to the height but diminished as the diameter decreased.

7. Gauze material. Steel and phosphor-bronze gave the same efficiency after flooding except at low vapour velocities, where unsealing of apertures appeared to be more pronounced in the case of the "Staybrite".

8. Inclination of the column from the vertical. It was shown that there was a gradual reduction in efficiency with increasing degree of tilt.

Gauze ring packed columns have been employed exclusively in the laboratory type fractionating equipment used in this investigation, and their efficiency has been shown to justify the claims made by Dixon.

The main/
The main disadvantage with gauze ring packed columns is that, when working at low pressures, the pressure drop is too great. For this type of work the recently developed spinning band (126), and rotary concentric tube (127) columns are very suitable.

The technique of fractional distillation has provided the main basis for this investigation. A high degree of separation has been obtained by this means alone, and in several cases where the pure bases were solid at room temperature, they have been isolated merely by cooling the appropriate finely cut fractions.

b) Separation by means of the Base Salts.

In the majority of the earlier researches on the separation and isolation of the tar bases, the separation and purification of the individual bases were carried out by means of their salts after an initial crude fractional distillation of the base mixture. Several salts have been used for this, including the picrates and the calcium chloride, mercuric chloride and zinc chloride double salts, and the methods have consisted mainly of fractional salting and fractional crystallisation.

In this investigation the method of fractional treatment with picric acid has been employed/
employed in cases where a narrow boiling range cut has been obtained, which has been thought to consist essentially of one component. The method employed consisted of treating a portion of the cut, in solution in ethyl alcohol, with the theoretical amount of picric acid, also dissolved in ethyl alcohol, in three or more separate portions, allowing the salt to crystallise out and filtering after each addition. In this way three or more fractions of picrate were obtained, and it was usually found that the impurities were concentrated in either the first or the last fraction. The purer picrate fractions were then recrystallised to constant melting point from a suitable solvent and finally recrystallised from a different solvent to ensure that a pure picrate of constant melting point had been obtained.

This method was found to be quite suitable for the isolation of the major constituents of most of the cuts examined, without resort to the tedious process of fractional crystallisation, and in the examination of the more complex cuts it was considered that the method of fractional acid extraction would be more efficient than fractional crystallisation of picrates.

c) **Fractional Acid Extraction.**

Processes of extraction are in some respects akin to those of distillation. In the latter case,
two components are separated by fractionation on a volatility basis, each "plate" growing progressively richer in the one or the other component. Likewise in multiple extraction of a solution of two substances there will be a progressive separation determined by relative solubilities. Hunter and Nash (129) have reviewed such methods of fractional extraction, but these methods would be laborious and inefficient when applied to the homologues of pyridine or quinoline owing to the similarity of their distribution coefficients.

Jantzen (78), however, devised a method of fractional acid extraction which he applied most successfully to the separation of quinoline and iso-quinoline homologues in a most thorough investigation of certain higher coal tar base fractions. The theory of the process has been discussed in detail by Jantzen, and it is sufficient here to describe merely the mode of carrying out such a separation, as follows:–

A portion of the mixed bases is neutralised with N. HCl to the end point as indicated by methyl red. Caustic soda solution (10N) is then added in portions equivalent to one tenth of the acid required for neutralisation, and the solution extracted with equal volumes of solvent after each addition, to give ten extracts, S.1 to S.10, containing equivalent amounts/
amounts of bases. The completion of the fractional acid extraction from this point is represented diagramatically in Fig. 2.

**Figure 2.**

Five portions of normal acid, $W.1 - W.5$, each portion being equivalent to one tenth of the acid required for the neutralisation of the bases, are prepared. $W.1$ is shaken with the solvent layer $S.1$, the acid layer drawn off and the solvent layer run to waste. The acid layer $W.1$ is then successively contacted with $S.2$ to $S.10$, thereby giving an acid layer containing a high proportion of the stronger bases, which is made alkaline with caustic soda and extracted with solvent to give $S.11$.

The whole process is then repeated a further four times with the remaining portions of acid, and finally the bases are obtained as ten solutions ranging in order of basicity.

The bases/
The bases are finally recovered from these index solutions, and refractive index measurements of each fraction taken to give an indication of the degree of separation attained. Provided that sufficient separation is attained the pure bases may then be isolated by means of their salts.

The efficiency of the process may be improved by increasing the number of solvent and acid portions.

If many separations were being carried out by this means, however, the process would become rather tedious and time-consuming, and for this reason Jantzen (loc. cit.) has designed various columns etc. by means of which the process may be carried out more easily. For the purpose of this investigation it has not been found necessary to construct any such column.

\[d\] Miscellaneous Methods.

Pyridine homologues which are substituted in the \(\alpha\)- or \(\gamma\)-positions react with cyclic aldehydes to yield condensation products which are solid and non-volatile in steam. This reaction, which usually leads to an equilibrium mixture, has been found to proceed to completion when applied to a mixture of 3- and 4-picolines and 2,6-lutidine. The 3-picoline does not itself react, but acts as a catalyst to the reaction/
reaction (46). This has provided a means of isolation of 3-picoline from the "β-picoline" fraction of coal tar, but no means has been found for regenerating the free bases from the condensation products of the α- and γ-substituted pyridines.

Cyclic aldehydes also react with 2- and 4-substituted quinolines to yield similar condensation products. It was thought that this might provide a convenient method for the identification and semi-quantitative estimation of the 2- and 4-substituted quinoline homologues, provided that the melting points of the various pure condensation products were known. This method, however, did not seem so promising when it was found that the great bulk of the poly-substituted quinolines present in the coal tar base mixture was substituted in the 2-position, and that even in close-cut fractions the occurrence of more than one quinoline homologue substituted in the 2-position was very probable.

Another possible application of this condensation reaction is as a means of getting rid of the quinolines substituted in the 2- and 4-positions, thereby either proving the absence of quinoline homologues not substituted in these positions, or else obtaining a mixture richer in the homologues not substituted in these positions, from which the pure components might then be isolated more easily. Unfortunately, insufficient time was available to explore/
explore this possibility.

Chromatographic absorption is another mode of separation which might find application in the study of the coal tar bases, although very little work appears to have been carried out so far.

Kondo (130) describes the separation of pyridine and 2-methylpyridine by adsorption on an alumina column, and it is possible that this method might be applicable to the higher homologues also.

Walker (131), using the more modern method of paper chromatography in the study of the coal tar bases, revealed the presence of pyridine, 2-methylpyridine, 2:6-dimethylpyridine and 2:4:6-trimethylpyridine. The method of separation was by ascending development, using a solvent prepared by shaking together equal volumes of butyl alcohol and 2N.HCl, discarding the aqueous layer and adding a small amount of methyl red.

It is felt, however, that the method of ion-exchange chromatography would afford a better means of separation than either of the above chromatographic techniques, as it would take advantage of the differences in the relative strengths of the bases. This method would, in effect, be very similar to Jantzen's method of fractional acid extraction. J. Idris Jones, in a study of the by-products/
by-products from the hydrogenation of pyridine with Raney Nickel (132), was able to separate N-n-amyl-piperidine from a mixture containing similar bases by means of a selective elution from an ion-exchange column, the resin being of the sulphonated cross-linked polystyrene type. It is possible that a good separation of pyridine or quinoline homologues might be achieved by a method similar to this, but insufficient time was available to explore this possibility.
CRUDE COAL TAR (1000 parts by weight)

Other Oil Fractions
- Naphthalene Oil (85.7) (Acid Extraction)
  - Naphthalene Oil Bases (1.54)

Benzol Absorbing Oil (79.5) (Acid Extraction)
- Benzol Absorbing Oil Bases (1.59)

DISTILLATION IN THE 20-GALLON STILL

A-Fractions (50°C Cuts)
B-Fractions (50°C Cuts)

DISTILLATION IN THE 30-PLATE COLUMN

C-Fractions (25 Shortrange Cuts)
- C2-C7

D-Fractions (50 Shortrange Cuts)
- C19(0.008) D20&D21(0.033) D27&D28(0.032) D44&D45(0.027) D46(0.025) D47(0.026) D48-50(0.044)

DISTILLATION IN THE 100-PLATE COLUMN

Quantitative estimates 1E Fractions of the lower pyridine homologues

1E Fractions
- 2:4:5-Trimethylpyridine
- 2:3:4-Trimethylpyridine
- 2:3:4:6-Tetramethylpyridine

2E Fractions
- 3-Methylisoquinoline

3E Fractions

4E Fractions

5E Fractions

6E Fractions

7E Fractions

8E Fractions

2:7-Dimethylquinoline

2:3-, 2:4 and 2:5-Dimethylquinolines.
PROCEDURE. (See Flow Sheet)

The procedure adopted for this investigation may be summarised by the following five stages:

1) Fractionation of both the Naphthalene Oil crude bases and the Benzol Absorbing Oil crude bases, separately, in the 20 gallon still made available by Messrs. Midland Tar Distillers Ltd. The purpose of these distillations was to free the volatile bases from water and pitch, and to provide suitable charges for the "30-plate" column by taking 5°C. cuts.

2) Fractionation of each of these 5°C cuts in the "30-plate" column, thus obtaining weight distribution balances for both the Naphthalene Oil Bases and the Benzol Absorbing Oil Bases, and reasonably close-cut fractions of the bases.

3) Subjection of several of the higher of these fractions to further fractionation in the "100-plate" column, thereby obtaining cuts suitable for the isolation of pure bases.

4) Separation and purification of the individual components from these close-cut fractions by methods referred to before.

5) Identification of the individual bases isolated. This was generally accomplished by comparison of their physical properties and the melting points of their derivatives with recorded data, and where possible by mixed melting points and comparison of infra-red absorption spectrograms.
FIGURE 3.

20 GALLON BATCH STILL.
APPARATUS.

20-Gallon Still.

The author is indebted to Messrs. Midland Tar Distillers Ltd. for permission to use the 20-gallon still in their works at Oldbury. This still was used for the initial fractionation of the crude tar bases, and was operated either at atmospheric pressure or under reduced pressure as required.

The following is a brief description of the plant and a sketch is shown in Figure 3.

The boiler consists of a cylindrical steel vessel (18" x 2') with six steel tubes running through the lower half, heating of the charge being carried out by six 2Kw. electrical heaters which are contained in these tubes. To the top of the boiler are fitted a filling funnel and a vapour up-riser pipe. This pipe, to which a manometer is fitted for use when operating at reduced pressures, is in the form of a right-angled curve which joins the foot of the fractionating column at the side.

The fractionating column is in the form of a steel tube, 3 inches in diameter and approximately 6 feet in length, and is packed with 1/4 inch diameter Raschig rings. To the dished bottom of this column is/
is fitted with a liquid return tube which returns the reflux liquid to the boiler. To the top of the column is fitted a pipe through which the hot vapours rise to the condenser.

The condenser is of the tubular water-cooled type with a weir at the bottom. Into this weir two tubes are fitted. The first tube, which protrudes a little distance into the weir, is the liquid return line and contains a sight glass for the purpose of obtaining an approximation to the reflux rate. The second tube, which is the take-off line, is fitted flush with the foot of the weir and has a steel needle-type valve for controlling the take-off rate. To the top of the condenser is fitted a tube which connects up with the receiver assembly and with the vacuum line.

The boiler, column and vapour and return lines are lagged with a casing of 1 inch of magnesia and 1 inch of "Stellite".

The receiver assembly consists of a steel vessel, in the line, and a Buchner flask with appropriate connections to the take-off, vacuum line and overhead. These connections are shown clearly in Figure 3.

When working under reduced pressure, the vacuum is maintained by a "Speedivac" pump and is variable through an air bleed. The vacuum line also contains/
contains a stainless steel buffer-vessel and a small catch-pot.

The column-head temperature is read by means of a simple mercury in glass thermometer which is situated in a pocket at the top of the fractionating column. Three further thermometers are situated in pockets spaced regularly along the length of the column, their purpose being to measure the temperature gradient in the column.

This still proved quite satisfactory for the task which it was called upon to perform, but it possessed the disadvantage of having no reliable means of measuring the rate of reflux, the sight-glass providing only a rough guide. Thus it was possible that the still was not always running at a constant reflux ratio and, consequently, the fractionating efficiency of the column may have varied slightly during the distillations.

No figures were available as to the fractionating efficiency of this column but it was thought that this would be equivalent to between 5 and 10 theoretical plates.

30-Plate, I.C.I. Gauze-Ring Packed, Column.

This column, based on similar ones in use in/
in the laboratories of the Anglo-Iranian Oil Co. Ltd.
and on Institute of Petroleum Specification 25/44, was supplied as a complete unit by Messrs. Griffin
and Tatlock Ltd., but had been extensively modified by Messrs. Benzie and Milne (24).

The following is a brief description of the still and a sketch is shown in Figure 4.

The still-pot is a 5 litre heavy-walled flask with a B.34 socket on the neck and a B.19 radial neck for a thermocouple. It is supported on an asbestos-wound ring which is supported above a heavy Sindanyo shelf which carries a 1 Kw. heater, lying directly below, but not touching the flask. This heater is controlled through a Variac transformer. The Sindanyo shelf is in turn supported by three springs and brackets to a tripod whose height is adjustable by a chain and screw mechanism. The flask, heater, etc. are enclosed in a double-walled lagging box which is lined with asbestos and packed with glass-wool.

To the neck of the boiler flask is connected a reflux-meter of the type designed by Messrs. Anglo-Iranian Oil Co. Ltd., with B.34 cone and socket, and operated by an external magnet.

The column itself is a heavy-walled glass tube having an internal diameter of 36 mm. and a packed/
packed length of 4 feet. It is surrounded by a lagging shield which consists of a brass tube, wound with three sections of resistance wire which serve as heaters and are supplied independently through three Variac transformers. A layer of "Versil" glass-wool is wound over these heater windings and the whole is bound with tape and painted with aluminium paint. The shield is supplied with three thermocouples for measurement of the temperature gradient in the column.

The still-head is of the simple weir type with twin internal spiral condensers, and take-off is through a grooved stop-cock to two 250 mls. graduated receivers. These receivers have connections to the vacuum system, as shown in Figure 4, which make it possible to empty and re-evacuate the lower receiver without affecting the pressure in the rest of the system.

The column is packed with 1/4" x 1/4" I.C.I. Staybrite rings of 60-mesh square weave gauze. The static hold-up has been estimated from figures provided by Messrs. I.C.I. Ltd. (133) for 2:2:4-trimethylpentane and is approximately 30gms. No figures are available from which the dynamic hold-up can be calculated, but this is believed to be correspondingly low.

The efficiency of this column, after pre-flooding and running to equilibrium for four hours, was estimated by Benzie and Milne (24) using Benzene /carbon tetrachloride/
carbon tetrachloride as the test mixture (134) and their results are shown below.

<table>
<thead>
<tr>
<th>Boil-up Rate (mls/hour)</th>
<th>Theoretical Plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,200</td>
<td>20.0</td>
</tr>
<tr>
<td>3,600</td>
<td>22.0</td>
</tr>
<tr>
<td>2,000</td>
<td>26.2</td>
</tr>
<tr>
<td>1,500</td>
<td>33.5</td>
</tr>
<tr>
<td>785</td>
<td>48.8</td>
</tr>
</tbody>
</table>

During the present investigation this column was run at a boil-up rate of 1,500 mls/hr., and at a reflux ratio of about 30:1.

Vacuum System: The vacuum system for this column was completely automatic, and variation from the set value was negligible over a period of 24 hours, provided that there was no great change in room temperature. The sensitivity of control of the system varied somewhat according to the working pressure, and at 100 mm. Hg. was less than 0.5 mm., which was sufficiently accurate for the distillations carried out in the column.

The system of control was substantially that described by Coulson and Warner (135), and the following is a description of its operation.

The cylindrical steel buffer vessel (A) has a capacity of about 5 litres, and is connected to a mercury manostat (a) which controls a "Speedivac" pump through a "Sunvic" Hot-Wire Vacuum Switch. The pressure in this primary buffer vessel is reduced to/
to about 20 mm. Hg. below the working pressure, and the manostat (a) is closed. Further reduction of pressure breaks the mercury contact in the manostat, thus breaking the control circuit of the Hot-Wire Vacuum Switch and shutting off the pump. The slight time delay which is associated with this type of relay protects the pump from too frequent stopping and starting and allows the pressure in the primary buffer vessel to vary within certain limits.

The pressure in the secondary buffer (B) and the rest of the system is then reduced to the required value, and the mercury-sealed manostat (b) is closed. Thus, when air leaks into the system, the mercury contact in the manostat (b) is made, causing a momentary opening of the solenoid valve which connects the primary and secondary buffer vessels, and bringing the pressure back to the set value.

The solenoid valve (British Thermostat Co. Ltd.) operates on 230 volts A.C. and, to avoid fouling of the mercury in the manostat (b), is controlled through an electronic valve relay, of the type described by Coulson and Warner (135), which operates a miniature telephone-type relay, which in its turn operates a heavy battery relay controlling the supply of current to the solenoid valve.

Since this column was left on total reflux unattended/
unattended overnight, it was considered advisable to arrange for automatic cutting off of the power supply in the event of a failure in the vacuum system or condenser water supply. This was arranged by connecting an insensitive manostat (c) (sensitivity - about 2 mm. Hg.) to a "trip-box". Thus, if the tap on the manostat were closed when working at the required pressure, a mercury contact would be made if the pressure in the system varied by more than about 2 mm. Hg. and this, working the relay system of the "trip-box", would cut off all power to the panel. The water control, which was attached to the condenser outlet and consisted of a counter-balanced perforated bucket through which the water flowed, worked in the same way, a mercury contact being made when the water supply failed.

All ground-glass joints in this system were secured with Audco Lubricant No. 657. No lubricant was found for the stop-cocks which would resist the powerful solvent effects of the pyridine or quinoline bases. Apiezon Grease M was used throughout the present investigation, but the bases soon dissolved this away, and the stop-cocks were then apt to leak. The most effective method found for preventing these leakages was to pack the outside of the cocks with some such lubricant as Audco Lubricant No. 356.
Figure 5.

100-plate column
I.C.I. gauge-reading packed
This column, which was almost entirely constructed by Messrs. Benzie and Milne (24) and was modified during the present investigation, was very similar in general details to the 30-plate column.

The following is a description of the still and a sketch is shown in Figure 5.

The still consists of a 2 litre heavy-walled flask with a B.24 socket on the neck. It is supported in an asbestos heating mantle ("Isomantle") which completely surrounds the flask. The lower half of the Isomantle is contained in an aluminium frame which is fixed to a heavy Sindanyo shelf. This shelf is supported by three springs and brackets to a tripod whose height is adjustable by a chain and screw mechanism.

The isomantle has been adopted as a means of heating the still-pot of this column, in preference to the radiator type of heater, as it lessens the risk of serious bumping. It also lessens the risk of a fire resulting from a broken flask. The heat input to the Isomantle is controlled through a Variac Transformer.

To the neck of the flask is fitted a ball and socket reflux-meter with B.24 cone and socket. Between this meter and the column itself is fitted a magnetic/
a magnetic valve of the type designed by Messrs. I.C.I. Ltd. (147), which consists of a short length of glass tubing with a B.24 joint at either end, in which is situated a simple "butterfly" type valve containing a short bar magnet and operated by an external system of movable magnets. The purpose of this valve is to limit the return of reflux liquid when flooding the column prior to carrying out a distillation. Thus, when the valve is closed, the reflux liquid builds up from the bottom of the column until the entire packing is submerged; then on gradually opening the valve, the reflux liquid drains back into the flask at a controlled rate while a steady reflux is maintained in the column-head.

The column itself consists of two sections of 20 mm. precision bore Pyrex tubing fitted with B.24 cone and socket joints. Each section is packed for a length of 82.5 cms. with 1/16" x 1/16" I.C.I. Staybrite rings of 100-mesh square weave gauze. This gives a total packed length of 165 cms. The packing is supported at the bottom of each section with a spiral of nichrome wire which rests on a slight constriction of the column wall, and a few glass rings are placed immediately above these spirals so that the small gauze rings do not fall through. The packing is held in position at the top of each section with a circle of Staybrite gauze fitting tightly just below the joint.
Each column section is provided with an electrically wound compensating lagging, consisting of a length of 1.25\" bore "Fibreglass" steam pipe lagging 0.75\" in thickness, covered with three thicknesses of asbestos paper, on which is wound 100 turns of "Brightray" nichrome tape with a resistance of 11 ohms per yard, making a total resistance of about 250 ohms. The turns of the winding are spaced more closely towards the top and bottom ends of the upper and lower sections respectively to compensate for end losses. The windings are held in position by a further layer of asbestos paper, hardened with a coating of sodium silicate solution, and by a close-fitting outer layer of 1.5\" Fibreglass lagging of 6\" external diameter.

At the centre of each lagging section is situated a differential thermocouple consisting of two copper leads joined by a short constantan lead. One junction of each thermocouple is attached to a small sheet copper collecting plate on the inner wall of the lagging, adjacent to the wall of the column, while the other junction, the E.M.F. of which opposes that of the first, is attached to a similar collecting plate in close thermal contact with, but electrically insulated from, the winding. Using a sensitive galvonometer with these thermocouples, any lateral heat flow is immediately indicated by a deflection, the direction of which indicates whether heat is flowing/
flowing to or from the column. Thus close adiabatic conditions may be easily maintained.

The lagging heaters are independently controlled through two Variac transformers, and the heat input is adjusted so that there is a slight but insignificant loss of heat from the column.

The still-head is of the tipping-bucket type as designed in the laboratories of Messrs. Anglo-Iranian Oil Co. Ltd. (136). It is a total reflux, variable take-off head. The reflux liquid, after returning from the main condenser, passes through a small auxiliary condenser to a small glass bucket, the overflow of which is returned to the column. The take-off is effected by an external solenoid which, when energised, attracts a small counterweight which is attached to the bucket and ejects a measured volume of liquid into the receivers. The rate of take-off is determined by the setting of a timer which controls the supply of current to the solenoid.

The vapour up-riser on this head is provided with a silvered vacuum jacket which is fitted with a Fibreglass lagging supplied with a heater winding and differential thermocouple to prevent excessive condensation of vapour when dealing with high-boiling fractions. The column-head temperature is read by means of a wide scale mercury thermometer for which a pocket is provided in the head. The main condenser is/
is of the double-surface spiral type and is fitted with a vacuum jacket.

This still-head proved very satisfactory in this present investigation, the absence of stop-cocks providing a decided advantage for vacuum operation. It possessed the disadvantage, however, that, when materials were distilling over which were solid at room temperature, the solid was apt to clog the liquid return lines. This difficulty was alleviated by providing these lines with heater windings so that, when any solid began to appear, the auxiliary condenser water could be drained and the heaters turned on.

The receiver assembly is very similar to that of the 30-plate column and is shown in Figure 3.

To eliminate the difficulties due to variation in the mains voltage supply which were experienced with the 30-plate column, the power supply to this column was fed through a constant voltage transformer (Advance Components Ltd.). This transformer has proved very useful, maintaining, for the most part, a constant output of 230 volts but, at times, "load shedding" has been so severe that the transformer has not been able to cope with the variations. It has, therefore, been found necessary to keep a close watch on the column whenever "load shedding" was liable to occur.
Throughout the present work this column has been operated at reduced pressure in order to avoid the danger of thermal decomposition of the bases, due to prolonged heating, as the time of distillation for a normal batch of 1 Kg. was about ten days and all the bases distilled boiled over 180°C / 760 mm. Hg.

The vacuum system of this column was very similar to that of the 30-plate column but followed more closely the system described by Coulson and Warner (135). It was thought necessary to describe here only the differences between this system and that of the 30-plate column as follows.

The low pressure buffer vessel (A, Fig. Z), manostat (a) and the pump serve both systems, and if the two stills are to be operated simultaneously at different pressures, the pressure in A is maintained at about 20 mm. below the lower working pressure.

The place of the buffer vessel B is taken by a large bolt-head flask, enclosed for safety in a metal casing. The solenoid valve is replaced by a flap valve of the type described by Coulson & Warner. This valve is supported inside the 10 litre buffer flask by a rubber bung through which passes the connection between the buffer vessel A and the valve and vacuum connections to still-head receiver system. To protect the valve from the possibility of damage due/
due to accidental flooding, a 2 litre catch-pot (bolt-head flask) is placed in the line between the 10 litre flask and the still. This gives a total effective buffering volume of approximately 12 litres, which is maintained at the still operating pressure and thus reduces the effect of leakages.

The manostat b is replaced by a sulphuric acid manostat of the type described by Hershberg and Huntress (137) which is more sensitive than the simple mercury type. This manostat can be rotated by a pivot and screw mechanism for ease in making minor adjustments. It is connected to the 10 litre flask via a small safety trap and, to eliminate the effect of ambient temperature, is enclosed in a thermostatically controlled box (Sunvic thermostat, type T.S.3) whose temperature is maintained at a few degrees above room temperature by means of a heater consisting of a 25 Watt lamp.

The electrical relay system between the sulphuric acid manostat and the flap valve consists of an electronic valve relay (135) which operates a 40 volt local battery circuit energising the coil on the flap valve.

The sensitivity of this system is of the order of 0.1 - 0.2 mm. Hg. at 100mm. Hg. operating pressure, and the useful working range of the still extends to about 20 mm. Hg., below which the pressure drop/
drop due to the column packing cancels out the advantage of lower working pressures.

As this column was run unattended overnight it was necessary to install safety cut-outs on the vacuum system and condenser water supply similar to those on the 30-plate column.

Automatic Receiver Changing.

Particulars about the construction of various types of automatic receiver changers have been published from time to time. The installation of such a device on the 100-plate column, if practicable, would have resulted in reducing greatly the time required for a distillation, as the still could then have been run continuously. It was considered impracticable, however, as it would have necessitated the use of an automatic temperature recorder, and no such instrument was available. There would also have been difficulties due to clogging of the lines with the solids distilling over and to probable leakages in the vacuum system.

During the latter part of this investigation a "Tektor Proximity Switch" (Fielden Electronics Ltd.) was installed on the 100-plate column, and by means of this device it was sometimes possible to leave the still taking off overnight with the Proximity Switch stopping the take-off at any required temperature.
The operation of this device was as follows: -

A thin strip of metal was secured to the column-head thermometer at the point where the cut was to be terminated. The metal strip was then connected to the cable of the Proximity Switch and the latter connected to the power supply of the solenoid on the still-head, turned on and set. Distillation was then allowed to continue, and when, owing to rise in the column-head temperature, the mercury thread in the thermometer rose up to the metal strip, it caused the capacity of a condenser, of which the metal strip formed one plate, to alter, and this, operating through a series of relays incorporated in the Proximity Switch, shut off the power to the solenoid, thereby putting the still on to total reflux.

Efficiency of the 100-Plate Column.

The following data for the column were calculated from figures supplied by Messrs. I.C.I. Ltd. (133).

Static Hold-up. - This was calculated from data given for the hold-up of 100 gms. of 1/16" 100-mesh Staybrite gauze rings using 2:2:4-trimethylpentane and draining for 10 minutes. It was found to be 21.2 gms.

Dynamic Hold-up. - The dynamic hold-up varies with the boil-up rate and using the figures given for 2:2:4-trimethylpentane an approximation was obtained of 84 gms. at 1000 mls./hr.
Theoretical Plates. - Benzie & Milne (24) obtained the following results for the efficiency of this column by calculation from figures supplied by Messrs. I.C.I. Ltd.

<table>
<thead>
<tr>
<th>Boil Up Rate (Gms./hr)</th>
<th>Theoretical Plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>136</td>
</tr>
<tr>
<td>1000</td>
<td>112</td>
</tr>
<tr>
<td>1200</td>
<td>95</td>
</tr>
<tr>
<td>1400</td>
<td>83</td>
</tr>
</tbody>
</table>

The efficiency of this column was too high to permit of its being estimated by the common test mixture of benzene - carbon tetrachloride. It can be measured, however, using the system of n-heptane - methylcyclohexane (138), and this was carried out as follows:

The still-pot was charged with a mixture of n-heptane and methylcyclohexane whose composition was calculated so that, when the still was running, the molar composition of the overheads would be the opposite of that of the contents of the still-pot. This was calculated using the figures of Leckey and Ewell (124), and on the assumptions that the still had an efficiency of approximately 100 theoretical plates, that the total hold-up was 100gms., and that the molar composition of the hold-up was 1:1.

A sampling tube which dipped well below the surface of the liquid was inserted in the still-pot.
The column was then flooded and the still run to equilibrium at the required boil up rate. When equilibrium had been attained samples were taken simultaneously from the overhead by means of the tipping-bucket, and from the still-pot by applying vacuum to the sampling tube.

The refractive indices of these samples were determined and hence the mole fractions of the two components were found from the tables (124). The plate efficiency was then calculated from the tables provided.

The plate efficiency of this column was determined at three different boil up rates, and the results are shown below.

<table>
<thead>
<tr>
<th>B.U.R.</th>
<th>Mole fractions of n-heptane</th>
<th>Theoretical</th>
<th>Plates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Still-head</td>
<td>Boiler</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>0.72</td>
<td>0.07</td>
<td>50</td>
</tr>
<tr>
<td>1200</td>
<td>0.81</td>
<td>0.015</td>
<td>80</td>
</tr>
<tr>
<td>1000</td>
<td>0.95</td>
<td>0.015</td>
<td>101</td>
</tr>
</tbody>
</table>

It can be seen that the values obtained were lower than those obtained by calculation, but these practical results confirm that at the boil up rate of 900-1000mls./hr. used throughout the present investigation, a fractionating efficiency equivalent to at least 100 theoretical plates will have been obtained.
EXPERIMENTAL.

A-Distillations.

Initial Fractionation of the Naphthalene Oil Bases.

180 litres of the crude Naphthalene Oil Bases were distilled in the 20-gallon still of Messrs. Midland Tar Distillers Ltd. in three batches of 54 litres, 54 litres and 72 litres as follows:

The measured volume of bases was charged to the still, and a suitable number of the still-pot heaters turned on. When the bases were refluxing steadily, and an even temperature gradient had been obtained in the fractionating column, the take-off line was opened and the take-off rate adjusted to about 2 litres per hour. Distillation was then continued until all the "hydrate" boiling below 110°C. had distilled. The still was allowed to cool, the "hydrate" treated with solid caustic soda and the liberated dry bases returned to the still.

The heaters were then turned on again, and when equilibrium had been attained in the column, the take-off line was re-opened and the take-off rate adjusted to about 2 litres per hour. Frequent readings of temperature and volume were taken, and the/
the distillate was divided up into five degree fractions. When the column-head temperature reached 220°C., the still was closed down and the residue run off, while still warm, and weighed. Similar cuts from the three distillations were bulked together.

Throughout these three A-distillations, which were all carried out in a precisely similar manner, an attempt was made to maintain a steady reflux rate but this may not always have been achieved as the only method of measuring the reflux rate was by a sight-glass on the liquid return line from the condenser.

This still was run for sixteen hours per day, and during the remaining eight hours, when it had to be left unattended, one or two heaters were turned off so that the bases were refluxing about half way up the column. This avoided loss of time in re-starting.

The results of these distillations are shown in Table I (overleaf).

Graph 1 shows the weights, densities and refractive indices plotted against the mid-points of the cuts, and indicates that a fair degree of fractionation was obtained in these distillations.
Graph 1.

NAPHTHALENE OIL BASES. (A-Distillations)

- Weight/50°C.
- $D_{20}$
- $n_{25}^D$
- $T_{60}$
Table I. (Naphthalene Oil Bases, A-Distillations)

<table>
<thead>
<tr>
<th>Distn Range of Fraction</th>
<th>Volumes</th>
<th>Total Volume</th>
<th>$D_2^0$</th>
<th>$H_2^5$</th>
<th>Total Weight</th>
<th>Weight % of the Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Charge A 54L</td>
<td>Charge B 54L</td>
<td>Charge C 72L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>4.75L.</td>
<td>3.75L.</td>
<td>5.90L.</td>
<td>14.40L.</td>
<td>1.000</td>
<td>14.40Kg</td>
</tr>
<tr>
<td>0 - 110°</td>
<td>4.70</td>
<td>4.28</td>
<td>6.20</td>
<td>15.18</td>
<td>0.999</td>
<td>1.4295</td>
</tr>
<tr>
<td>110 - 135</td>
<td>2.35</td>
<td>1.98</td>
<td>2.25</td>
<td>6.58</td>
<td>0.967</td>
<td>1.4932</td>
</tr>
<tr>
<td>135 - 140</td>
<td>3.15</td>
<td>2.85</td>
<td>2.95</td>
<td>8.95</td>
<td>0.946</td>
<td>1.4987</td>
</tr>
<tr>
<td>140 - 145</td>
<td>0.80</td>
<td>2.87</td>
<td>4.88</td>
<td>8.55</td>
<td>0.942</td>
<td>1.4990</td>
</tr>
<tr>
<td>145 - 150</td>
<td>1.41</td>
<td>1.16</td>
<td>3.17</td>
<td>5.74</td>
<td>0.941</td>
<td>1.4990</td>
</tr>
<tr>
<td>150 - 155</td>
<td>2.68</td>
<td>1.59</td>
<td>2.90</td>
<td>7.17</td>
<td>0.938</td>
<td>1.4990</td>
</tr>
<tr>
<td>155 - 160</td>
<td>3.97</td>
<td>3.85</td>
<td>2.00</td>
<td>9.82</td>
<td>0.934</td>
<td>1.4990</td>
</tr>
<tr>
<td>160 - 165</td>
<td>2.65</td>
<td>2.22</td>
<td>5.30</td>
<td>10.17</td>
<td>0.931</td>
<td>1.4995</td>
</tr>
<tr>
<td>165 - 170</td>
<td>1.56</td>
<td>2.20</td>
<td>2.07</td>
<td>5.83</td>
<td>0.933</td>
<td>1.5030</td>
</tr>
<tr>
<td>170 - 175</td>
<td>2.32</td>
<td>3.22</td>
<td>2.65</td>
<td>8.19</td>
<td>0.943</td>
<td>1.5133</td>
</tr>
<tr>
<td>175 - 180</td>
<td>2.02</td>
<td>1.45</td>
<td>3.00</td>
<td>6.47</td>
<td>0.951</td>
<td>1.5220</td>
</tr>
<tr>
<td>180 - 185</td>
<td>1.05</td>
<td>1.44</td>
<td>1.55</td>
<td>4.04</td>
<td>0.958</td>
<td>1.5270</td>
</tr>
<tr>
<td>185 - 190</td>
<td>2.15</td>
<td>1.14</td>
<td>1.00</td>
<td>4.29</td>
<td>0.951</td>
<td>1.5317</td>
</tr>
<tr>
<td>190 - 195</td>
<td>1.80</td>
<td>1.87</td>
<td>2.60</td>
<td>6.27</td>
<td>0.968</td>
<td>1.5382</td>
</tr>
<tr>
<td>195 - 200</td>
<td>1.92</td>
<td>1.90</td>
<td>3.20</td>
<td>7.02</td>
<td>0.973</td>
<td>1.5455</td>
</tr>
<tr>
<td>200 - 205</td>
<td>1.10</td>
<td>1.00</td>
<td>1.45</td>
<td>3.55</td>
<td>0.979</td>
<td>1.5500</td>
</tr>
<tr>
<td>205 - 210</td>
<td>0.67</td>
<td>0.70</td>
<td>1.40</td>
<td>2.84</td>
<td>0.981</td>
<td>1.5532</td>
</tr>
<tr>
<td>210 - 220</td>
<td>0.85</td>
<td>1.20</td>
<td>1.55</td>
<td>3.60</td>
<td>0.990</td>
<td>1.5590</td>
</tr>
<tr>
<td>Residue</td>
<td>30.5 lb</td>
<td>31.5 lb</td>
<td>40.5 lb</td>
<td></td>
<td></td>
<td>47.80</td>
</tr>
</tbody>
</table>
B-Distillations.

Initial Fractionation of the Benzol Absorbing Oil Bases.

162 Litres of the crude Benzol Absorbing Oil Bases were distilled in the 20-gallon still in three batches of 54 litres, as follows:

The measured volume of bases was charged to the still and the still run to equilibrium. When equilibrium had been attained the take-off line was opened and the take-off rate adjusted to about 2 litres per hour. Distillation was then continued, taking frequent readings of temperature and volume, and dividing the distillate up into suitable cuts: The first cut was taken up to 150°C., the second from 150 -170°C., and from this point to 240°C. 5°C. cuts were taken. When the column-head temperature reached 240°C. the still was shut down, allowed to drain and the residue run to storage while still hot.

When all three batches had been distilled to 240°C., the three residues were re-charged to the still and distilled as follows, at reduced pressure to reduce the risk of thermal decomposition.

All the stop-cocks being in their appropriate positions, the vacuum pump motor was turned on and the system evacuated to 10" Hg. The air-bleed valve was set at a position to maintain the pressure at/...
at this level and the heaters turned on. When the bases were refluxing steadily and an even temperature gradient had been obtained in the fractionating column, the take-off line was opened and the take-off rate adjusted to 2 litres per hour. Distillation was then continued at the same pressure and taking 5°C. cuts up to 220°C./10⁻² Hg. At this point the still was shut down and an attempt made to drain off the residue while it was still hot. The residue had set hard, however, and had to be extracted with acetone. This extraction still left quite an amount of solid matter in the still-pot which could not be extracted.

The results of these distillations can be seen in Table 2.(overleaf). Graph la shows the weights, densities and refractive indices of the cuts plotted against the mid-points of the cuts.

It will be noted that the losses in these distillations are very high. This is partly due to the fact that coking took place and the weights found for the residues were low as these did not include the solid material which could not be discharged from the still. A contributary factor was that the still had to be discharged, cleaned and re-charged at one point in the distillations as Messrs. Midland Tar Distillers Ltd. required the use of their still for another purpose.
Graph Ia.

BENZOL ABSORBING OIL BASES. (B-Distillations.)

Weight % of charge distilling per 5°c.

- \( \sum_{20} \)
- \( \Sigma_{4} \)
- \( \Sigma_{2.5} \)

MID-POINTS OF 5°C CUTS (ATM. PRESS)
Table 2. (Benzol Absorbing Oil Bases, B-Distillations)

<table>
<thead>
<tr>
<th>Distn Range of Fraction</th>
<th>Volumes Charge 1 54L.</th>
<th>Volumes Charge 2 54L.</th>
<th>Volumes Charge 3 54L.</th>
<th>Total Volume</th>
<th>D20</th>
<th>D40</th>
<th>Total Weight of the Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>97 - 150°</td>
<td>5.36L.</td>
<td>5.36L.</td>
<td>4.72L.</td>
<td>16.46L.</td>
<td>0.997</td>
<td>1.4208</td>
<td>16.40Kg 9.39</td>
</tr>
<tr>
<td>150 - 170</td>
<td>2.90</td>
<td>1.33</td>
<td>2.98</td>
<td>7.21</td>
<td>0.942</td>
<td>1.4989</td>
<td>6.80 3.89</td>
</tr>
<tr>
<td>170 - 175</td>
<td>0.75</td>
<td>0.68</td>
<td>0.50</td>
<td>1.93</td>
<td>0.940</td>
<td>1.5042</td>
<td>1.81 1.04</td>
</tr>
<tr>
<td>175 - 180</td>
<td>0.68</td>
<td>0.98</td>
<td>0.35</td>
<td>2.01</td>
<td>0.940</td>
<td>1.5064</td>
<td>1.89 1.08</td>
</tr>
<tr>
<td>180 - 185</td>
<td>0.80</td>
<td>1.33</td>
<td>1.78</td>
<td>3.91</td>
<td>0.944</td>
<td>1.5107</td>
<td>3.69 2.11</td>
</tr>
<tr>
<td>185 - 190</td>
<td>0.52</td>
<td>0.40</td>
<td>1.20</td>
<td>2.12</td>
<td>0.947</td>
<td>1.5138</td>
<td>2.01 1.15</td>
</tr>
<tr>
<td>190 - 195</td>
<td>0.70</td>
<td>0.60</td>
<td>0.57</td>
<td>1.87</td>
<td>0.952</td>
<td>1.5167</td>
<td>1.78 1.02</td>
</tr>
<tr>
<td>195 - 200</td>
<td>1.20</td>
<td>1.70</td>
<td>1.55</td>
<td>4.45</td>
<td>0.957</td>
<td>1.5214</td>
<td>4.26 2.44</td>
</tr>
<tr>
<td>200 - 205</td>
<td>1.35</td>
<td>1.10</td>
<td>1.05</td>
<td>3.50</td>
<td>0.963</td>
<td>1.5260</td>
<td>3.37 1.93</td>
</tr>
<tr>
<td>205 - 210</td>
<td>1.70</td>
<td>2.18</td>
<td>1.78</td>
<td>5.66</td>
<td>0.970</td>
<td>1.5308</td>
<td>5.49 3.14</td>
</tr>
<tr>
<td>210 - 215</td>
<td>0.65</td>
<td>0.60</td>
<td>0.68</td>
<td>2.13</td>
<td>0.987</td>
<td>1.5366</td>
<td>2.10 1.20</td>
</tr>
<tr>
<td>215 - 220</td>
<td>0.30</td>
<td>0.35</td>
<td>0.77</td>
<td>1.42</td>
<td>0.995</td>
<td>1.5442</td>
<td>1.41 0.81</td>
</tr>
<tr>
<td>220 - 225</td>
<td>0.72</td>
<td>0.45</td>
<td>1.36</td>
<td>2.53</td>
<td>1.025</td>
<td>1.5601</td>
<td>2.59 1.48</td>
</tr>
<tr>
<td>225 - 230</td>
<td>3.70</td>
<td>1.40</td>
<td>1.50</td>
<td>6.60</td>
<td>1.044</td>
<td>1.5785</td>
<td>6.89 3.94</td>
</tr>
<tr>
<td>230 - 235</td>
<td>7.40</td>
<td>5.22</td>
<td>5.31</td>
<td>17.93</td>
<td>1.065</td>
<td>1.5962</td>
<td>19.10 10.93</td>
</tr>
<tr>
<td>235 - 240</td>
<td>6.45</td>
<td>2.50</td>
<td>4.27</td>
<td>13.22</td>
<td>1.077</td>
<td>1.6064</td>
<td>14.24 8.15</td>
</tr>
<tr>
<td>Residue</td>
<td>18.74</td>
<td>23.15</td>
<td>25.07</td>
<td>66.96</td>
<td>8.13</td>
<td>1.081</td>
<td>1.59842</td>
</tr>
<tr>
<td>-190°/10&quot;Hg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.56</td>
<td>1.077</td>
<td>1.6082</td>
</tr>
<tr>
<td>190-195 &quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.83</td>
<td>1.068</td>
<td>1.6065</td>
</tr>
<tr>
<td>195-200 &quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.64</td>
<td>1.063</td>
<td>1.6035</td>
</tr>
<tr>
<td>200-205 &quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.89</td>
<td>1.060</td>
<td>1.6025</td>
</tr>
<tr>
<td>205-210 &quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.22</td>
<td>1.058</td>
<td>1.6025</td>
</tr>
<tr>
<td>210-215 &quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.70</td>
<td>1.057</td>
<td>1.6025</td>
</tr>
<tr>
<td>215-220 &quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>22.25</td>
<td>12.73</td>
<td></td>
</tr>
</tbody>
</table>
C-Distillations.

Second Fractionation of the Naphthalene Oil Bases.

These distillations were carried out in the 30-plate column at a boil up rate of 1500 mls./hr. and a reflux ratio of approximately 30:1.

First of all the size of batch to be used had to be decided as there were two possible alternatives:

1) To take a fixed proportion of the five degree cuts from the A-distillations (e.g. 1/3). This would enable a weight balance to be drawn up simply and without resort to approximations. It would be very inconvenient for working, however, as, taking 1/3 as the proportion, the batch size would vary between approximately 1 and 3 Kg. There would be the additional disadvantage that much time would be consumed in the distillation of the more common cuts (such as the β-picoline fraction), which are of little interest in this investigation, whereas insufficient of the smaller cuts would be obtained, unless the proportion were set at a high level.

2) To take a uniform sample of each of the five degree cuts (e.g. 2 litres). This would complicate the calculation of a weight balance, as each batch could only be distilled down to a residue of about 200 cc., and an approximation would have to be/
be made as to the composition of this residue. It would be very convenient to work, however, as a batch of 2 litres could be completed in exactly one week (approximately 50 hrs. working), and workable quantities of the smaller, though important, cuts would be obtained. It was therefore decided to adopt this latter alternative.

Approximately 2 litre samples of each of the A fractions 1 - 11 inclusive, A.1 having been dried previously with solid NaOH, were distilled at atmospheric pressure in the 30-plate column, as follows:

The charge was weighed into the still-pot along with some tile chips. The heaters were adjusted to give a boil up rate of 1500 mls./hr., as shown by the reflux meter, and an even temperature gradient in the fractionating column, as shown by the thermocouple readings. When this had been attained the column packing was flooded by suddenly applying vacuum to the column. The flooding was then allowed to subside gradually, while maintaining a steady reflux in the column, by slowly releasing the vacuum. The still was allowed to run to equilibrium for three hours.

When equilibrium had been attained, the take-off line was opened and the take-off rate was adjusted to 50 mls./hr. Distillation was then allowed to proceed at this rate, frequent readings being taken of column-head temperature, volume of distillate, thermocouple/
thermocouple readings (indicating the still-pot and column temperatures), Variac settings and boil up rate. The column-head temperatures were corrected to 760 mm. Hg. by the Crafts Equation:

\[
\Delta T = c(273 + t)(760 - p)
\]

where \( \Delta T \) is the correction factor to be added. 
\( c \) is 0.00012 
\( t \) °C. is the observed temperature. 
and \( p \) mm. is the observed pressure.

Cuts were taken to coincide with the distillation flats and those with the same distillation range from different batches were bulked together. The distillations were continued throughout the day, and during the night the still was left on total reflux. Each of the distillations was continued down to a residue of approximately 200 gms., the distillation being stopped, when possible, on a climb in the distillation graph. After draining the column, the residue was weighed and the next batch was weighed in on top of this residue.

As it had been observed during the distillation of the higher boiling fractions, that there had been a tendency for the column-head temperature to fluctuate, and as it was thought that there was a possibility of thermal decomposition of the bases due to the prolonged heating at the high temperatures attained, it was decided to carry out the remainder of the C-distillations at the reduced pressure of 100 mm. Hg.
The procedure for these reduced pressure distillations was precisely similar to the atmospheric pressure distillations, except that the vacuum was set before heating was commenced and flooding was accomplished by momentarily reducing the pressure.

During the first part of the first distillations under diminished pressure, as there was considerable overlap of the five degree cuts from the A-distillations, it was necessary to convert the temperatures to 760 mm. Hg., so that the cuts could be bulked with cuts of the same distillation range from the lower boiling batches. This was achieved by the application of Dühring's Rule, using the figures given by Riley & Bailey (140). The distillation flats acted as a check to this conversion.

In the final batches distillation was only carried as far as 145°C./100mm., as it was considered that there would be some bases boiling around this temperature remaining in the residues from the A-distillations, and no quantitative estimate of their amount was possible.

Finally a quantity of the water azeotrope (C.1) was treated with caustic soda to liberate the bases which were then dried over solid caustic soda and subjected to a distillation at atmospheric pressure in the 30-plate column down to the smallest possible/
DISTILLATIONS LC, 2C, 3C & 4C.

(Carried out in the 30-plate column at atmospheric pressure.)
possible residue. This residue was then assumed to consist entirely of the cut C.7, as the distillation was still on this flat when closed down.

The following are the weight balances obtained for the individual batches, the cuts being as follows:

C.1. 0-115°  2. 115-117°  3. 117-129°  4. 129-130°
C.17 183-186°.


Distillations :

1.C. Charge 1620gms.
Fract. No. 1. 2. 3. 4. 5. 6. 7.
Weight 115. 342. 184. 220. 233. 92. 250 gms.

2.C. Charge 2338gms.
Fract. No. 1. 2. 3. 4. 5. 6.
Weight 411. 213. 201. 591. 242. 65 gms.

Fract. No. 1. 2. 3. 4. 5. 6. 7.
Weight 59. 9. 254. 357. 73. 180. 1474 gms.

4.C./
DISTILLATIONS 8C, 9C, 10C & 11C.

(Carried out in the 30-plate column at atmospheric pressure.)
Graph 3

DISTILLATIONS 5C, 6C, & 7C.

(Carried out in the 30-plate column at atmospheric pressure.)
<table>
<thead>
<tr>
<th>Fract. No.</th>
<th>Weight</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>33.6</td>
</tr>
<tr>
<td>2</td>
<td>30.5</td>
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<tr>
<td>3</td>
<td>30.2</td>
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<tr>
<td>5</td>
<td>12.9</td>
</tr>
<tr>
<td>6</td>
<td>7.5</td>
</tr>
</tbody>
</table>
DISTILLATIONS 12C, 13C, 14C A15C.
(Carried out in the 30-plate column at a pressure of 100 mm. Hg.)
<table>
<thead>
<tr>
<th>Charge</th>
<th>Previous Residue</th>
<th>Fractions</th>
<th>Residue</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.C.</td>
<td>1842gms</td>
<td>1806gms</td>
<td>299gms.</td>
<td>9gms.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fr. No</td>
<td>Weight</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1. 3. 6. 7. 8. 9 .10. 11. 12. 13. 14. 15. 16. 17.</td>
<td>10. 8. 5.15.97.188.63.159.368.142.132.125.190.304gms.</td>
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<tr>
<td></td>
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<td>Fr. No</td>
<td>Weight</td>
<td></td>
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<td></td>
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<td>6 . 7 . 8. 9 .10. 11. 12. 13. 14. 15. 16. 17.</td>
<td>6 . 5 . 57. 31. 48.138.270.143. 74. 36.175.537gms.</td>
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</tr>
<tr>
<td>11.C.</td>
<td>1827gms</td>
<td>1570gms</td>
<td>540gms.</td>
<td>16gms.</td>
</tr>
<tr>
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<td>Fr. No</td>
<td>Weight</td>
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<tr>
<td></td>
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<td>6 . 7 . 8. 9 .10. 11. 12. 13. 14. 15. 16. 17.</td>
<td>9.56.39.19.112.195. 84.120. 18. 55.678.345.358gms.</td>
<td></td>
</tr>
<tr>
<td>12.C.</td>
<td>1840gms</td>
<td>2088gms</td>
<td>280gms.</td>
<td>12gms.</td>
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<tr>
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<td>Fr. No</td>
<td>Weight</td>
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<td>7 . 8 . 9.10. 11. 12. 13. 14. 15. 16. 17. 18. 19.</td>
<td>5.7.37.13.11.106.134.30.66.67.54.408.155.216.144.120gms.</td>
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</tr>
<tr>
<td>13.C.</td>
<td>1849gms</td>
<td>1573gms</td>
<td>552gms.</td>
<td>4gms.</td>
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<tr>
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<td>Fr. No</td>
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<tr>
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<td></td>
<td>6.7. 8. 9.10. 11. 12.13.14.15.16. 17. 18. 19. 20. 21.</td>
<td>5.5.11.7. 9.27.46.27.60.46.110.195.82.60.103.550.692gms.</td>
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<tr>
<td>14.C.</td>
<td>1870gms</td>
<td>2037gms</td>
<td>343gms.</td>
<td>42gms.</td>
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<tr>
<td>15.C.</td>
<td>1902gms</td>
<td>1887gms</td>
<td>340gms.</td>
<td>18gms.</td>
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<tr>
<td></td>
<td></td>
<td>Fr. No</td>
<td>Weight</td>
<td></td>
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</tbody>
</table>
Graph 6

DISTILLATIONS 16°C, 17°C, & 18°C.

(Carried out in the 30-inch column at a pressure of 100mm. Hg.)
Weight 4 5. 9. 6. 9.16. 6. 9.34.22.28.33.224.492.420.258.204 gms.

17.C. Charge 1870gms. Previous Residue 389gms.
Weight 7. 6. 5.11. 6. 6.11.16.28.75.292.296.118.186 gms.

18.C. Charge 1936gms.
Weight 5. 4. 4. 5. 3. 3. 7. 5.13.24.39.170.171. 68.184 gms.

Graphs of the volume distilled against the temperature of distillation, for all of these C-
distillations are shown in graphs 2 - 6 inclusive.
(Note. Fractions denoted with an asterisk were incomplete.)

Total Weight Balance For The Naphthalene Oil Bases.

In order to obtain a total "weight / temperature" balance for any batch, it was necessary
to make the assumption that the residue from each distillation was of the same composition as the
residue obtained from the next higher batch on distillation to the same temperature. Thus, as it was
usual to distil each batch to a temperature of about 5° C. above that of the previous batch, it was assumed that/
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</table>

**TOTAL WEIGHT BALANCE OF NAPHTHALENE OIL BASES.** (Table 3)

Total weight of bases processed... 142.00Kg.
Water removed in A-distillations... 14.40Kg.
Loss on A-distillations... 3.17Kg.
Residue from the A-distillations... 47.40Kg.

These temperatures are at a pressure of 100mm. Hg.
Graph 7.

**DISTRIBUTION CURVE FOR THE TOTAL NAPHTHALENE OIL BASES.**

Total weight of dry bases processed 161.26 kg
Total loss on A & C-distillations ... 4.16 kg
Total Residue .................. 52.20 kg
that this distillate was derived from the previous residue and from the batch in process, in quantities proportional to the amount of each present. By continuation of this type of calculation a total weight balance for each of the batches was obtained.

The weight balance for the total crude Naphthalene Oil Bases was then obtained by multiplying the weight of each individual cut by the factor - Weight of the total A-fraction / Weight of batch taken.

The results are shown in Table 3.

A graph (7) was then prepared of the weight distilled per degree centigrade against the temperature of distillation, making use of this table, the distribution inside the various cuts being estimated from the distillation graphs. The boiling points of the bases which had already been isolated from coal tar are indicated on this graph and it can be seen that the distillation "peaks" correspond very well with theme.

Examination of the C-Fractions.

The specific gravities and refractive indices of all the C-fractions were determined and are shown in Table 4. From a study of these constants and of Graph 7 it can be seen that a good degree of separation was achieved in these C-distillations.

Table 4/
<table>
<thead>
<tr>
<th>Fract. No.</th>
<th>Distrn. Range</th>
<th>( D_{25} )</th>
<th>( n_{25}^D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.2</td>
<td>115-117°/760mm.</td>
<td>0.9757</td>
<td>1.5052</td>
</tr>
<tr>
<td>C.3</td>
<td>117-129°</td>
<td>0.9530</td>
<td>1.5008</td>
</tr>
<tr>
<td>C.4</td>
<td>129-132°</td>
<td>0.9397</td>
<td>1.4982</td>
</tr>
<tr>
<td>C.5</td>
<td>130-132°</td>
<td>0.9396</td>
<td>1.4982</td>
</tr>
<tr>
<td>C.6</td>
<td>132-140°</td>
<td>0.9378</td>
<td>1.4984</td>
</tr>
<tr>
<td>C.7</td>
<td>140-145°</td>
<td>0.9368</td>
<td>1.4998</td>
</tr>
<tr>
<td>C.8</td>
<td>145-157°</td>
<td>0.9357</td>
<td>1.4999</td>
</tr>
<tr>
<td>C.9</td>
<td>157-160°</td>
<td>0.9263</td>
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</tr>
<tr>
<td>C.10</td>
<td>160-162°</td>
<td>0.9265</td>
<td>1.4990</td>
</tr>
<tr>
<td>C.11</td>
<td>162-169°</td>
<td>0.9243</td>
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<td>C.12</td>
<td>169-173°</td>
<td>0.9196</td>
<td>1.4991</td>
</tr>
<tr>
<td>C.13</td>
<td>173-175°</td>
<td>0.9206</td>
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<td>C.14</td>
<td>175-179°</td>
<td>0.9235</td>
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</tr>
<tr>
<td>C.15</td>
<td>179-181°</td>
<td>0.9365</td>
<td>1.5154</td>
</tr>
<tr>
<td>C.16</td>
<td>181-183°</td>
<td>0.9466</td>
<td>1.5249</td>
</tr>
<tr>
<td>C.17</td>
<td>183-186°</td>
<td>0.9658</td>
<td>1.5406</td>
</tr>
<tr>
<td>C.18</td>
<td>122.5-124°/100mm.</td>
<td>0.9724</td>
<td>1.5440</td>
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<td>C.19</td>
<td>124-126°</td>
<td>0.9492</td>
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</tr>
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<td>C.20</td>
<td>126-131°</td>
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<td>C.21</td>
<td>131-135°</td>
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<td>C.23</td>
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Graph/
Graph 8 shows the densities and refractive indices plotted against the mid-points of the cuts.

In order to obtain a quantitative estimate of the amounts of pyridine, 2-, 3- & 4-methylpyridines and 2:6-dimethylpyrididine present in the total crude Naphthalene Oil Bases, the lower fractions were examined as follows:

C.2. This fraction was assumed to consist entirely of pyridine as the boiling point, density and refractive index corresponded well with the values given for pure pyridine. The purity, as estimated by titration with standard sulphuric acid using screened methyl orange as indicator, was found to be 99%.

C.3. This fraction was assumed to consist entirely of a mixture of pyridine and 2-methylpyrididine. A small sample of the fraction was freed from non-basic material by acidifying with HCl, steam-distilling the non-basic material, making alkaline with NaOH and distilling off the purified bases in steam. After drying the purified bases by refluxing over solid KOH, the percentages of the two components were estimated by the method of Hamer, Pomfret & Stubbings (141).

Results

<table>
<thead>
<tr>
<th>Pyridine</th>
<th>45%</th>
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<tr>
<td>2-Methylpyridine</td>
<td>55%</td>
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</table>

C.4./
C.4. Owing to the very close similarity of the boiling point, density and refractive index of this fraction with those given for 2-methylpyridine, it was assumed that this cut consisted entirely of 2-methylpyridine. The purity as estimated by acid titration was found to be 100%.

C.5. The refractive index and density of this fraction were almost identical with those of C.4. The fraction did, however, contain pyrrole, as was shown by the "match test", but the quantity of this compound present must have been very small as, on picration, an almost quantitative yield of 2-methylpyridine picrate was obtained. It was therefore assumed that the fraction contained at least 95% of 2-methylpyridine.

C.7. This fraction was assumed to consist of a mixture of 3- and 4-methylpyridines and 2:6-dimethylpyridine. A sample of the fraction was freed from non-basic material, which was present only as traces, and dried by refluxing over solid KOH. The percentages of all three constituents in the sample were then found by the method of S.J. Angyal (142)

Results. 3-Methylpyridine......32.9%
        4-Methylpyridine......16.9%
        2:6-Dimethylpyridine..50.2%

C.6. This fraction was intermediate between the flats C.4-5 and C.7 and was assumed to consist/
consist of a mixture of the two. As no quantitative method of estimation was available, the approximation was made that it consisted of a 50:50 mixture of 2-methylpyridine and the fraction C.7.

From the above estimations and Table 3, the percentages of these five components present in the total crude Naphthalene Oil Bases were calculated. These may be of some industrial importance.

**Results.**

- Pyridine............... 2.26%
- 2-Methylpyridine....... 5.73%
- 3-Methylpyridine....... 3.60%
- 4-Methylpyridine....... 1.85%
- 2:6-Dimethylpyridine... 5.50%

**Note.** The percentages given for the last three components will be slightly low as they were also present in the fraction C.8 but could not be estimated therein.

Unfortunately there are no simple methods by which a quantitative estimate of the individual pyridine homologues in the higher fractions may be obtained, and insufficient time was available to attempt to isolate all the components.

It may be noted from a study of Graph 8 that there is a sharp rise in density and refractive index as the fractions C.17 and 18 are reached, which is explained by the presence of aniline. A further rise/
rise takes place as fractions C.24 and 25 are reached, and this is explained by the presence of toluidines and xylidines, and also of Naphthalene, of which a large amount was found to be present in fraction C.25. The presence of primary amines in fractions C.14 - 25 was shown qualitatively by means of diazotisation.

None of the Naphthalene Oil Base fractions was further examined, with the exception of C.21 which was subjected to a further fractionation in the 100-plate column in the hope of isolating tetramethylpyridines. This is described later (Distillation 1.E).
D-Distillations.

Second Fractionation of the Benzol Absorbing Oil Bases.

These distillations were carried out in the 30-plate column, in a manner precisely similar to that used for the C-distillations, using a 2 litre batch size (where possible) of each B-fraction, a boil up rate of 1500 mls./hr. and a take-off rate of 50 mls/hr.

The B-fractions 1-4 inclusive were fractionated at atmospheric pressure, column-head temperatures being converted to 760 mm. Hg. as in the C-distillations.

The other fractions (B.5 - 23) were distilled at 100 mm. Hg., the column-head temperatures of the overlapping cuts being converted to 760 mm. Hg. as in the C-distillations.

In the distillation of the last three fractions, when the column-head temperatures reached 180°C./100mm. Hg., the pressure was further reduced to 50 mm. Hg. (to reduce the risk of thermal decomposition), the column re-flooded and allowed to regain equilibrium under total reflux and then distillation was continued at 50 mm. Hg. The final distillation was continued to 178°C./50mm.

In the latter half of these D-distillations it was found that the column-head temperature fell when the still was left on total reflux for any length of/
of time. The temperature very soon regained its original value, however, once distillation was re-commenced.

In distillations 19D - 23D inclusive a great amount of difficulty was experienced due to "load shedding" and, in spite of constant supervision, it was found that the boil up rate varied considerably, as did the heating conditions in the column. For this reason the degree of fractionation achieved in these latter distillations was not constant, and the reliability of the results obtained may be slightly impaired thereby.

A further difficulty experienced in the higher of the D-distillations was that of bumping. This was successfully overcome, however, by packing the boiler flask with glass wool to a level higher than that of the liquid.

The cuts taken during the D-distillations were as follows:-

D.1. 0-115° D.2. 115-117° D.3. 117-129°
D.4. 129-132° D.5. 132-143.5° D.6. 143.5-145.5°
D.16. 183-186°
D.17./
Graph 9

DISTILLATIONS 1D, 2D, 3D & 4D.

(Carried out in the 30-plate column at atmospheric pressure.)
The results of the D-distillations were as follows:-

1.D. Charge 1967gms.

<table>
<thead>
<tr>
<th>Fr. No</th>
<th>1.</th>
<th>2.</th>
<th>3.</th>
<th>4.</th>
<th>5.</th>
<th>6.</th>
<th>7.</th>
<th>8.</th>
<th>9.</th>
<th>10.</th>
<th>11.</th>
<th>12.</th>
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</thead>
<tbody>
<tr>
<td>Weight</td>
<td>48.106.222.78.205.260.234.162.132.114.82.108. gms</td>
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2.D. Charge 1803gms. Previous Residue 240gms.

<table>
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<th>Fr. No</th>
<th>Water.</th>
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<th>5.</th>
<th>6.</th>
<th>7.</th>
<th>8.</th>
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<th>12.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>66.156.55.324.152.198.312.148.302. gms.</td>
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Fractions 989gms. Residue 525gms. Loss 2gms.

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<th>5.</th>
<th>6.</th>
<th>7.</th>
<th>8.</th>
<th>9.</th>
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<th>13.</th>
<th>14.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>20.9.143.34.32.164.132.192.304.53. gms.</td>
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</table>

4.D./
Graph 10.

DISTILLATIONS 6D, 6D, 7.4 6D.

(Carried out in the 30-plate column at a pressure of 100mm. Hg.)

TEMPERATURE / 100 mm. Hg.

VOLUME DISTILLED
<table>
<thead>
<tr>
<th>Date</th>
<th>Charge</th>
<th>Previous Residue</th>
<th>Fractions</th>
<th>Residue</th>
<th>Loss</th>
<th>Fr. No</th>
<th>Water</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.D.</td>
<td>1104gms.</td>
<td>525gms.</td>
<td>991gms.</td>
<td>617gms.</td>
<td>21gms.</td>
<td>7, 8, 9, 10, 11, 12, 13, 14, 15, 16</td>
<td>26, 19, 28, 18, 104, 72, 158, 187, 112, 97, 170</td>
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<tr>
<td>5.D.</td>
<td>1834gms.</td>
<td>617gms.</td>
<td>1832gms.</td>
<td>616gms.</td>
<td>3gms.</td>
<td>7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18</td>
<td>24, 42, 20, 24, 124, 142, 214, 148, 132, 106, 58, 432, 356</td>
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</tr>
<tr>
<td>6.D.</td>
<td>1450gms.</td>
<td>616gms.</td>
<td>1571gms.</td>
<td>616gms.</td>
<td>-7gms.</td>
<td>5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19</td>
<td>14, 7, 4, 6, 4, 9, 53, 70, 42, 72, 43, 62, 44, 267, 559, 315</td>
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<tr>
<td>7.D.</td>
<td>1110gms.</td>
<td>736gms.</td>
<td>866gms.</td>
<td>736gms.</td>
<td>10gms.</td>
<td>6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20</td>
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<tr>
<td>8.D.</td>
<td>1728gms.</td>
<td>736gms.</td>
<td>1928gms.</td>
<td>540gms.</td>
<td>4gms.</td>
<td>7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22</td>
<td>16, 3, 2, 5, 10, 10, 14, 20, 12, 20, 30, 102, 58, 460, 366, 380, 420</td>
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<tr>
<td>9.D.</td>
<td>1735gms.</td>
<td>540gms.</td>
<td>1954gms.</td>
<td>290gms.</td>
<td>31gms.</td>
<td>8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20</td>
<td>8, 2, 2, 9, 9, 12, 9, 10, 12, 41, 58, 158, 176</td>
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<td></td>
<td>21, 22, 23, 24, 25</td>
<td>222, 338, 256, 517, 106</td>
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<tr>
<td>10.D.</td>
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Graph 11

DISTILLATIONS 9D, 10D, 11D & 12D.
(Carried out in the 30-plate column at a pressure of 100mm. Hg.)
10.D. Charge 1830gms. Previous Residue 290gms.
Weight 12. 7. 5. 5.10. 7. 9.12.26.46.173.108.160.128.168.
Fract. No 24. 25. 26.27.28.29.30.31.32.33.34.35.36.37.
Weight 470.166.236.436.60.47.23.22.18.14.14.12.10.16 gms.

Note. Batches 11 - 24.D. were fractionated prior to the fractionation of batches 1 - 10.D. In order to obtain a complete weight balance for these lower batches it was therefore necessary to distil batch 10.D. until no residue was left. This was achieved by mixing the batch with some very high boiling bases and distilling the mixture until all of batch 10.D. had distilled over.

11.D. Charge 1860gms.
Weight 36 .13. 9. 7.11. 6. 7.34.68.80.134.110.467.161.250.190.

Fr. No water.20.21.22.23. 24.25. 26. 27. 28.

Fr. No water.18.19.20.21.22.23. 24. 25. 26. 27. 28. 29. 30. 31.
Weight 48 . 4. 7.13.19.15.36.120.146.184.300.157.128.321.258.

14.D.
Graph 13.

DISTILLATIONS 17D, 18D, 19D & 20D.
(Carried out in the 30-plate column at a pressure of 100mm Hg.)
Graph 12.

DISTILLATIONS 13D, 14D, 15D & 16D.

(Carried out in the 30-plate column at a pressure of 100mm. Hg.)
14.D. Charge 1854gms. Previous Residue 570gms
Fr. No | water | 18.19.20.21.22.23.24.25.26.27.28.29.30.31.32.33
Weight | 16.2.6.6.8.6.10.64.85.84.112.126.215.187.790.169.94

Fractions 1868gms. Residue 496gms. Loss 17gms.
Fr. No | water | 24.25.26.27.28.29.30.31.32.33.34.35.36
Weight | 22.17.25.31.30.46.130.262.545.182.104.157.147.228 gms.

Fr. No | water | 26.27.28.29.30.31.32.33.34.35.36.37.38.39
Weight | 12.6.6.5.14.25.34.404.355.278.20.170.380.144.167 gms.

17.D. Charge 2095gms. Previous Residue 432gms.
Fr. No | water | 19.20.21.22.23.24.25.26.27.28.29.30.31
Weight | 20.6.4.4.3.2.2.5.7.8.7.7.13.50.416
Fr. No | 32.33.34.35.36.37.38.39
Weight | 224.100.48.44.258.196.102.224 gms.

18.D. Charge 2138gms. Previous Residue 594gms.
Fractions 2143gms. Residue 588gms. Loss 1gms.
Fr. No | water | 23.24.25.26.27.28.29.30.31.32.33.34
Weight | 10.2.3.3.4.4.6.13.24.246.246.126.362
Fr. No | 35.36.37.38.39.40
Weight | 76.350.392.88.144.44 gms.

19.D./
Graph 14.

DISTILLATIONS 21D, 22D & 23D.

(Carried out in the 30-plate column at pressures of 100 & 50mm Hg.)
Fr. No water.31.32.33.34. 35. 36. 37. 38. 39. 40. 41.

Fr. No water.31.32.33.34.35.36. 37. 38. 39. 40. 41.
Weight 4 . 6.10.12. 8.32.64.442.260.160.168.182 gms.

Fr. No water.35.36.37.38.39. 40. 41. 42. 43. 44. 45. 46.

Fr. No water.35.36.37.38.39.40.41.42. 43. 44. 45. 46. 47.
Weight 10 . 8.10.42.36.34.52.54.124.178.238.574.982 gms.

Fr. No water.37.38.39.40.41.42.43.44.45. 46. 47. 48. 49. 50.
Weight 10 .10. 4. 4.14.22.22.33.35.46.286.464.612.652.544 gms.

Note. Fractions denoted with an asterisk were incomplete.

Graphs of volume distilled against temperature of distillation for all of these D-distillations are shown in Graphs 9 - 14 inclusive.
## TOTAL WEIGHT BALANCE ON BENZOL ABSORBING OIL BASES. (Table 5)

Total weight of bases processed........174.7 Kg.
Loss on B-distillations..................25.5 Kg.
Residue from the B-distillations........22.3 Kg.

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<th>D.2</th>
<th>D.3</th>
<th>D.4</th>
<th>D.5</th>
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<th>D.7</th>
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<th>D.9</th>
<th>D.10</th>
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<td>157°</td>
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<td>2:4-Dimethylpyridine</td>
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<td>3:5-Dimethylpyridine</td>
<td>160.8°</td>
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<td>N-P-Toluidine</td>
<td>200.4°</td>
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<td>m-Toluidine</td>
<td>203.3°</td>
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<tr>
<td>2-Ethylquinoline</td>
<td>212°</td>
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</tr>
<tr>
<td>3-Ethylquinoline</td>
<td>215°</td>
<td></td>
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</tr>
<tr>
<td>4-Ethylquinoline</td>
<td>220°-222°</td>
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<td>1-Ethylisoquinoline</td>
<td>223°</td>
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<tr>
<td>2-Ethylisoquinoline</td>
<td>229°</td>
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<td></td>
</tr>
<tr>
<td>3-Ethylisoquinoline</td>
<td>234.25°</td>
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<td>4-Ethylisoquinoline</td>
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<td>3410hylisoquinoline</td>
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<td>Quinoline</td>
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<td>3-Methylisoquinoline</td>
<td>255.25°</td>
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</tr>
</tbody>
</table>

**Graph 15.**

**DISTRIBUTIONOGRAPH FOR THE TOTAL BENZOL ABSORBING OIL BASES.**

Total weight of dry bases processed 164.7 kg.
Total loss on 3 & 4 distillations... 26.0kg.
Total Residue.......................... 23.3kg.

![Graph showing the distribution of compounds](image-url)
Total Weight Balance for the Benzol Absorbing Oil Bases.

"Weight distilled / temperature of distillation balances" were calculated for each of these batches using the same assumptions and procedure as are described in the section on the C-distillations. The weight balance for the total crude Benzol Absorbing Oil bases was then obtained by multiplying the weight of each individual cut by the factor - Weight of the total B-fraction / weight of batch taken.

The results are shown in Table 5.

A graph (15) was then prepared of the weight distilled per degree centigrade against the temperature of distillation, making use of this table, the distribution inside the various cuts being estimated from the distillation graphs. The boiling points of the bases which have already been isolated from coal tar are indicated on this graph, and it can be seen that the distillation "peaks" correspond very well with these.

Examination of the D-Fractions.

The specific gravities and refractive indices of all the D-Fractions were determined and are shown in Table 6. From a study of these constants and of Graph 15 it can be seen that a good degree of separation was achieved in these D-distillations.
Graph 16.

DENSITIES & REFRACTIVE INDICES OF D-FRACTIONS.

- Density
- Refractive Index
<table>
<thead>
<tr>
<th>Fract. No.</th>
<th>Distn. Range</th>
<th>D_{4}^{25}</th>
<th>n_{D}^{25}</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.1</td>
<td>0-115°/760mm.</td>
<td></td>
<td>1.4551</td>
</tr>
<tr>
<td>D.2</td>
<td>115-117°</td>
<td>0.9712</td>
<td>1.5041</td>
</tr>
<tr>
<td>D.3</td>
<td>117-129°</td>
<td>0.9534</td>
<td>1.5020</td>
</tr>
<tr>
<td>D.4</td>
<td>129-132°</td>
<td>0.9397</td>
<td>1.4989</td>
</tr>
<tr>
<td>D.5</td>
<td>132-143.5°</td>
<td>0.9371</td>
<td>1.4992</td>
</tr>
<tr>
<td>D.6</td>
<td>143.5-145.5°</td>
<td>0.9364</td>
<td>1.5000</td>
</tr>
<tr>
<td>D.7</td>
<td>145.5-157°</td>
<td>0.9346</td>
<td>1.4998</td>
</tr>
<tr>
<td>D.8</td>
<td>157-160°</td>
<td>0.9276</td>
<td>1.4990</td>
</tr>
<tr>
<td>D.9</td>
<td>160-162°</td>
<td>0.9263</td>
<td>1.4989</td>
</tr>
<tr>
<td>D.10</td>
<td>162-169°</td>
<td>0.9252</td>
<td>1.5002</td>
</tr>
<tr>
<td>D.11</td>
<td>169-172°</td>
<td>0.9243</td>
<td>1.5011</td>
</tr>
<tr>
<td>D.12</td>
<td>172-175°</td>
<td>0.9265</td>
<td>1.5008</td>
</tr>
<tr>
<td>D.13</td>
<td>175-179°</td>
<td>0.9204</td>
<td>1.5030</td>
</tr>
<tr>
<td>D.14</td>
<td>179-181°</td>
<td>0.9306</td>
<td>1.5050</td>
</tr>
<tr>
<td>D.15</td>
<td>181-183°</td>
<td>0.9310</td>
<td>1.5064</td>
</tr>
<tr>
<td>D.16</td>
<td>183-186°</td>
<td>0.9352</td>
<td>1.5100</td>
</tr>
<tr>
<td>D.17</td>
<td>122-124°/100mm.</td>
<td>0.9341</td>
<td>1.5145</td>
</tr>
<tr>
<td>D.18</td>
<td>124-126°</td>
<td>0.9427</td>
<td>1.5180</td>
</tr>
<tr>
<td>D.19</td>
<td>126-131°</td>
<td>0.9494</td>
<td>1.5180</td>
</tr>
<tr>
<td>D.20</td>
<td>131-135°</td>
<td>0.9502</td>
<td>1.5165</td>
</tr>
<tr>
<td>D.21</td>
<td>135-137°</td>
<td>0.9516</td>
<td>1.5232</td>
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<tr>
<td>D.22</td>
<td>137-138.5°</td>
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<td>1.5288</td>
</tr>
<tr>
<td>D.23</td>
<td>138.5-140°</td>
<td>0.9596</td>
<td>1.5302</td>
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<tr>
<td>D.24</td>
<td>140-144°</td>
<td>0.9774</td>
<td>1.5350</td>
</tr>
<tr>
<td>D.25</td>
<td>144-148°</td>
<td>0.9745</td>
<td>1.5400</td>
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<tr>
<td>D.26</td>
<td>148-152°</td>
<td>0.9659</td>
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</table>

Continued over.
Table 6. (Continued)

<table>
<thead>
<tr>
<th>Fract. No.</th>
<th>Distn. Range</th>
<th>$D_4^{25}$</th>
<th>$n_D^{25}$</th>
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</thead>
<tbody>
<tr>
<td>D.27</td>
<td>152-155°/100mm.</td>
<td>0.9716</td>
<td>1.5370</td>
</tr>
<tr>
<td>D.28</td>
<td>155-158.5°</td>
<td>0.9890</td>
<td>1.5450</td>
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<tr>
<td>D.29</td>
<td>158.5-161.5°</td>
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<td>1.5560</td>
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<td>D.30</td>
<td>161.5-163°</td>
<td>1.0490</td>
<td>1.5580</td>
</tr>
<tr>
<td>D.31</td>
<td>163-164°</td>
<td>1.0716</td>
<td>1.6075</td>
</tr>
<tr>
<td>D.32</td>
<td>164-166°</td>
<td>1.0773</td>
<td>1.6120</td>
</tr>
<tr>
<td>D.33</td>
<td>166-168°</td>
<td>1.0781</td>
<td>1.6125</td>
</tr>
<tr>
<td>D.34</td>
<td>168.5-169°</td>
<td>1.0771</td>
<td>1.6120</td>
</tr>
<tr>
<td>D.35</td>
<td>167.5-168.5°</td>
<td>1.0750</td>
<td>1.6105</td>
</tr>
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<td>D.36</td>
<td>168.5-170°</td>
<td>1.0748</td>
<td>1.6105</td>
</tr>
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<td>D.37</td>
<td>170-172°</td>
<td>1.0680</td>
<td>1.6090</td>
</tr>
<tr>
<td>D.38</td>
<td>172-173°</td>
<td>1.0606</td>
<td>1.6062</td>
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<td>D.39</td>
<td>173-174°</td>
<td>1.0559</td>
<td>1.6040</td>
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<td>D.40</td>
<td>174-176°</td>
<td>1.0526</td>
<td>1.6003</td>
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<td>D.41</td>
<td>176-178°</td>
<td>1.0502</td>
<td>1.5970</td>
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<td>D.42</td>
<td>178-180°</td>
<td>1.0505</td>
<td>1.5970</td>
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<td>D.43</td>
<td>158-161°/50mm.</td>
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<td>D.44</td>
<td>161-163°/50mm.</td>
<td>1.0541</td>
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<tr>
<td>D.45</td>
<td>163-165°</td>
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<td>D.49</td>
<td>174-176°</td>
<td>1.0511</td>
<td>1.6038</td>
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<tr>
<td>D.50</td>
<td>176-178°</td>
<td>1.0481</td>
<td>1.6028</td>
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</table>
Graph 16 shows the densities and refractive indices of the fractions plotted against the mid-points of their distillation ranges. The "peaks" which appear on this graph at about 128° & 145°C./100mm. are explained by the presence of primary aromatic amines which were detected by qualitative tests, and the higher densities and refractive indices obtained for the fractions boiling over 160°C./100mm. are due to the quinoline and isoquinoline homologues which form the main bulk of these fractions.

The further examination of the D-fractions was confined to certain chosen ranges from which it was hoped that previously unidentified coal tar bases might be isolated. A description of this work is given in the next section. (Distillations 2.E. - 9.E.)
E-Distillations.

The isolation of pure bases from the C- or D-fractions without further fractional distillation would have been, in most cases, an arduous task, and for this reason it was decided to subject certain chosen ranges to further fractional distillation in the "100-plate" column. The fractions chosen were those from which it was considered most likely that previously unidentified bases might be isolated.

The chosen fractions were first freed from traces of non-basic material which had been present in the crude bases and were still present at this stage. This was accomplished by acidifying with concentrated hydrochloric acid, removing the non-basic material by either steam distillation or extraction with ether and regenerating the bases by neutralisation with caustic soda. In batches 1.E - 4.E the non-basic material was removed by steam distillation and the purified bases were recovered from the neutralised solution by this means also. In batches 5.E - 8.E steam distillation was unsuitable owing to the high boiling ranges of the fractions, so the non-basic material was removed by extraction with ether and the purified bases were recovered from the neutralised solution by extraction with ether and removal of the ether from the resulting extract by distillation, after/
after drying over caustic soda. The purified bases were dried by refluxing over solid caustic soda prior to distillation in the "100-plate column".

The E-distillations were carried out in the "100-plate" column under diminished pressure at a boil-up rate of 1000mls./hour and a take-off rate of 10mls./hour, the procedure being as follows:

The charge was weighed into the boiler flask, which had previously been packed with glass wool to prevent bumping during the distillation. The vacuum was set to the required value. The boil-up rate was then adjusted to 1000mls./hour and the column flooded by closing the magnetic valve. (Note: When traces of water were found to be still present, these were removed prior to flooding.) After slowly deflooding the column, the vacuum and boil-up rate were checked and the column heaters brought to the correct temperature as indicated by zero readings on the differential thermocouple galvanometer. The column was then run to equilibrium for 10 - 12 hours and the take-off started at the correct rate. Distillation was then continued, taking short range cuts to correspond with distillation "flats", and maintaining the correct boil-up rate and adiabatic conditions throughout the column.

The still was run continuously throughout each batch, being left on total reflux overnight.

After/
After the installation of the Tektor Proximity Switch, however, it was sometimes possible to leave the still taking off overnight when on a distillation "flat".

**Distillation 1.E.**

Naphthalene Oil Bases. C.21 (131-135°C./100mm.)

This range was refractionated in the hope of isolating 2:3:5:6- and 2:3:4:6-tetramethylpyridines, which boil at 131° and 135°C./100mm. respectively (24) and have not hitherto been reported as coal tar constituents.

3.76 Kg. of this cut was obtainable from 184 Kg. of the crude bases (i.e. 2.04%).

A portion of the fraction was first freed from non-basic material. A yield of 2.10% non-basic material was obtained.

A sample of the purified bases was then fractionated in the "100-plate" column at a pressure of 100 mm. Hg. The weight balance for the distillation is shown below and the distillation graph is shown in Graph 17.

Charge.........916gms. \( D_4^{25} 0.9569 \) \( n_D^{25} 1.5364 \)

Fractions.......766gms.

Residue.........140gms.

Loss............ 10gms.

Fract. No./
DISTILLATION 1.B

(Carried out in the 100-plate column at a pressure of 100mm Hg.)
From the table and graph it can be seen that the only distillation "flats" obtained were at about 123°C./100mm. and 134°C./100mm., and that no "flat" was obtained corresponding to the boiling point of 2:3:5:6-tetramethylpyridine.

Converting the distillation temperature of the 123°C. "flat" to 760mm. a value of 190°C. was obtained which is in good agreement with the boiling point given for 2:4:5-trimethylpyridine (9), a compound which has been isolated from coal tar previously. That this "flat" does consist mainly of 2:4:5-trimethylpyridine has been proved, and the isolation of this compound is fully described in the next section.
Converting the distillation temperature of the 134°C. "flat" to 760mm. a value of 201°C. was obtained which is close to the values given for the o- and p-toluidines (200.7 and 200.4°C. respectively) which have been isolated from coal tar previously (17). As the fractions distilling in this region were found to consist almost entirely of primary bases it was assumed that these fractions consisted essentially of o- and p-toluidines. The solid distilling at the top of the range, on recrystallisation from ether, gave a melting point of 45°C. which is identical with that given for p-toluidine, and a mixed melting point of the solid with an authentic sample of p-toluidine showed no lowering.

As this investigation was not concerned with primary bases this range was not examined further.

Distillation 2.E.

Benzol Absorbing Oil Bases. D.19. (126-131°C./100mm.)

This range was refractionated in the hope of isolating 2:3:5:6-tetramethylpyridine.

3.07 Kg. of this cut was obtainable from 175 Kg. of the crude wet bases (i.e. 1.76%).

A portion of the fraction was first freed from non-basic material. A yield of 0.78% non-basic material was obtained.

A/
DISTILLATIONS 2E & 3E.

(Carried out in the 100-plate column at a pressure of 100mm. Hg.)
A sample of the purified bases was then fractionated in the "100-plate" column at a pressure of 100 mm. Hg. The weight balance for this distillation is shown below and the distillation graph is shown in Graph 18.

Charge........1000gms. \( D^2_{25} 0.9494 \) \( n^2_{D} 1.5180 \)
Fractions.... 863gms.
Residue...... 100gms.
Loss........... 37gms.

<table>
<thead>
<tr>
<th>Fract. No.</th>
<th>Distn. Range</th>
<th>Weight</th>
<th>( n^2_{D} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td>10gms.</td>
<td></td>
</tr>
<tr>
<td>2E/1</td>
<td>114-122.5°/100mm.</td>
<td>32gms.</td>
<td>1.5030</td>
</tr>
<tr>
<td>2E/2</td>
<td>122.5-123°/100mm.</td>
<td>55gms.</td>
<td>1.5050</td>
</tr>
<tr>
<td>2E/3</td>
<td>123-124°/100mm.</td>
<td>79gms.</td>
<td>1.5090</td>
</tr>
<tr>
<td>2E/4</td>
<td>124-124.5°/100mm.</td>
<td>137gms.</td>
<td>1.5255</td>
</tr>
<tr>
<td>2E/5</td>
<td>124.5-126.9°/100mm.</td>
<td>91gms.</td>
<td>1.5242</td>
</tr>
<tr>
<td>2E/6</td>
<td>126.9-127°/100mm.</td>
<td>193gms.</td>
<td>1.5190</td>
</tr>
<tr>
<td>2E/X</td>
<td>124.8-126.9°/100mm.</td>
<td>13gms.</td>
<td>rejected</td>
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<td>2E/7</td>
<td>127-128.5°/100mm.</td>
<td>79gms.</td>
<td>1.5175</td>
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<td>2E/8</td>
<td>128.5-130°/100mm.</td>
<td>56gms.</td>
<td>1.5130</td>
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<tr>
<td>2E/9</td>
<td>130-131°/100mm.</td>
<td>42gms.</td>
<td>1.5185</td>
</tr>
<tr>
<td>2E/10</td>
<td>131-131.3°/100mm.</td>
<td>44gms.</td>
<td>solid</td>
</tr>
<tr>
<td>2E/11</td>
<td>131.3-131.4°/100mm.</td>
<td>20gms.</td>
<td>solid</td>
</tr>
<tr>
<td>2E/12</td>
<td>131.4-132.5°/100mm.</td>
<td>22gms.</td>
<td>solid</td>
</tr>
</tbody>
</table>

From the above table and the distillation graph it can be seen that the "flats" occurred as follows/
follows:

1) At about 123°C./100mm. This "flat" was assumed to be of the same composition as the first "flat" in distillation I.E.

2) At 124 - 124.5°C./100mm. The examination of this fraction is described in the next section.

3) At 126°C./100mm. Converting to 760mm., a distillation temperature of 193°C. was obtained which corresponds well with the value of 192-193°C. given for 2:3:4-trimethylpyridine (8), a compound which has been reported as a coal tar constituent previously. The isolation of this compound is described in the next section.

4) At 131 - 131.5°C./100mm. The isolation of 2:3:5:6-tetramethylpyridine from this range is described in the next section.

Distillation 3.E.

Benzol Absorbing Oil Bases D.20 & 21. (131-137°C./100mm.)

This range was refraccionated in the hope of isolating 2:3:4:6-tetramethylpyridine.

3.61 Kg. of this range was obtainable from 175 Kg. of the crude wet bases. (i.e. 2.06%)  

The fractions D.20 & D.21 were mixed in quantities proportional to their total yields. A portion of the mixture was freed from non-basic material and fractionated in the "100-plate" column under/
under a pressure of 100mm. Hg. The yield of non-basic material amounted to 0.80%. The weight balance is shown below and the distillation graph is shown in Graph 18.

Charge .......... 1000gms.
Fractions ...... 886gms.
Residue......... 98gms.
Loss............ 16gms.

<table>
<thead>
<tr>
<th>Fract. No.</th>
<th>Distr. Range</th>
<th>Weight</th>
<th>$n^2_{D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td>6gms.</td>
<td></td>
</tr>
<tr>
<td>3E/1</td>
<td>115-122.5°/100mm.</td>
<td>32gms.</td>
<td>1.5065</td>
</tr>
<tr>
<td>3E/2</td>
<td>122.5-124°/100mm.</td>
<td>33gms.</td>
<td>1.5145</td>
</tr>
<tr>
<td>3E/3</td>
<td>124-127°/100mm.</td>
<td>24gms.</td>
<td>1.5147</td>
</tr>
<tr>
<td>3E/4</td>
<td>127-128.5°/100mm.</td>
<td>31gms.</td>
<td>1.5147</td>
</tr>
<tr>
<td>3E/5</td>
<td>128.5-130°/100mm.</td>
<td>28gms.</td>
<td>1.5148</td>
</tr>
<tr>
<td>3E/6</td>
<td>130-130.3°/100mm.</td>
<td>31gms.</td>
<td>1.5208</td>
</tr>
<tr>
<td>3E/6a</td>
<td>130.8-131°/100mm.</td>
<td>34gms.</td>
<td>1.5225</td>
</tr>
<tr>
<td>3E/7</td>
<td>131-131.5°/100mm.</td>
<td>104gms.</td>
<td>solid</td>
</tr>
<tr>
<td>3E/8</td>
<td>131.5-132°/100mm.</td>
<td>36gms.</td>
<td>solid</td>
</tr>
<tr>
<td>3E/9</td>
<td>132-133.5°/100mm.</td>
<td>43gms.</td>
<td>1.5095</td>
</tr>
<tr>
<td>3E/10</td>
<td>133.5-134.5°/100mm.</td>
<td>69gms.</td>
<td>1.5095</td>
</tr>
<tr>
<td>3E/11</td>
<td>134.5-135°/100mm.</td>
<td>62gms.</td>
<td>1.5160</td>
</tr>
<tr>
<td>3E/12</td>
<td>135-135.2°/100mm.</td>
<td>128gms.</td>
<td>1.5202</td>
</tr>
<tr>
<td>3E/13</td>
<td>135.2-136°/100mm.</td>
<td>82gms.</td>
<td>1.5232</td>
</tr>
<tr>
<td>3E/14</td>
<td>136-137.2°/100mm.</td>
<td>143gms.</td>
<td>1.5250</td>
</tr>
</tbody>
</table>
From the distillation graph it can be seen that the "flats" occurred as follows:

1) At 131 - 131.5°C./100mm. The examination of this range is described in the next section.

2) At 135°C./100mm. The isolation of 2:3:4:6-tetramethylpyridine from this range is described in the next section.

3) At 136°C./100mm. The fraction 3E/14 was found to consist almost entirely of primary bases. Converting the distillation temperature to 760mm., a value of 204.5°C. was obtained which is fairly close to the literature value for the boiling point of m-toluidine (203.3°C), a compound which has been previously identified in coal tar. This range, therefore, was not examined further.

Distillation 4.E.

Benzol Absorbing Oil Bases D.27 & 28. (152-158.5°C./100mm.)

Pentamethylpyridine has neither been isolated from any natural source nor has it been prepared, but, calculating its boiling point by means of an empirical formula derived by Eguchi (9), a value of 227.3°C./760mm. was obtained (i.e. approximately 155.5°C./100mm.). This compound would, in all probability, be solid at room temperature and, therefore, would be easily isolated from narrow boiling range fractions.
Graph 19

DISTILLATION 4E

(Carried out in the 100-plate column at a pressure of 100mm. Hg.)

TEMPERATURE OF DISTILLATION

VOLUME DISTILLED
This range (152-158.5°/100mm.), therefore, was refractionated in the hope of isolating penta-methylpyridine, in spite of the fact that these D-fractions had been found to consist essentially of primary bases.

3.50 Kg. of this range was obtainable from 175 Kg. of the crude wet bases. (i.e. 2.0%)

The fractions D.27 & D.28 were mixed in quantities proportional to their total yields. A portion of the mixture was freed from non-basic material and fractionated in the "100-plate" column under a pressure of 100mm. Hg. The yield of non-basic material amounted to 3.18%. The weight balance is shown below and the distillation graph in Graph 19.

Charge 1090gms. Fractions 980gms. Residue 110gms.

<table>
<thead>
<tr>
<th>Fract. No.</th>
<th>Distn. Range</th>
<th>Weight</th>
<th>(n_D^{25})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td>20gms.</td>
<td></td>
</tr>
<tr>
<td>4E/1</td>
<td>140-148° /100mm.</td>
<td>36gms.</td>
<td>1.5177</td>
</tr>
<tr>
<td>4E/2</td>
<td>148-150° /100mm.</td>
<td>88gms.</td>
<td>1.5240</td>
</tr>
<tr>
<td>4E/3</td>
<td>150-151.5° /100mm.</td>
<td>136gms.</td>
<td>1.5335</td>
</tr>
<tr>
<td>4E/4</td>
<td>151.5-152° /100mm.</td>
<td>106gms.</td>
<td>1.5363</td>
</tr>
<tr>
<td>4E/5</td>
<td>152-152.5° /100mm.</td>
<td>60gms.</td>
<td>1.5380</td>
</tr>
<tr>
<td>4E/6</td>
<td>152.5-153° /100mm.</td>
<td>84gms.</td>
<td>1.5370</td>
</tr>
<tr>
<td>4E/7</td>
<td>153-154° /100mm.</td>
<td>138gms.</td>
<td>1.5355</td>
</tr>
<tr>
<td>4E/8</td>
<td>154-155° /100mm.</td>
<td>75gms.</td>
<td>1.5355</td>
</tr>
<tr>
<td>4E/9</td>
<td>155-156° /100mm.</td>
<td>53gms</td>
<td>1.5360</td>
</tr>
<tr>
<td>4E/10</td>
<td>156-156.5° /100mm.</td>
<td>84gms.</td>
<td>1.5380</td>
</tr>
<tr>
<td>4E/11</td>
<td>156.5-158.5° /100mm.</td>
<td>100gms.</td>
<td>1.5390</td>
</tr>
</tbody>
</table>
No solid material could be frozen out from any of these fractions even on cooling to as low a temperature as \(-70^\circ C\), and, as it was found that all the fractions consisted essentially of primary amines, they were not examined further.

Batches D.44 - D.50 inclusive were refractionated, as this range had not been exhaustively examined in the past and as considerable doubts were entertained as to the reliance which could be placed on the weight balance obtained for this range in the D-distillations.

All these batches were refractionated in the "100-plate" column under a pressure of 50mm. Hg.

Distillation 5.E.

Benzol Absorbing Oil Bases D.44 & 45. (161-165°C./50mm.)

The fractions D.44 and D.45 were mixed in quantities proportional to their yields, and a portion of the mixture was freed from non-basic material which amounted to 5.12%. The weight balance for the distillation of this purified material is shown below and the distillation graph is shown in Graph 20.

<table>
<thead>
<tr>
<th>Fract. No./m.</th>
<th>Charge</th>
<th>Fractions</th>
<th>Residue</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1164gms.</td>
<td>1072gms.</td>
<td>70gms.</td>
<td>22gms.</td>
</tr>
</tbody>
</table>

Fract. No./
Graph 26.

DISTILLATIONS 5E, 6E, 7E & 8E.
(Carried out in the 100-plate column
at a pressure of 50mm Hg.)
<table>
<thead>
<tr>
<th>Fract. No.</th>
<th>Distn. Range</th>
<th>Weight</th>
<th>$n_D^{25}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>154.8-157°/50mm.</td>
<td>16gms.</td>
<td>Solid</td>
</tr>
<tr>
<td>5E/1</td>
<td>157-158°/50mm.</td>
<td>8gms.</td>
<td></td>
</tr>
<tr>
<td>5E/2</td>
<td>158-159°/50mm.</td>
<td>21gms.</td>
<td>1.5995</td>
</tr>
<tr>
<td>5E/3</td>
<td>159-160°/50mm.</td>
<td>36gms.</td>
<td>1.6042</td>
</tr>
<tr>
<td>5E/4</td>
<td>160-161°/50mm.</td>
<td>127gms.</td>
<td>1.6070</td>
</tr>
<tr>
<td>5E/5</td>
<td>161-162°/50mm.</td>
<td>122gms.</td>
<td>1.6080</td>
</tr>
<tr>
<td>5E/6</td>
<td>161-162°/50mm.</td>
<td>190gms.</td>
<td>1.6062</td>
</tr>
<tr>
<td>5E/7</td>
<td>162-162°/50mm.</td>
<td>128gms.</td>
<td>1.6020</td>
</tr>
<tr>
<td>5E/8</td>
<td>162-162.3°/50mm.</td>
<td>158gms.</td>
<td>1.6020</td>
</tr>
<tr>
<td>5E/9</td>
<td>162.3-165.8°/50mm.</td>
<td>112gms.</td>
<td>1.5980</td>
</tr>
<tr>
<td>5E/10</td>
<td>165.8-165.8°/50mm.</td>
<td>58gms.</td>
<td>1.5975</td>
</tr>
</tbody>
</table>

Distillation 6.E.

Benzol Absorbing Oil Bases D.46. (165-168°/50mm.)

The yield of non-basic material from this fraction amounted to 3.85%. The purified material was charged on top of the residue from the previous distillation. The weight balance for the distillation is shown below and the distillation graph is shown in Graph 20.

Charge........... 1066gms + 70gms of previous residue
Fractions....... 1012gms.
Residue......... 132gms.
Loss............ -8gms.
Fract. No./
<table>
<thead>
<tr>
<th>Fract. No.</th>
<th>Distn. Range</th>
<th>Weight</th>
<th>nD&lt;sub&gt;25&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td>26gms.</td>
<td></td>
</tr>
<tr>
<td>6E/0</td>
<td></td>
<td>5gms.</td>
<td></td>
</tr>
<tr>
<td>6E/1</td>
<td>160-162° /50mm.</td>
<td>64gms.</td>
<td>1.5995</td>
</tr>
<tr>
<td>6E/2</td>
<td>162-162.3°/50mm.</td>
<td>78gms.</td>
<td>1.5985</td>
</tr>
<tr>
<td>6E/3</td>
<td>162.3-165.5°/50mm.</td>
<td>130gms.</td>
<td>1.5945</td>
</tr>
<tr>
<td>6E/4</td>
<td>165.5-166° /50mm.</td>
<td>265gms.</td>
<td>1.6060</td>
</tr>
<tr>
<td>6E/5</td>
<td>166-166.2°/50mm.</td>
<td>206gms.</td>
<td>1.6110</td>
</tr>
<tr>
<td>6E/6</td>
<td>166.2-166.8°/50mm.</td>
<td>62gms.</td>
<td>1.6120</td>
</tr>
<tr>
<td>6E/7</td>
<td>166.8-167° /50mm.</td>
<td>90gms.</td>
<td>1.6136</td>
</tr>
<tr>
<td>6E/8</td>
<td>167-168.5°/50mm.</td>
<td>86gms.</td>
<td>1.6085</td>
</tr>
</tbody>
</table>

**Distillation 7.E.**

Benzol Absorbing Oil Bases D.47. (168-170°C./50mm.)

The yield of non-basic material from this fraction amounted to 5.45%. The purified material was charged on top of the residue from the previous distillations. The weight balance for the distillation is shown below and the distillation graph is shown in Graph 20.

- **Charge** ......... 1066gms. + 132gms. of previous residue.
- **Fractions** ....... 1036gms.
- **Residue** ......... 172gms.
- **Loss** ............ -10gms.

Fract. No./
<table>
<thead>
<tr>
<th>Fract. No.</th>
<th>Distn. Range</th>
<th>Weight</th>
<th>$n_D^{25}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td>42gms.</td>
<td></td>
</tr>
<tr>
<td>7E/0</td>
<td></td>
<td>10gms.</td>
<td></td>
</tr>
<tr>
<td>7E/1</td>
<td>162.5-166° /50mm.</td>
<td>54gms.</td>
<td>1.6018</td>
</tr>
<tr>
<td>7E/2</td>
<td>166-166.2°/50mm.</td>
<td>170gms.</td>
<td>1.6093</td>
</tr>
<tr>
<td>7E/3</td>
<td>166.2-166.7°/50mm.</td>
<td>96gms.</td>
<td>1.6110</td>
</tr>
<tr>
<td>7E/4</td>
<td>166.7-167°/50mm.</td>
<td>156gms.</td>
<td>1.6120</td>
</tr>
<tr>
<td>7E/5</td>
<td>167-168.5°/50mm.</td>
<td>108gms.</td>
<td>1.6060</td>
</tr>
<tr>
<td>7E/6</td>
<td>168.5-169°/50mm.</td>
<td>352gms.</td>
<td>1.6030</td>
</tr>
<tr>
<td>7E/7</td>
<td>169-169°/50mm.</td>
<td>48gms.</td>
<td>1.6010</td>
</tr>
</tbody>
</table>

**Distillation 8.E.**

Benzol Absorbing Oil Bases D.48-50. (170-178°C./50mm)

Fractions D.48, D.49 and D.50 were mixed in quantities proportional to their total yields. The non-basic material removed from this fraction amounted to 5.60%. The purified material was charged on top of the residue from the previous distillations. The weight balance for the distillation is shown below and the distillation graph is shown in Graph 20.

Charge........1470gms. + 172gms. of previous residue.
Fractions.....1542gms.
Residue......110gms.
Loss.........-10gms.

Fract. No./
DISTRIBUTION GRAPH FOR THE HIGHER BENZOL ABSORBING OIL BASES. (Graph 21.)

(Obtained from the distillations 5E - 8E, the weights being those obtainable from 175 kg. of the total crude wet bases.)
<table>
<thead>
<tr>
<th>Fract. No.</th>
<th>Distn. Range</th>
<th>Weight</th>
<th>nD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td>76gms.</td>
<td></td>
</tr>
<tr>
<td>8E/0</td>
<td></td>
<td>4gms.</td>
<td></td>
</tr>
<tr>
<td>8E/1</td>
<td>165-168.5°/50mm.</td>
<td>58gms.</td>
<td>1.6005</td>
</tr>
<tr>
<td>8E/2</td>
<td>168.5-169°/50mm.</td>
<td>136gms.</td>
<td>1.6005</td>
</tr>
<tr>
<td>8E/3</td>
<td>169-169.2°/50mm.</td>
<td>110gms.</td>
<td>Solid</td>
</tr>
<tr>
<td>8E/4</td>
<td>169.2-170°/50mm.</td>
<td>24gms.</td>
<td>Solid</td>
</tr>
<tr>
<td>8E/5</td>
<td>170-170.5°/50mm.</td>
<td>32gms.</td>
<td>Solid</td>
</tr>
<tr>
<td>8E/6</td>
<td>170.5-170.7°/50mm.</td>
<td>36gms.</td>
<td>Solid</td>
</tr>
<tr>
<td>8E/7</td>
<td>170.7-170.8°/50mm.</td>
<td>36gms.</td>
<td>Solid</td>
</tr>
<tr>
<td>8E/8</td>
<td>170.8-173.5°/50mm.</td>
<td>122gms.</td>
<td>1.6030</td>
</tr>
<tr>
<td>8E/9</td>
<td>173.5-174°/50mm.</td>
<td>134gms.</td>
<td>1.6030</td>
</tr>
<tr>
<td>8E/10</td>
<td>174-174.2°/50mm.</td>
<td>252gms.</td>
<td>1.6047</td>
</tr>
<tr>
<td>8E/11</td>
<td>174.2-174.2°/50mm.</td>
<td>250gms.</td>
<td>1.6053</td>
</tr>
<tr>
<td>8E/12</td>
<td>174.2-174.2°/50mm.</td>
<td>162gms.</td>
<td>1.6065</td>
</tr>
<tr>
<td>8E/13</td>
<td>159-174°/50mm.</td>
<td>18gms.</td>
<td>1.6195</td>
</tr>
<tr>
<td>8E/14</td>
<td>174-175°/50mm.</td>
<td>102gms.</td>
<td>1.6105</td>
</tr>
</tbody>
</table>

A graph (21) was prepared of the weight distilled per °C. against the temperature for the range covered by these four batches, using the same assumptions and procedure as were used in the construction of distribution graphs for the C- and D-distillations. The boiling points of bases which had already been reported as coal tar constituents are indicated on this graph.

From/
From this graph it can be seen that the most profitable ranges for close examination were those occurring between 168° and 175°C./50mm. Hg., and a description of the examination of these fractions is included in the next section. A description of the isolation of 3-methylisoquinoline from the fore-runnings of distillation 5.E. is also included.
EXAMINATION OF THE E-FRACTIONS.

All the E-fractions examined in this work have consisted essentially of tertiary bases of the pyridine, quinoline or isoquinoline type. The isolation of the pure components from these fractions has been effected by methods described earlier in this thesis.

The pure compounds isolated have generally been identified by the following means:

1) Comparison of their physical constants (melting point, boiling point, density and refractive index) with values given in the literature.

2) Preparation of three or more derivatives for each compound isolated and comparison of their melting points with values given in the literature. This method was particularly useful in the case of methylated quinolines as Manske (86) had published the melting points of the picrates, styphnates and trinitro-m-cresolates of all the possible mono- and dimethylquinolines, which he had prepared by unambiguous routes, and had shown that the identity of any mono- or dimethylquinoline could be established conclusively by the determination of the melting points of its picrate, styphnate and trinitro-m-cresolate. Where possible, additional confirmation was obtained by carrying out mixed melting points with authentic samples.

3)
3) The infra-red absorption spectrograms for all the compounds isolated have been prepared through the courtesy of Dr. E.A. Coulson of the Department of Scientific and Industrial Research and compared with reference spectra where available. (* and of Mr. L.J. Bellamy of the Ministry of Supply.)

Fraction 1E/2. (122.5-123.5°C./100mm.)

Isolation of 2:4:5-Trimethylpyridine.

This fraction consisted entirely of tertiary bases and showed an equivalent weight of 121 on titration with standard hydrochloric acid using screened methyl orange as indicator. This value is in perfect agreement with the equivalent weight of trimethylpyridines (C₆H₈N = 121), and the main constituent of the fraction has been shown to be 2:4:5-trimethylpyridine, a compound which has been reported as a coal tar constituent previously.(60, 61)

75 Gms. of the fraction was treated with the theoretical amount of picric acid (based on the equivalent weight found) as a saturated solution in boiling 95% ethyl alcohol. This treatment was carried out in three stages, one third of the total amount of picric acid being added at each stage and the precipitated picrates filtered and washed, after thorough cooling. In this manner the following three batches of picrate were obtained.

1E/2a/

1E/2b. Colour - Similar to a. Crystalline form - as 1E/2a. m.p. - 159-160°C. Yield - 55.2gms.

1E/2c. Colour - Paler than above. Cryst. form - non-homogeneous. m.p. - 140-152°C. Yield - 38.5gms.

Fractions 1E/2a and 1E/2b were bulked together and recrystallised from 95% alcohol giving a product which melted at 160-161°C. Repeated recrystallisations from alcohol did not alter this melting point nor did a recrystallisation from acetone. This latter crystallisation showed that a pure product had been obtained.

The resulting yield of pure picrate was then treated with caustic soda to liberate the free base which was steam distilled out, dried over solid caustic soda and redistilled.

The physical characteristics of this pure base were determined, and the picrolonate and methiodide were prepared by the normal methods and recrystallised to constant melting points.

Below are listed the physical characteristics of the base and the melting points of its derivatives, along with the literature values of these constants for 2:4:5-trimethylpyridine and also mixed melting points of the derivatives with the derivatives prepared from an authentic sample of 2:4:5-trimethylpyridine/
pyridine.

B.p. 189.5°C/755mm. Literature value 189.6°C/760mm. (9)

D\(_4^{25}\) 0.9327 " " 0.9330 (9)

n\(_D^{25}\) 1.5055 " " 1.5054 (9)

Picrate m.160-161°C " " 161°C. (9)

Mixed melting point 160-161°C.

Picrolonate m.218°C. Literature value 218°C. (24)
The mixed melting point showed no lowering.

Methiodide m.244°C. Literature value 244°C. (24)
The mixed melting point showed no lowering.

The agreement of the above figures together with the evidence of mixed melting points was sufficient to prove that this compound was 2:4:5-trimethylpyridine.

Additional confirmation was provided by the infra-red absorption spectrogram (Appendix II) which was found to be identical with the spectrogram obtained by Benzie and Milne for 2:4:5-trimethylpyridine.

A microscopic examination of the crystalline form of the picrate fraction 1E/2c showed that this consisted of a mixture of which the main constituent was identical in crystalline form with 2:4:5-trimethylpyridine picrate. This picrate fraction was not examined further.

No quantitative estimate of the amount of 2:4:5-trimethylpyridine present in the crude Naphthalene Oil Bases was possible from these results as it was isolated.
isolated from fraction C.21 whose boiling range (131-135°C./100mm.) was well above the boiling point of the pure compound (123°C./100mm.) and, therefore, much larger proportions of this compound would be expected to occur in the lower C-fractions which were not thoroughly examined.

The presence of 2:4:5-trimethylpyridine in the bases derived from the Benzol Absorbing Oil was also shown by the isolation of a picrate from fractions 2E/3 and 2E/4 which melted at 160-161°C. and whose mixed melting point with 2:4:5-trimethylpyridine picrate showed no lowering.

Fraction 2E/6. (126.9-127°C./100mm.)

Isolation of 2:3:4-Trimethylpyridine.

This fraction consisted entirely of tertiary bases and showed an equivalent weight of 120.5 on titration with standard hydrochloric acid using screened methyl orange as indicator. This value is in good agreement with the equivalent weight of trimethylpyridines ($C_9H_{11}N = 121$), and the main constituent of the fraction has been shown to be 2:3:4-trimethylpyridine, a compound which has been reported as a coal tar constituent previously (61).

60 Gms. of the fraction was treated with the/
the theoretical amount of picric acid (based on the equivalent weight found) as a saturated solution in boiling 95% alcohol. This treatment was carried out in three stages, one third of the total amount of picric acid being added at each stage and the precipitated picrate filtered and washed after thorough cooling. In this manner the following three batches of picrate were obtained.

2E/6a Colour - Bright yellow. Crystalline form - homogeneous.
- m.p. - 162-164°C. Yield 53gms.

2E/6b Colour - As 2E/6a Crystalline form - as 2E/6a
- m.p. - 162-163°C. Yield 58gms.

2E/6c Colour - Darker than above. Cryst. Form - heterogeneous
- m.p. - 150-154°C. Yield 20gms.

Owing to their great similarity, the fractions 2E/6a and 2E/6b were bulked together. On repeated recrystallisation of these combined fractions from alcohol a product was obtained which melted sharply at 164°C. The melting point of this product could not be raised by further recrystallisation from alcohol nor by recrystallisation from acetone. It was considered, therefore, that a pure product had been obtained, and the free base was regenerated from this total yield of pure picrate in the manner described for 2:4:5-trimethylpyridine, and dried and redistilled.

The physical characteristics of this pure base/
base were determined and the picrolonate and methiodide were prepared by the normal methods and recrystallised to constant melting points.

Below are listed the physical characteristics of the base and the melting points of its derivatives together with the literature values of these constants for 2:3:4-trimethylpyridine. Unfortunately no authentic sample of 2:3:4-trimethylpyridine was available for comparison.

B.p. 193°/755mm. Literature value 192-193° (8)

\[ D_2^{25} \quad 0.9490 \quad \text{"} \quad \text{"} \quad D_2^{23} \quad 0.9511 \quad (74) \]

\[ n_D^{25} \quad 1.5130 \quad \text{"} \quad \text{"} \quad n_D^{22} \quad 1.5129 \quad (74) \]

Picrate m.164°C

\[ \text{"} \quad \text{"} \quad 164.5°C. \quad (8) \]

Picrolonate m.242°C (Ex. alcohol) \[ \text{"} \quad 239°C. \quad (74) \]

Methiodide m.160°C (Ex. absolute alcohol)

The agreement of the above figures was sufficient to prove that this compound was 2:3:4-trimethylpyridine. An infra-red absorption spectrum was obtained for this compound (Appendix II), but unfortunately no reference spectrum was available for direct comparison.

On repeated recrystallisation of picrate fraction 2E/6c from alcohol a product was finally obtained which melted at 164°C. and whose mixed melting point with 2:3:4-trimethylpyridine picrate showed no lowering. It was considered, therefore, that the fraction/
Fraction 2E/6c consisted essentially of 2:3:4-trimethylpyridine picrate together with small quantities of some impurity, probably 2:4:5-trimethylpyridine picrate. The fraction was not examined further.

A quantitative estimate of the amount of 2:3:4-trimethylpyridine in the crude Benzol Absorbing Oil Bases was made on the assumption that the whole of fraction 2E/6 consisted of this compound. The value found was - 0.34% on the total crude wet bases. i.e. 0.0068% on the Benzol Absorbing Oil.

The assumption that the whole of fraction 2E/6 consisted of 2:3:4-trimethylpyridine was not strictly correct, but the presence of this compound in the neighbouring fractions 2E/5 and 2E/7 would have more than compensated for the impurities in 2E/6. For this reason and because the neighbouring D-fraction 18 might also have contained a proportion of 2:3:4-trimethylpyridine (the other neighbouring fraction, D.20, contained only negligible quantities, as can be seen from the graph of distillation 3.E), the above estimate will be low, and the actual percentage might have been anything up to two times as great as this estimated value.

It is interesting to note that no indication of the presence of this compound in the Naphthalene Oil Bases was obtained from distillation 1.E.
Fractions 2E/10 - 12. (131-132.5°C./100mm.)
and 3E/7 and 8. (131-132°C./100mm.)

Isolation of 2:3:5:6-Tetramethylpyridine.

The solid which separated out from these fractions has been proved to be 2:3:5:6-Tetramethylpyridine, a compound which has not hitherto been reported as a constituent of coal tar. (Note. A preliminary note has been published on this part of the investigation.) (139).

The solid which separated out from these fractions was filtered off and washed with petroleum ether ("40-60°") After repeated recrystallisations of this solid material from petroleum ether, a product was obtained which consisted of small white glistening platelets with a pleasant odour and a melting point of 76°C, which could not be raised by further recrystallisations from the same solvent. From this pure product, the picrate, picrolonate and methiodide were prepared and recrystallised to constant melting points.

These melting points are listed below, and in each case they are identical with the melting points of the same derivatives prepared from a tertiary base (C₅H₁₃N), of the same melting and boiling points, isolated from the mixed pyridine bases in shale oil by Benzie and Milne (24). Mixed melting points showed no lowering either in the case of the base itself/
itself or of its derivatives.

Picrate (Ex. alcohol) m. 176°C.
Picrolonate (Ex. alcohol) m. 259-260°C (decomp.)
Methiodide (Ex. absolute alcohol) m. 178°C.

Benzie and Milne suggested tentatively that their compound was 2:3:5:6-tetramethylpyridine on the basis of a comparison of its dissociation constant with those of other methylated pyridines, and this was further supported by analogy of the tetramethylpyridines to the tetramethylbenzenes.

There are few references in the literature to the preparation of this compound. Oparina (60), however, obtained a solid tertiary base in the reaction products on passing a mixture of formaldehyde, methyl-ethyl ketone and ammonia over alumina in a heated copper tube. This solid base melted at 73-74°C. and its picrate melted at 173-174°C. This work has been repeated in this college by R.T. Smith, who obtained a solid product which on purification melted at 76°C. and the picrate of which melted at 176°C. The mode of preparation of this compound strongly indicates the 2:3:5:6-configuration. The identity of this base with that isolated from coal tar was proved by the fact that the mixed melting points of the pure bases and of the picrates showed no lowering, and also by the fact that the infra-red absorption spectrograms for the two samples were identical (Appendix II).
Oparina (105) has recently repeated his earlier work and obtained a product which melted at 81°C. and the picrate of which melted at 173.5°C. On partial oxidation of this free base with permanganate he obtained 2:6-dimethylpyridine-3:5-dicarboxylic acid which on distillation with lime yielded 2:6-dimethylpyridine. Oxidation with excess permanganate yielded a crude tetracarboxylic acid which on heating lost carbon dioxide to give an acid melting at 308-309°C. From the mother liquors of the oxidation the 3:5-dicarboxylic acid and 2:5-dimethylpyridine-3:6-dicarboxylic acid were obtained.

This work proves quite conclusively that the product obtained by Oparina was 2:3:5:6-tetramethylpyridine, and, on the grounds that their reaction conditions were almost identical, it can be assumed that the product obtained by Smith was also 2:3:5:6-tetramethylpyridine, in spite of discrepancies in the melting points, and hence that the base isolated from coal tar was 2:3:5:6-tetramethylpyridine.

In order to obtain an approximate quantitative estimate of the amount of 2:3:5:6-tetramethylpyridine present in the crude tar bases, a portion of the bulked fractions 2E/10-12 and 3E/7 & 8 was subjected to the following treatment.

The/
The sample was cooled with a "dry ice"/methyl alcohol mixture, the solid filtered off and the liquid removed for re-freezing. The solid was washed with a small quantity of chilled petroleum ether, the ether removed from the washings by distillation and the resulting residue bulked with the above liquid fraction for re-freezing. This whole series of operations was repeated until no more solid could be separated.

Finally a liquid portion was obtained consisting entirely of tertiary bases and amounting to 17.5% of the bulked fractions.

3:4:5-Trimethylpyridine has neither been isolated from any natural nor has it been prepared, but, calculating its boiling point by means of an empirical formula derived by Eguchi (9), a value of 199.3°C./760mm. was obtained, i.e. approximately the same as that of the solid base. It was therefore considered possible that 3:4:5-trimethylpyridine might be present in the liquid residue, and for this reason the liquid was subjected to a fractional treatment with picric acid as has been described before. In this manner the following three batches of picrate were obtained:

A. m. 172-174°C.  B. m. 174-176°C.  C. m. 160-170°C.

On recrystallisation of the bulked fractions A. and B. from 95% alcohol a product was obtained which melted/
melted at 176°C and whose mixed melting point with 2:3:5:6-tetramethylpyridine picrate showed no lowering. On repeated recrystallisation of fraction C, an identical product was obtained, thus proving that the liquid consisted essentially of 2:3:5:6-tetramethylpyridine with only traces of impurities. As no indication of the presence of 3:4:5-trimethylpyridine had been found, this range was not examined further.

The investigation described above showed that the bulked fractions 2E/10-12 and 3E/7 & 8 consisted almost entirely of 2:3:5:6-tetramethylpyridine. A quantitative estimate of the amount of this compound present in the total oils was made, using the same approximations as were used in the estimation of 2:3:4-trimethylpyridine. The value found was 0.46% on the total crude wet bases. i.e. 0.0092% on the Benzol Absorbing Oil. Here again it must be remembered that the true value might have been anything up to two times as great as this approximation.

It is interesting to note that, as in the case of 2:3:4-trimethylpyridine, no indication of the presence of 2:3:5:6-tetramethylpyridine in the bases derived from the Naphthalene Oils was obtained from distillation 1.E. In addition, the presence of the o- and p-toluidines in the Naphthalene Oil Bases was shown in distillation 1.E., but no indication of their presence/
presence in the Benzol Absorbing Oil Bases was obtained from distillations 2.E. and 3.E. These facts illustrate the profound differences which exist between base fractions of the same boiling range derived from different tar oil fractions. This difference is probably due to the fact that in the distillation of the crude tar the bases distil over as some type of complex with phenols, and the boiling points of these complexes may not vary in the same order as those of their base constituents.

For this reason the absence of a base in any single tar oil fraction does not prove the absence of that base in the total tar.

Fraction 3E/12. (135-135.2°C./100mm.)

**Isolation of 2:3:4:6-Tetramethylpyridine.**

This fraction, which consisted for the most part of tertiary bases together with a small amount of primary bases, showed an equivalent weight of 133 on titration with standard hydrochloric acid using screened methyl orange as indicator. This value is in good agreement with the equivalent weight of the tetramethylpyridines (C$_9$H$_{13}$N = 135), and the main constituent of the fraction has been shown to be 2:3:4:6-tetramethylpyridine, a compound which has not hitherto been reported as a constituent of coal tar.

70 Gms./
70 Gms. of the fraction was treated with the theoretical amount of picric acid (based on the equivalent weight found) as a saturated solution in boiling 95% ethyl alcohol. This treatment was carried out in three stages, one third of the total amount of picric acid being added at each stage, and the precipitated picrate filtered and washed after thorough cooling. In this manner the following three batches of picrate were obtained.

3E/12a Colour - As 3E/12b. Crystalline form - homogeneous.
   m.p. - 110-120°C. Yield - 70gms.

3E/12b Colour - As 3E/12a. Crystalline form - homogeneous.
   m.p. - 110-120°C. Yield - 60gms.

3E/12c Colour - Darker than above. Cryst. form - heterogeneous.
   m.p. - 150-170°C (decompn.) Yield - 38gms.

Owing to their great similarity the fractions 3E/12a and 3E/12b were bulked together. On repeated recrystallisation of these fractions from alcohol a product was obtained which melted sharply at 122.5-123°C. The melting point of this product could not be raised by further recrystallisation from alcohol, nor by recrystallisation from acetone.

It was considered therefore that a pure product had been obtained, and the free base was regenerated from the total yield of pure picrate. The free base was then dried and redistilled.
The physical characteristics of this pure base were determined, and the picrolonate and the methiodide were prepared by the normal methods and recrystallised to constant melting points.

Below are listed the physical characteristics of the base and the melting points of its derivatives along with the literature values of these constants for 2:3:4:6-tetramethylpyridine. The mixed melting points of the picrate and picrolonate with the same derivatives obtained from a sample of 2:3:4:6-tetramethylpyridine, isolated from the mixed pyridine bases in shale oil by Benzie and Milne (24), showed no lowering.

E.p. 203°C/750mm. Literature value 203.5°C/760mm. (9)

D_25^o 0.9322 " " 0.9345 (24)

n_25^D 1.5087 " " 1.5084 (9)

Picrate (Ex. acetone) m. 122.5-123°C. Literature value........ 122.5-123°C. (24)

Picrolonate (Ex. alcohol) m. 225.5°C. (decompn.) Literature value............ 225.5°C. (24)

Methiodide (Ex. absolute alcohol) m. 192-193°C.

The agreement of the above figures, together with the evidence of mixed melting points, was sufficient to prove that this compound was 2:3:4:6-tetramethylpyridine. Additional confirmation was provided by the infra-red absorption spectrogram (Appendix II) which was found to be identical with the spectrogram obtained for 2:3:4:6-tetramethylpyridine by Benzie and/
and Milne.

The picrate fraction \(3E/12c\) was shown to contain a proportion of a primary base by regeneration of the free bases and diazotisation. This primary base was probably \(m\)-toluidine which has previously been reported as a coal tar constituent (17) and which boils at \(203.3^\circ C./760\) mm. The fraction was not examined further as it was considered most likely that it consisted of a mixture of \(m\)-toluidine and 2:3:4:6-tetramethylpyridine.

The investigation described above showed that the fraction \(3E/12\) consisted essentially of 2:3:4:6-tetramethylpyridine contaminated with a small proportion of \(m\)-toluidine. An approximate quantitative estimate of the amount of this tetramethylpyridine present in the total oils was made using the same approximations as were used before.

The value found was 0.26% on the total crude wet bases, i.e. 0.0052% on the Benzol Absorbing Oil.

Here again it must be remembered that the true value might have been considerably greater than this approximation, even more so than in the case of 2:3:5:6-tetramethylpyridine where the solid character of the base facilitated its isolation from a wider distillation range.

Fraction/
Isolation of 3-Methylisoquinoline.

The solid which separated from this fraction has been proved to be 3-methylisoquinoline, a compound which has been reported as a coal tar constituent previously (78).

The solid which separated from the fraction on thorough cooling was filtered off and washed with petroleum ether. After repeated recrystallisation of this solid material from petroleum ether a product was obtained with a melting point of 64.5°C. which could not be raised by further recrystallisations from the same solvent. From this pure product the picrate, sulphate and methiodide were prepared and recrystallised to constant melting points.

The melting points of the free base and of its derivatives are shown below together with the literature values of these constants for 3-methylisoquinoline.

**Free base** m.64.5°C.
**Literature Value** 64.7°C.(78)

**Picrate (Ex. alcohol)** m.199-200°C.
**Literature value** ......... 197-198°C.(25)

**Sulphate (Ex. absolute alcohol)** m.154.5°C.
**Literature value** ............... 154.5-155°C.(78)

**Methiodide (Ex. alcohol)** m.221°C.
**Literature value** ............. 219°C.(143)

Unfortunately/
Unfortunately no authentic sample of 3-methylisoquinoline was available for carrying out mixed melting points, but the agreement of the above figures was sufficient to prove that this compound was 3-methylisoquinoline.

An infra-red absorption spectrogram was obtained for this compound (Appendix II) but no reference spectrum was available for comparison.

No quantitative estimate of the amount of 3-methylisoquinoline in the total oil could be obtained from the above investigation, as the fraction was obtained from the fore-runnings of distillation 5.E., and it was to be expected that the greater part of the 3-methylisoquinoline present would occur in the lower D-fractions whose distillation ranges were more close to the boiling point of the pure base.

The fraction 5E/1 was not examined further.

Fractions 7E/6 and 8E/2. (168.5-169°C./50mm.)

Isolation of 2:7-Dimethylquinoline.

A solid base has been isolated from the fractions 7E/6 and 8E/2, which has been proved to be 2:7-dimethylquinoline, a compound which has not hitherto been isolated from any natural source.
On cooling a portion of the bulked fractions 7E/6 and 8E/2 with a freezing mixture of ice and salt, a white solid separated out. This solid base was filtered off, washed with petroleum ether and recrystallised repeatedly from petroleum ether to constant melting point. Finally a product was obtained consisting of clear needle-shaped crystals which melted at 61°C. From this pure base the picrate, styphnate and trinitro-m-cresolate were prepared and recrystallised to constant melting points.

These melting points are listed below together with the literature values of these constants for 2:7-dimethylquinoline. A mixed melting point of the free base with an authentic sample of 2:7-dimethylquinoline, prepared according to the method described by Doebner and Miller (144) from m-toluidine, paraldehyde and concentrated hydrochloric acid, showed no lowering. (Note - The product obtained by means of the Doebner & Miller synthesis from m-toluidine and paraldehyde was assigned the 2:5- formula by Decker and Remfry (147), but Manske (86) has since shown that this is untrue and that the true configuration is that of 2:7-dimethylquinoline.)

Free base............. m. 61°C.
Literature value..... 61°C. (86)

Picrate (Ex. acetone) m. 196°C.
Literature value....... 196°C. (86)

Styphnate (Ex. acetone) m. 220°C.
Literature value....... 222°C. (86)

Trinitro-/
Trinitro-m-cresolate (Ex. "cellosolve") m.250°C. Literature value.................. 250°C.(86)

The agreement of the above figures, together with the evidence of the mixed melting point, was sufficient to prove that this compound was 2:7-dimethylquinoline.

Additional confirmation was obtained from the infra-red absorption spectrogram (Appendix II), which was found to be identical with that obtained for the authentic sample of 2:7-dimethylquinoline which had been prepared.

In order to obtain an approximate estimate of the amount of 2:7-dimethylquinoline present in the tar oil, a portion of the bulked fractions 7E/6 and 8E/2 was subjected to the following treatment.

The sample was cooled with a "dry ice"/methyl alcohol mixture, the solid filtered off and the liquid removed for re-freezing. The solid was washed with a small quantity of chilled petroleum ether, the ether removed from the washings by distillation and the resulting residue bulked with the above liquid fraction for re-freezing. This whole series of operations was repeated until no more solid could be separated.

In this manner a total liquid residue which amounted to 20% of the bulked fractions was finally obtained.
obtained, and all the solid obtained, although melting below 61°C., melted at an intermediate temperature when mixed with pure 2:7-dimethylquinoline, thus proving that it consisted of substantially pure 2:7-dimethylquinoline.

This investigation showed that the bulked fractions 7E/6 and 8E/2 contained at least 80% of 2:7-dimethylquinoline, in addition to the amount of this compound which still remained in the liquid residue.

An estimate of the amount of 2:7-dimethylquinoline present in the tar oil was made on the assumption that the bulked fractions 7E/6 and 8E/2 consisted entirely of 2:7-dimethylquinoline, as it was considered that the 2:7-dimethylquinoline content of the neighbouring E-fractions would more than compensate for the impurities in the bulked fractions. The value found was 0.78% on the total crude wet bases. i.e. 0.016% on the Benzol Absorbing Oil.

Note - This will be a closer approximation to the true value than was obtained for the previous compounds, as the fractions 7E/6 and 8E/2 were derived from a wider range of D-fractions and there was little chance of any 2:7-dimethylquinoline occurring in any of the other D-fractions.
Fractions 8E/3 - 8E/7. (169-170.8°C./50mm.)

Isolation of 2:6-Dimethylquinoline.

A solid base has been isolated from the fractions 8E/3 - 8E/7, which has been proved to be 2:6-dimethylquinoline, a compound which has not hitherto been isolated from any natural source.

The solid base which separated from these fractions was filtered off, washed with petroleum ether and recrystallised from petroleum ether to constant melting point. Finally a product was obtained which consisted of clear needle-shaped crystals with a melting point of 60°C. This melting point was identical to that of an authentic sample of 2:6-dimethylquinoline prepared according to the method of Doebner and Miller (144) from p-toluidine and paraldehyde, and a mixed melting point showed no lowering.

From the pure base the picrate, styphnate and trinitro-m-cresolate were prepared and recrystallised to constant melting points. These melting points are listed below together with the literature values of the melting points of these derivatives of 2:6-dimethylquinoline.

Picrate (Ex. absolute alcohol) m.191°C.
Literature value................. 191°C.(86)

Styphnate/
Styphnate (Ex. absolute alcohol) m.199°C.
Literature value.......................... 200°C. (86)

Trinitro-m-cresolate (Ex. "cellosolve") m.207°C.
Literature value.......................... 206°C.

The agreement of the above figures, together with the evidence of the mixed melting point of the free base, was sufficient to prove that this compound was 2:6-dimethylquinoline.

Additional confirmation was obtained from the infra-red absorption spectrogram (Appendix II) which was found to be identical to that obtained for the authentic sample of 2:6-dimethylquinoline which had been prepared.

In order to obtain an estimate of the amount of 2:6-dimethylquinoline present in the total oil, a portion of the bulked fractions 8E/3-8E/7 was subjected to the same treatment as was used in the evaluation of the 2:7-dimethylquinoline.

In this manner a yield of solid was obtained which consisted of essentially pure 2:6-dimethylquinoline, and the total liquid residue amounted to 53% of the bulked fractions.

An estimate of the amount of 2:6-dimethylquinoline present in the total oil was made on the approximation that 50% of the liquid residue consisted of 2:6-dimethylquinoline, i.e. a total of 73.5% of the/
the bulked fractions consisted of 2:6-dimethylquinoline. As a result of this approximation and on account of the fact that neighbouring E-fractions might have contained some 2:6-dimethylquinoline, the error in the value obtained may be as high as ±50%.

The value found was 0.36% on the total crude wet bases, i.e. 0.0072% on the Benzol Absorbing Oil.

Fractions 8E/9 - 8E/12. (173.5-174.2°C./50mm.)

Isolation of 2:4-Dimethylquinoline.

A pure liquid base has been isolated from these fractions and has been proved to be 2:4-di-methylquinoline, a compound which has not hitherto been reported as a coal tar constituent.

As no pure picrate could be isolated from any of these fractions by fractional treatment with picric acid and recrystallisation of the resulting picrate fractions, it was decided to carry out a fractional acid extraction on the bulked fractions 8E/9 and 8E/10.

This fractional acid extraction was carried out in a manner precisely similar to that described on page 28, using as a starting material 200gms. of the bulked fractions 8E/9 and 8E/10. The weights and/
and refractive indices of the ten base fractions, which were finally obtained by distilling the ether from the fractions S.6 - S.15 and then distilling the bases in vacuo, are shown below.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Weight</th>
<th>$n_{D}^{25}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F.1</td>
<td>5gms.</td>
<td>1.5965</td>
</tr>
<tr>
<td>F.2</td>
<td>16gms.</td>
<td>1.6010</td>
</tr>
<tr>
<td>F.3</td>
<td>18gms.</td>
<td>1.6025</td>
</tr>
<tr>
<td>F.4</td>
<td>17gms.</td>
<td>1.6035</td>
</tr>
<tr>
<td>F.5</td>
<td>21gms.</td>
<td>1.6045</td>
</tr>
<tr>
<td>F.6</td>
<td>18gms.</td>
<td>1.6045</td>
</tr>
<tr>
<td>F.7</td>
<td>20gms.</td>
<td>1.6045</td>
</tr>
<tr>
<td>F.8</td>
<td>19gms.</td>
<td>1.6045</td>
</tr>
<tr>
<td>F.9</td>
<td>22gms.</td>
<td>1.6045</td>
</tr>
<tr>
<td>F.10</td>
<td>29gms.</td>
<td>1.6022</td>
</tr>
</tbody>
</table>

Owing to their great similarity the fractions F.5 - F.9 inclusive were bulked together. A sample of the bulked fractions was treated with the theoretical amount of picric acid (calculated for dimethylquinoline.) as a saturated solution in boiling 95% alcohol. This treatment was carried out in three stages, one third of the total amount of picric acid being added at each stage and the picrate precipitated, filtered and washed after thorough cooling.

In this manner three picrate fractions were obtained.
obtained which did not differ in either melting point (189-192°C.), crystalline form (needle-shaped crystals) or colour (yellow - darkening rapidly on exposure to light). The three fractions were therefore bulked together. On repeated recrystallisation of these bulked fractions from "cellosolve" a product was finally obtained which melted at 196°C. This melting could not be raised by further recrystallisation from "cellosolve" nor by recrystallisation from acetone. It was considered therefore that a pure picrate had been obtained.

The free base was regenerated from the pure picrate by treatment with caustic soda and extraction with ether. The ether was distilled from this extract, after drying over solid caustic soda, and the free base was distilled at a pressure of 100mm. Hg.

The physical characteristics of this pure base were determined, and the styphnate and trinitro-m-cresolate were prepared by the normal methods and recrystallised to constant melting points.

Below are listed the physical characteristics of the base and the melting points of its derivatives, together with the literature values of these constants for 2:4-dimethylquinoline.

B.p. 174°C./100mm. Hg.
An authentic sample of 2:4-dimethylquinoline was prepared according to the method of Vaughan (148) from aniline and acetone via the "acetone anil", and from this sample the picrate was prepared and recrystallised from "cellosolve" to constant melting point (196°C). A mixed melting point of this picrate with the coal tar base picrate showed no lowering.

The agreement of the above figures, together with the evidence of the mixed melting points of picrates, was sufficient to prove that this compound was 2:4-dimethylquinoline.

Additional confirmation was obtained from a comparison of the infra-red absorption spectrograms of the sample isolated from coal tar and the synthetic sample (Appendix II).

From the above investigation it can be seen that the combined fractions F.5 - F.9 consisted almost entirely of 2:4-dimethylquinoline with only traces of impurities. The fractions F.5 - F.9 amounted to 50%
50% of the combined fractions 8E/9 and 10 and, as it could be seen from the refractive indices of the other F-fractions that no other major constituent was present, it was assumed that the combined fractions 8E/9 and 10 contained at least 75% of 2:4-dimethylquinoline.

An estimate of the 2:4-dimethylquinoline content of the combined fractions 8E/11 and 12 was made by means of the m-nitrobenzaldehyde condensation product.

The condensation product of 2:4-dimethylquinoline with m-nitrobenzaldehyde was prepared as follows: -

1 Gm. of pure 2:4-dimethylquinoline was heated with 1 gm. of m-nitrobenzaldehyde in an oil bath at 170°C. for six hours. On cooling, the reaction mixture solidified. The solid product was washed with a little alcohol and dried in vacuo.

Yield 1.3gms. (66% based on formula i)
m.p. 160-162°C.

On repeated recrystallisation of this from benzene a product was obtained consisting of almost colourless prisms which melted at 166-167°C. This melting point does not agree with the value of 184°C. given by Spallino and Cucchiaroni (149). It was found, however, that on boiling the product for two hours/
hours with acetic anhydride and cooling, a yellow powder was obtained which melted at 180-183°C. and whose melting point was raised to 186-187°C by repeated recrystallisation from acetic anhydride.

It was considered that the product melting at 166-167°C. was of the formula -

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2-\text{CHOH} \quad \text{NO}_2 \\
\end{align*}
\]

which was dehydrated on boiling with acetic anhydride to yield -

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \equiv \text{CH} \quad \text{NO}_2 \\
\end{align*}
\]

A 10gm. sample of the combined fractions 6E/11 and 12 was heated with 10gms of m-nitrobenzaldehyde in an oil bath at 130°C. for six hours. On cooling, the reaction mixture solidified. The solid product was washed with a little alcohol and dried in vacuo.

Yield 12gms. (61.2% on formula i)

m.p. 158-160°C.

This yield was recrystallised from benzene.

Yield 11gms. m.p. 161-163°C.

This melting point approximates the melting point of the product obtained in 66.3% yield from pure 2:4-dimethylquinoline, and on repeated recrystallisation from benzene a product was obtained which melted at 166-
166-167°C. The mixed melting point of this product with that of the same melting point obtained from pure 2:4-dimethylquinoline showed no lowering, thus proving the identity of the two compounds.

Summarising the above results:-

1) A crude condensation product which melted at 160-162°C. was obtained in 66.3% yield from pure 2:4-dimethylquinoline.

2) A crude sample of the same condensation product, which melted at 158-160°C., was obtained from the combined fractions 8E/11 and 12 in 61.2% yield. Although this melting point was slightly below that of the corresponding product from pure 2:4-dimethylquinoline, it was raised to a higher level by one recrystallisation from benzene with a resultant reduction in yield to 56.1%.

On the basis of these results it was reasonable to assume that at least 75% of the combined fractions 8E/11 and 12 consisted of 2:4-dimethylquinoline.

An estimate of the 2:4-dimethylquinoline content of the total Benzol Absorbing Oil Bases was calculated on the assumption that the combined fractions 8E/9 - 12 contained 75% of 2:4-dimethylquinoline. The value found was 1.12% on the total crude wet bases, i.e. 0.022% on the Benzol Absorbing Oil.
It is possible that the true content of 2:4-dimethylquinoline may have been anything up to 50% greater than this estimated value.

Fraction 8E/14. (174-175°C./50mm.)

Isolation of 2:3-Dimethylquinoline.

A solid base has been isolated from fraction 8E/14 which has been proved to be 2:3-dimethylquinoline, a compound which has not hitherto been reported as a coal tar constituent.

The solid, which separated from the fraction on prolonged standing, was filtered off and washed with petroleum ether. No more solid could be separated from the fraction, even on freezing to as low a temperature as -70°C. The solid base was recrystallised to constant melting point from petroleum ether. Finally a product was obtained consisting of clear prism shaped crystals which melted at 70°C. This melting point was identical with that of an authentic sample of 2:3-dimethylquinoline prepared from isatin and methyl ethyl ketone by the method of Pfitzinger (145) as modified by Plant and Rosser (146), and a mixed melting point showed no lowering.

From the pure base the picrate, styphnate and/
and trinitro-m-cresolate were prepared and recrystallised to constant melting points. These melting points are listed below together with the literature values for the melting points of these derivatives of 2:3-dimethylquinoline.

Picrate (Ex. absolute alcohol) m.235°C. Literature value .................. 235°C. (86)

Styphnate (Ex. absolute alcohol) m.242°C. Literature value .................. 243°C.

Trinitro-m-cresolate (Ex. "cellosolve") m.248°C. Literature value .................. 248°C.

The agreement of the above figures, together with the evidence of the mixed melting point of the free base, was sufficient to prove that this compound was 2:3-dimethylquinoline.

Additional confirmation was obtained from the infra-red absorption spectrogram (Appendix II), which was found to be identical with that obtained for the authentic sample of 2:3-dimethylquinoline which had been prepared.

No estimate of the amount of this compound present in the total oil could be obtained, as it occurred in the last fraction of the E-distillations and it was to be expected that the greater part of compound which had been present in the crude bases would be retained in the residues from the D- and E-distillations.
DISCUSSION AND SUMMARY.

The starting materials for this investigation were the nitrogenous bases extracted by sulphuric acid from both the Naphthalene Oil and the Benzol Absorbing Oil fractions of vertical retort coal tar. These bases consist for the most part of pyridine, quinoline and isoquinoline homologues, together with smaller quantities of primary bases.

Each fraction of bases has been subjected to a two-fold fractional distillation, the first of these fractionations having been carried out in a Raschig-ring packed column of efficiency equivalent to 5 - 10 theoretical plates, and the second stages of the fractionations carried out in a "Dixon gauze-ring" packed column of efficiency equivalent to approximately 30 theoretical plates.

From the results of these distillations "weight / temperature of distillation" balances have been drawn up for both fractions of bases. The distillation "flats" indicated in these distribution graphs correspond well with the boiling points of the bases previously isolated from coal tar, and from the graphs an estimate can be obtained of the relative abundance of the individual components (or groups of components when several boil close together).
The fractions obtained from these two-fold fractional distillations have been studied as follows.

**Naphthalene Oil Bases.**

A high proportion of these bases distilled at temperatures below 145°C., and quantitative estimates have been made of the individual constituents occurring within this range.

The results obtained were:

- Pyridine .................. 2.26% (on total crude wet base)
- 2-Methylpyridine......... 5.73%
- 3-Methylpyridine......... 3.60%
- 4-Methylpyridine......... 1.85%
- 2:6-Dimethylpyridine... 5.50%

Note - The results obtained for the last three compounds were probably slightly low as some of these bases would have been carried over into the higher cuts which were not examined.

These low-boiling bases have widespread industrial uses and, at the present time, are extracted commercially from the lower boiling tar oil fractions only. There are indications that the present demand for these bases exceeds the supply, and it is possible that the Naphthalene Oils might provide a useful auxiliary source.

A more profitable use for high-boiling tar bases, such as those obtained from the Naphthalene Oils, might be provided by some form of catalytic cracking to pyridine.

Little/
Little work appears to have been carried out on this possibility, but the Philips Petroleum Co. (152) have patented a process for conversion of alkyl-pyridines to pyridine by passing the alkyl-pyridines, with an excess of benzene or some other alkyl group acceptor, in the vapour phase over a clay type catalyst at 455-650°C. The example given, however, refers to mixed ethylpyridines, and it is doubtful whether the method would prove satisfactory if applied to the methylpyridines derived from coal tar. Prior to the recent war, however, the I.G. Farbenindustrie (153) were investigating a process for the conversion of high-boiling bases into pyridine. The process consisted of passing the vapours of the mixed bases, with hydrogen and a small proportion of hydrogen sulphide, through a nickel-chrome steel tube at about 860°C. Although the yield was only about 50% of the theoretical, the erection of a larger plant had been considered, but the war caused this plan to be abandoned.

A fraction of the Naphthalene Oil Bases (b. 131-135°C./100 mm. Hg.) has been subjected to a further fractional distillation in a "Dixon gauze ring" packed column, of efficiency equivalent to approximately 100 theoretical plates, in the hope of isolating tetramethylpyridines. No trace was found of tetra-methylpyridines but 2:4:5-trimethylpyridine was isolated from this fraction.
Benzol Absorbing Oil Bases.

From the distribution graph it can be seen that a high proportion of these bases distilled at a temperature corresponding with the boiling point of quinoline, and it is possible that these bases may provide a useful commercial source of quinoline.

The following fractions of these bases have been subjected to further fractionation in the "100-plate" column in the hope of isolating bases not previously reported as coal tar constituents:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Boiling Range</th>
<th>Distillation</th>
</tr>
</thead>
<tbody>
<tr>
<td>126-131°C./100mm. Hg.</td>
<td>Distillation 2.E.</td>
<td></td>
</tr>
<tr>
<td>131-137°C./</td>
<td>Distillation 3.E.</td>
<td></td>
</tr>
<tr>
<td>152-158.5°C./</td>
<td>Distillation 4.E.</td>
<td></td>
</tr>
<tr>
<td>161-165°C./50mm. Hg.</td>
<td>Distillation 5.E.</td>
<td></td>
</tr>
<tr>
<td>165-168°C./</td>
<td>Distillation 6.E.</td>
<td></td>
</tr>
<tr>
<td>168-170°C./</td>
<td>Distillation 7.E.</td>
<td></td>
</tr>
<tr>
<td>170-178°C./</td>
<td>Distillation 8.E.</td>
<td></td>
</tr>
</tbody>
</table>

Eight compounds have been isolated and positively identified from the narrow boiling range cuts obtained by these distillations, and, where possible, approximate estimates of the amounts of these present have been made.

These compounds are listed below together with the boiling ranges of the cuts from which they have been isolated. The estimates of their content in the crude wet Benzol Absorbing Oil Bases are included.
included, together with the possible error involved in the individual estimations.

<table>
<thead>
<tr>
<th>Boiling Range</th>
<th>Compound</th>
<th>Content</th>
<th>Possible Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>126.9-127°C/100mm.</td>
<td>2:3:4-Trimethylpyridine</td>
<td>0.34%</td>
<td>+100%</td>
</tr>
<tr>
<td>131-132.5°C/100mm.</td>
<td>2:3:5:6-Tetramethylpyridine</td>
<td>0.46%</td>
<td>+100%</td>
</tr>
<tr>
<td>135-135.2°C/100mm.</td>
<td>2:3:4:6-Tetramethylpyridine</td>
<td>0.26%</td>
<td>+100%</td>
</tr>
<tr>
<td>154.8-157°C/50mm.</td>
<td>3-Methylisoquinoline</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>168.5-169°C/50mm.</td>
<td>2:7-Dimethylquinoline</td>
<td>0.78%</td>
<td>+20%</td>
</tr>
<tr>
<td>169-170.8°C/50mm.</td>
<td>2:6-Dimethylquinoline</td>
<td>0.36%</td>
<td>+50%</td>
</tr>
<tr>
<td>173.5-174.2°C/50mm.</td>
<td>2:4-Dimethylquinoline</td>
<td>1.12%</td>
<td>+50%</td>
</tr>
<tr>
<td>174 - 175°C./50mm.</td>
<td>2:3-Dimethylquinoline</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

The six compounds underlined in red have not hitherto been reported as coal tar constituents.

From the distillations 5.E - 8.E inclusive a more accurate distribution graph has been constructed for the range distilling between 161 and 175°C./50mm. Hg.

From a study of the results obtained in this investigation the following notable facts stand out.

1) Of the nineteen possible methyl homologues of pyridine, seventeen have now been identified in coal tar. The remaining two, 3:4:5-trimethylpyridine and pentamethylpyridine, have neither been isolated from any natural source nor has either been prepared synthetically. The absence of these two compounds from/
from coal tar has not been proved, however, during this investigation.

2) Of the dimethylquinolines isolated, all have been substituted in the 2-position, and in the boiling range which has been closely examined no trace of poly-substituted quinolines not substituted in the 2-position, although several such compounds boil within this range.

It is interesting to note that all the poly-substituted quinoline homologues isolated from the mixed petroleum bases have been substituted in the 3-position.

The only claim to the isolation of a poly-substituted quinoline from any natural source has been that of Ganguli & Guha (93) to the isolation of 5:8-dimethylquinoline from coal tar, and some doubt has been cast on this claim.

3) The percentage of 2:4-dimethylquinoline found was much higher than that of either 2:6- or 2:7-dimethylquinoline. Jantzen in his investigation of higher coal tar bases (78) found the following percentages for the monomethylquinolines.

<table>
<thead>
<tr>
<th>Position</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methylquinoline</td>
<td>10.60%</td>
</tr>
<tr>
<td>3- &quot;</td>
<td>1.79%</td>
</tr>
<tr>
<td>4- &quot;</td>
<td>5.70%</td>
</tr>
<tr>
<td>5- &quot;</td>
<td>0.30%</td>
</tr>
<tr>
<td>6- &quot;</td>
<td>1.80%</td>
</tr>
<tr>
<td>7- &quot;</td>
<td>1.35%</td>
</tr>
<tr>
<td>8- &quot;</td>
<td>1.46%</td>
</tr>
</tbody>
</table>
It may be noticed that 2-methylquinoline was found to be the most abundant, followed by 4-methylquinoline, and that the other methylquinolines were present to a much smaller extent.

These facts taken together seem to indicate that the percentages of individual methylated quinolines present in coal tar bear some relation to the reactivity of the substituent methyl groups.
ACKNOWLEDGEMENTS.

The author's thanks are due in the first instance to Principal H.B. Nisbet of the Heriot-Watt College, under whose supervision this research has been carried out, for his interest and advice throughout the course of the work, and to the Coal Tar Research Association whose grant has made this investigation possible.

Thanks are due also to many others whose names have been mentioned in the text of this thesis, and to members of the staff of the Heriot-Watt College.
APPENDIX I.

PYRIDINE, QUINOLINE AND ISOQUINOLINE HOMOLOGUES
ISOLATED PREVIOUSLY FROM COAL TAR.

Pyridine. First isolated by Williams in 1854 (6)
b. 115.3°C (7); D$_4^{25}$ 0.9776 (8); n$_D^{25}$ 1.5068 (9).
Picrate m.167°C (9); Chloroplatinate m.268°C (9);
Isolations etc - (7) - (16) and (18) - (23).

2-Methylpyridine. First isolated by Anderson in 1846 (2).
b. 129.3°C (9); D$_4^{25}$ 0.9400 (9); n$_D^{25}$ 1.4980 (24).
Picrate m.165.5°C (24), 168°C (25); Picrolonate m.212° (24), 214-5°C (25); Methiodide m.224° (8), 229.5°C (24)
Isolations etc - (8, 9, 11, 13, 14, 16, 20 and 26)

3-Methylpyridine. First isolated by Mohler in 1888 (27).
b.144°C (9); D$_4^{25}$ 0.9515 (7); n$_D^{25}$ 1.5036 (9).
Picrate m.149° (8&9), 153°C (25); Picrolonate m.206-7°C (24);
Chloroplatinate m.208°C (9).
Isolations etc - (8, 9, 13 and 28 - 52)
Note: - The great amount of literature published on
the isolation of 3-methylpyridine is due to the fact
that it cannot be separated from 4-methylpyridine and
2:6-dimethylpyridine by direct fractional distillation,
and much work has recently been carried out on its
isolation by other means, with a view to its conversion
to nicotinic acid or nicotinamide.

4-Methylpyridine. First isolated by Ladenburg in 1885 (53)
b. 145.3°C (9)/
b. 145.3°C (9); D$_4^{25}$ 0.9502 (9); n$_D^{25}$ 1.5029 (9)
Picrate m.167.5-168°C (25); Picrolonate m. 256°C (24), 262-3°C (25)
Isolations etc :- (9, 13, 27, 29, 32, 35 - 38, 40, 41, 43, 45, 49, 51, 52, 53 and 54)

2:3-Dimethylpyridine First isolated by Ahrens in 1906 (63).
b. 160.6°C (9); D$_4^{25}$ 0.9419 (9); n$_D^{25}$ 1.5055 (24)
Picrate m. 188°C (9); Picrolonate m. 225-226°C (24)
Methiodide m. 206-207°C (24)
Isolations etc :- (9, 55 and 63)

2:4-Dimethylpyridine First isolated by Ladenburg in 1888 (51).
b. 157.3°C (9); D$_4^{25}$ 0.9271 (9); n$_D^{25}$ 1.4982 (24).
Picrate m. 182.5-183°C (24); Picrolonate m. 209-211°C (24)
Methiodide m. 118.5-119.5°C (24)
Isolations etc :- (9, 13, 16, 51, 56, 57, 58 and 60 -62)

2:5-Dimethylpyridine First isolated by Lunge & Rosenburg in 1887 (56)
b. 157°C (9); D$_4^{25}$ 0.9261 (9); n$_D^{25}$ 1.4982 (9).
Picrate m. 170°C (25); Picrolonate m. 171-172°C (25);
Chloroplatinate m. 214°C (9).
Isolations etc :- (9, 56, 59, 60, 61, 62 and 64)

2:6-Dimethylpyridine First isolated by Ladenburg in 1885 (54)
b. 144°C (9); D$_4^{25}$ 0.9183 (9); n$_D^{25}$ 1.4952 (24)
Picrate m. 163-163.5°C (24); Picrolonate m. 208-9°C (24);
Methiodide m. 238°C (24).
Isolations etc :- (8, 9, 13, 16, 27, 29, 32, 35-38, 40, 41, 43, 45, 51, 54, 56, 60, 61, 63 and 65-70).

3:4-Dimethylpyridine/
3:4-Dimethylpyridine First isolated by Ahrens in 1896 (71).  
b. 178.9°C (9); D$_4^{25}$ 0.9537 (9); n$_D^{25}$ 1.4952 (24).  
Picrate m.163°C (9); Picrolonate m.223-226°C (24).  
Methiodide m.120-121°C (24)  
Isolations etc: (9, 26, 71 and 72).

3:5-Dimethylpyridine First isolated by Ahrens and Gorkow in 1904 (64).  
b. 171.6°C (9); D$_4^{25}$ 0.9385 (9); n$_D^{25}$ 1.5032 (9).  
Picrate m.244°C (9); Picrolonate m.239-240°C (24).  
Chloroplatinate m.263°C (9)  
Isolations etc: (9, 64 and 73)

2:3:4-Trimethylpyridine First isolated by Komatsu and Mohri in 1931 (61).  
B. 192-193°C (8); D$_4^{23}$ 0.9511 (74); n$_D^{22}$ 1.5129 (74).  
Picrate m.164.5°C (8); Picrolonate m.239°C (74).  
Isolations etc: (61)

2:3:5-Trimethylpyridine First isolated by Komatsu and Mohri in 1931 (61).  
b. 186.6°C (9); D$_4^{25}$ 0.9310 (9); n$_D^{25}$ 1.5057 (9).  
Picrate m.184°C (9); HgCl$_2$ compound m.110°C (9).  
Isolations etc: (9, 60, 61)

2:3:6-Trimethylpyridine First isolated by Eckert and Loria in 1917 (73).  
b. 172.8°C (9); D$_4^{25}$ 0.9220 (9); n$_D^{25}$ 1.5057 (24).  
Picrate m.148°C (9); Picrolonate m.228-229°C (25).  
Chloroplatinate m.220°C (9)  
Isolations etc: (9, 60, 61, 63, and 73)  
2:4:5-
2:4:5-Trimethylpyridine  First isolated by Ahrens in 1896 (71).
b. 189.8°C (9); $D_d^{25} 0.9330$ (9); $n_d^{25} 1.5057$ (24). 1.5054 (9).
Ficrate m.161°C (9); Picrolonate m.218°C (24);
Chloroplatinate m.192°C (9).
Isolations etc : - (9, 60, 61, and 71) (73)

2:4:6-Trimethylpyridine First isolated by Mohler in 1888 (27).
b. 170.3°C (9); $D_d^{25} 0.9101$ (9); $n_d^{25} 1.4959$ (9).
Ficrate m.157°C (9); Picrolonate m.230°C (24);
Chloroplatinate m.220°C (9).
Isolations etc : - (9,16,26,27,58,63,72,73 and 76)

2:3:4:5-Tetramethylpyridine First isolated by Ahrens in 1895 (105)
b. 233°C (105)
Isolations etc : - (61 and 105)

2-Methyl-4-ethylpyrididine First isolated by Weidel and Pick in 1884 (77)
b. 179-180°C (9); $D_d^{25} 0.9130$ (9); $n_d^{25} 1.4953$ (9).
Ficrate m.141-2°C (24); Picrolonate m.186-7°C (24);
Chloroplatinate m.203°C (8).
Isolations etc. : - (9, 24 and 77)

2-Methyl-6-ethylpyrididine First isolated by Jones in 1950 (106).
b. 160-161°C (106); $n_d^{20} 1.4946$ (106).
Ficrate m.160-161°C (106)
Isolations etc : - (9 and 106)

Quinoline/
Quinoline First isolated by Runge & Fischer in 1834 (3)
b. 238.05°C (78); $D_2^0$ 1.0929 (78); $n_D^0$ 1.6268 (78).
Picrate m.203°C (78); Picrolonate m.219-220°C (25)
Sulphate m.164-164.5°C (78).
Isolations etc. :- (3, 42, 78 and 80 - 84)

2-Methylquinoline First isolated by Jacobsen and Reimer in 1883 (85)
b. 247.6°C (78); $D_2^0$ 1.0585 (78); $n_D^0$ 1.6126 (78).
Picrate m.195°C (86); Styphnate m. 219°C (86);
Trinitro-m-cresolate m.223°C (86)
Isolations etc. :- (25, 78, 80, 82, 85 and 88)

3-Methylquinoline First isolated by Jantzen in 1932 (78)
b. 259.55°C (m.15-17°C); $D_2^0$ 1.0673; $n_D^0$ 1.6172 (78)
Picrate m.190°C (86); Styphnate.m.190°C (86);
Trinitro-m-cresolate m.223°C (86).
Isolations etc. :- (25 and 78)

4-Methylquinoline First isolated by Pforte in 1925
m. 9-10°C; b. 264.2°C; $D_2^0$ 1.0868; $n_D^0$ 1.6206 (78)
Picrate m.220°C (86); Styphnate m.237°C (86)
Trinitro-m-cresolate m.254°C (86)
Isolations etc. :- (25, 78, 89, 90 and 91)

5-Methylquinoline First isolated by Jantzen in 1932 (78)
m. 19°C; b. 262.7°C; $D_2^0$ 1.0832; $n_D^0$ 1.6220 (78)
Picrate m.223°C (86); Styphnate m.218°C (86);
Trinitro-m-cresolate m.214°C (86)

6-Methylquinoline First isolated by Jantzen in 1932 (78)
b. 258.6°C/
b. 258.6°C; $D_{4}^{20}$ 1.0654; $n_{D}^{20}$ 1.6157 (78).
Picrate m.235°C (86); Styphnate m.234°C (86);
Trinitro-m-cresolate m.238°C (86).

7-Methylquinoline  First isolated by Jantzen in 1932 (78)
m. 39°C; b. 257.6°C; $D_{4}^{20}$ 1.0609; $n_{D}^{20}$ 1.6150 (78).
Picrate m.242°C (86); Styphnate m.242°C (86);
Trinitro-m-cresolate m.244°C (86).
Isolations etc. :- (25 and 78)

8-Methylquinoline  First isolated by Jantzen in 1932 (78)
b. 247.75°C; $D_{4}^{20}$ 1.0719; $n_{D}^{20}$ 1.6164 (78).
Picrate m.205°C (86); Styphnate m.202°C (86);
Trinitro-m-cresolate m.199°C (86).
Isolations etc. :- (25 and 78)

2:8-Dimethylquinoline  First isolated by Jantzen in 1932 (78)
m. 23.2-23.6°C; b. 225.25°C; $D_{4}^{20}$ 1.0394; $n_{D}^{20}$ 1.6022 (78).
Picrate m.183°C (86); Styphnate m.194°C (86);
Trinitro-m-cresolate m.209°C (86).
Isolations etc. :- (25, 78 and 92).

5:8-Dimethylquinoline  First isolated by Ganguli and Guha in 1934 (93)?
Picrate m.186°C (86); Styphnate m.184°C (86);
Trinitro-m-cresolate m.180°C (86).

Note. Ganguli and Guha claim to have isolated this compound from anthracene oil bases by means of a crude fractional distillation and fractional crystallisation of the picrates obtained from a fraction b. 100 - 110°C/2mm./
b. 100 - 110°C/2mm. They claim that they obtained a picrate which melted at 198°C, which is the value given by Berend (128) for the picrate of 5:8-dimethylquinoline prepared from 2-amino-p-xylene, and that a mixed melting point of their sample with a sample prepared according to the method of Berend showed no lowering. They also claim that a mixed melting point of the chloroplatinate of the two samples showed no lowering from the observed value of 234°C (decompn.).

Manske et alia, however, in a recent and very reliable work (86), in which they prepared all the mono- and dimethylquinolines, found that the melting point of the picrate of 5:8-dimethylquinoline, prepared from 2-amino-p-xylene, was 186°C.

It is considered that this observation casts considerable doubt on the claim of Ganguli and Guha, especially in view of the fact that they give no physical constants for their base.

Isoquinoline First isolated by Hoogewerf van Dorp in 1885
m. 24.8°C; b. 243.25°C; D\textsubscript{4} 1.0980; n\textsubscript{D} 1.6146 (78)
Picate m. 224-5°C (25); Sulphate m. 209-209.5°C.
Isolations etc. ; - (15, 25, 17, 78, 91 and 94-98)

1-Methylisoquinoline First isolated by Jantzen in 1932 (78)
m. 10.1-10.4°C; b. 255.25°C; D\textsubscript{4} 1.0777; n\textsubscript{D} 1.6153 (78)
Picate m. 233.4°C (99); Sulphate m. 255.5-256°C (78)

3-Methylisoquinoline First isolated by Jantzen in 1932
m. 64.7°C/
m. 64.7°C (78); b. 252.25°C (78).

Picrate m.197-198°C (25); Sulphate m.154.5-155°C (78)

5 or 7-Methylisoquinoline First isolated by Jantzen in 1932 (78)
m. 76°C (78); b. 264.9°C (78).
Sulphate m.218-219°C (78).

6-Methylisoquinoline First isolated by Jantzen in 1932 (78)
m. 85-86°C (78); b. 265.5°C (78)
Sulphate m.191-192°C (78)

1:3-Dimethylisoquinoline First isolated by Jantzen in 1932 (78)
m. 29.8-30°C (78); b. 262.4°C (78)
Picrate m.180°C (100); Sulphate m.242-243°C (78)

2:4:6-Trimethylquinoline First isolated by Kruber in 1938 (101)
m. 65.5°C (102); b. 286-288°C (101).
Hydrochloride m.268-272°C (103); Hydrobromide m.265-270°C (104)
APPENDIX II.

INFRA-RED ABSORPTION SPECTRA.

During the course of the present investigation the opportunity was taken of having infra-red absorption spectrograms prepared for all of the compounds isolated.

The infra-red absorption spectrogram of a pure compound is unique and cannot be duplicated by that of any other compound. Accordingly, such spectra provide qualitative identification of any unknown pure compound whose infra-red spectrum has been obtained previously.

The infra-red spectra of organic compounds are characterised by absorption bands which occur repeatedly at specific frequencies. These have been correlated empirically with the presence of certain bonds and atomic groupings. Thus, even in the absence of a reference spectrogram for a given compound, it is generally possible by careful examination of its infra-red absorption spectrogram to recognise at least some of the chemical linkages present. It is also frequently possible to determine the geometrical arrangement of the atoms within the molecule by the presence of certain groups of absorption bands. Thus a decision can often be reached as to whether a molecule is cis or trans, ortho, meta or para, enolic or ketonic etc.

Benzie/
INFRARED ABSORPTION SPECTROGRAM

No

MICRONS WAVE LENGTH

PERCENT ABSORPTION

CM.\(^{-1}\) WAVE NUMBERS

MICRONS WAVE LENGTH

CM.\(^{-1}\) WAVE NUMBERS

COMPOUND 2:4:5-Trimethylpyridine

SOURCE Coal Tar

PURITY

STATE Liquid

CELL LENGTH 0.050mm.

SPECTROMETRIC Measurement Hilger D.209 Double-beam Spectrometer (Rocksalt Prism)
Benzie and Milne (24) have published infra-red absorption spectrograms for three of the compounds investigated during this work, namely 2:4:5-trimethylpyridine and 2:3:4:6- and 2:3:5:6-tetramethylpyridines, and in each of these cases excellent agreement was obtained between the spectrograms obtained for the bases isolated during the present work and those published by Benzie and Milne. In the case of 2:3:4-trimethylpyridine, however, no spectrogram had been published previously, and therefore it was not possible to make any direct comparison.

Unfortunately, no infra-red absorption spectrograms had been published for either 3-methylisoquinoline or the dimethylquinolines isolated. In the case of the dimethylquinolines, however, authentic samples of each were prepared, and the spectrograms obtained for these synthetic samples were found to be in agreement with those obtained for the bases isolated from coal tar.

The spectrograms of the nine compounds examined are reproduced together with short notes on each.

2:4:5-Trimethylpyridine.

The excellent agreement with the spectrogram obtained by Benzie and Milne (loc. cit.) confirmed that this compound was 2:4:5-trimethylpyridine. All the pyridine homologues have an intense, rather broad band/
INFRARED ABSORPTION SPECTROGRAM

No

MICRONS WAVE LENGTH

100 80 60 40 20

5.0 5.25 5.5 6.0 6.5 7.0 7.5 8.0 9.0 10.0 11.0 12.0 13.0 15.0 17.0 20.0 25.0

CM.\(^{-1}\) WAVE NUMBERS

2000 19 18 17 16 1500 14 13 12 11 1000 9 8 7 6 5 4

PERCENT ABSORPTION

100 80 60 40 20

2.0 2.25 2.5 2.75 3.0 3.5 4.0 5.0

CM.\(^{-1}\) WAVE NUMBERS

5000 45 4000 35 3000 25 2000

COMPUND  2:3:4-Trimethylpyridine

SOURCE  Coal Tar

PURITY

STATE  Liquid

CELL LENGTH  0.050 mm.

SPECTROMETRIC Hilger D.209 Double-beam Spectrometer (Rocksalt Prism)

DESIGNED BY CHEMICAL RESEARCH LABORATORY, TEDDINGTON MIDDEN, AND PUBLISHED BY H.M.S.O.
band at 750-855 cm$^{-1}$ which is quite probably due to ring deformation. In the case of 2:4:5-trimethylpyridine this band occurs at 855 cm$^{-1}$. The band due to the -C-CH$_3$ deformation which normally occurs at 1375-1390 cm$^{-1}$ is also strongly marked, while the band due to -CH$_2$-CH$_3$ (760-780 cm$^{-1}$) is absent.

2:3:4-Trimethylpyridine.

The clean spectrum of this compound indicates that the sample was pure, while the strong general resemblance to the spectrograms of 2:4:5-trimethylpyridine and of 2:4:6-trimethylpyridine (154) is in keeping with the suggestion that the compound had the formula assigned to it. Unfortunately, no reference spectrum was available for direct comparison, but the above notes on the spectrogram of 2:4:5-trimethylpyridine apply very similarly in the case of this spectrogram and support the view that this compound was 2:3:4-trimethylpyridine.

2:3:5:6-Tetramethylpyridine.

The spectrum of this compound was found to be identical to the spectrum obtained for the base isolated by Benzie & Milne, and to the spectrum obtained for the sample of 2:3:5:6-tetramethylpyridine prepared by Smith, thus confirming that this compound was 2:3:5:6-tetramethylpyridine.

2:3:4:6-Tetramethylpyridine.
INFRARED ABSORPTION SPECTROGRAM

No

MICRONS WAVE LENGTH

5.0 5.25 5.5 6.0 6.5 7.0 7.5 8.0 9.0 10.0 11.0 13.0 15.0 17.0 20.0 25.0

PERCENT ABSORPTION

0 20 40 60 80 100

CM.−1 WAVE NUMBERS

2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600

MICRONS WAVE LENGTH

2.0 2.25 2.5 2.75 3.0 3.5

CM.−1 WAVE NUMBERS

5000 4500 4000 3500 3000 2500 2000

COMPOUND
2,3-Dimethylquinoline

SOURCE
Coal Tar

PURITY
Satd. Solns. in CS₂ and in CCl₄

STATE
Satd. Solns. in CS₂ and in CCl₄

CELL LENGTH
0.050mm.

SPECTROMETRIC MEASUREMENTS
Hilger D.209 Double-beam Spectrometer (Rocksalt Prism)

Corrected for Solvent Absorption

DESIGNED BY CHEMICAL RESEARCH LABORATORY, TEDDINGTON MIDDX.
AND PUBLISHED BY H.M.S.O.
INFRARED ABSORPTION SPECTROGRAM

No

MICRONS WAVE LENGTH

PERCENT ABSORPTION

MICRONS WAVE LENGTH

CM. -1 WAVE NUMBERS

2.0 2.25 2.5 2.75 3.0 3.5 4.0 5.0

2000 18 17 16 1500 12 11 1000 10 9 8 7 6 5 4

2.0 2.25 2.5 2.75 3.0 3.5 4.0 5.0

5000 45 40 35 30 25 20 15 10 5 0

COMPOUND 2:7-Dimethylquinoline

SOURCE Coal Tar

PURITY Satd. Solns. in C32 and in CCl4

STATE Satd. Solns. in C32 and in CCl4

CELL LENGTH 0.050 mm.

SPECTROMETRIC MEASUREMENT Hilger D.209 Double-beam Spectrometer (Roghaillt Prism)

Corrected for Solvent Absorption

DESIGNED BY CHEMICAL RESEARCH LABORATORY, TEDDINGTON MIDDX.
AND PUBLISHED BY H.M.S.O.
INFRARED ABSORPTION SPECTROGRAM

No

MICRONS WAVE LENGTH

2000 19 18 17 16 15 14 WAVE NUMBERS

MICRONS WAVE LENGTH

2.0 2.25 2.5 2.75 3.0 3.5 4.0 5.0 CM. \(^{-1}\)

PERCENT ABSORPTION

2000 19 18 17 16 15 14 WAVE NUMBERS

5000 45 40 35 30 25 20 CM. \(^{-1}\)

COMPOUND
2:6-Dimethylquinoline

SOURCE
Coal Tar

PURITY

STATE
Satd. Solns in CS\(_2\) and in CCl\(_4\)

CELL LENGTH
0.050mm

SPECTROMETRIC MEASUREMENT
Hilger D.209 Double-beam Spectrometer (Rocksalt Prism)

Corrected for Solvent Absorption

DESIGNED BY CHEMICAL RESEARCH LABORATORY, TEDDINGTON MIDDX.
AND PUBLISHED BY H.M.S.O.
2:3:4:6-Tetramethylpyridine.

The perfect agreement of the spectrogram of this compound with that obtained by Benzie & Milne confirmed that this compound was 2:3:4:6-tetramethylpyridine.

3-Methylisoquinoline.

The infra-red absorption spectrogram of this compound was obtained, but no reference spectrum was available for direct comparison. The general nature of the spectrum, however, is in agreement with the supposition that this compound was 3-methylisoquinoline.

2:6-Dimethylquinoline.

The spectrum obtained for this compound was found to be identical to that obtained for an authentic sample of 2:6-dimethylquinoline, thus confirming that this compound was 2:6-dimethylquinoline.

2:7-Dimethylquinoline.

The spectrogram obtained for this compound was found to be identical to that obtained for an authentic sample of 2:7-dimethylquinoline, thus confirming that this compound was 2:7-dimethylquinoline.

2:3-Dimethylquinoline.

The spectrogram obtained for this compound was found to be identical to that obtained for an authentic sample of 2:3-dimethylquinoline, thus confirming/
INFRA-RED ABSORPTION SPECTROGRAM

Compound
- 2:4-Dimethylquinoline

Sources
- Synthetic and Coal Tar

State
- Liquid

Cell Length
- Capillary Film

Spectrometric Measurements by the Ministry of Supply, Chemical Inspectorate, C.36, Royal Arsenal, Woolwich.
confirming that this compound was 2:3-dimethyquinoline.

Note: - The concentrations used in the measurement of the above four spectra varied as is indicated by the band near 3000cm⁻¹.

2:4-Dimethyquinoline

The spectrum obtained for this compound is shown opposite together with the spectrum of the sample of 2:4-dimethyquinoline which had been prepared. The upper graph is that of the synthetic sample. It may be noted that the spectrogram of the synthetic sample contains the following three bands which are not present in the natural sample.

At about 690cm⁻¹ - which is characteristic of mono-substituted aromatic compounds.

At about 1270cm⁻¹ - which is characteristic of aniline.

At about 3300cm⁻¹ - which indicates a hydrogen-bonded NH or OH group.

There is very little doubt that these differences are due to the presence of traces of some impurity in the synthetic material, probably some unreacted aniline, and the overall agreement of the two spectra confirmed that the compound isolated from the taf bases was 2:4-dimethyquinoline.

Most of the above spectrograms were prepared through the courtesy of Dr. E.A. Coulson of the Department of Scientific and Industrial Research and the measurements were carried out by Mr. J.L. Hales at the Chemical Research Laboratory, Teddington. In the cases of the synthetic samples of 2:3-, 2:4-, 2:6- and 2:7-dimethyquinolines and of the natural sample of 2:4-dimethyquinoline, however, the spectra were prepared through the courtesy of Mr. E.T. Osborne of the Ministry of Supply and the measurements were carried out by Mr. I.J. Bellamy at the Chemical Inspectorate, Royal Arsenal, Woolwich.
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