

Characteristics of Organic Material in Colorado Oil Shale

The constitution of the organic material (kerogen) in Colorado oil shale was studied by degrading the organic material into smaller fragments for analysis and identification. First, samples of organic material were prepared by the partial removal of minerals from oil shale according to the procedure shown in figure 56. This procedure involved extracting a rich oil shale with benzene to remove 1.7 percent of natural oil or bitumen. The insoluble residue was leached with dilute acetic acid to remove mineral carbonates, then washed with water and acetone. After drying, the residue was centrifuged in benzene-carbon tetrachloride mixtures of different gravities. The resulting concentrates, which contained up to 91.3 percent organic material, were used for the degradation studies.

Oxidation with alkaline potassium permanganate has been used extensively by other investigators to determine the general structure of the organic material in coal, oil shale, and other naturally occurring substances. Products obtained by the partial oxidation of coal in this manner have been designated "regenerated humic acids." This term is also applied here to a related product obtained from oil shale.

The regenerated humic acids derived from Colorado oil shale differ from those derived from coal and certain other oil shales. This is shown in table 35. Extensive, or complete oxidation of Colorado kerogen (or its regenerated humic acids) with alkaline potassium permanganate yielded principally carbon dioxide and oxalic acid with only small amounts (2 percent, or less) of non-volatile, nonoxalic acids. There was no evidence that these nonvolatile, nonoxalic acids from Colorado kerogen contained benzenoid acids which are indicative of highly condensed aromatic structures. However, other kerogens, such as those from Pumpherstons (Scotland) oil shale and Ermelo (South Africa) torbanite, yielded greater amounts of the latter acids, indicating the presence of condensed aromatic structures. The products from Colorado kerogen (table 35) resembled those from carbohydrates, aliphatic acids, and terpene compounds of low molecular weight rather than products from aromatic hydrocarbons or terpene compounds of high molecular weight.

Products obtained from Colorado kerogen by other degradation methods were also examined. These methods included oxidation of kerogen by nitric acids, hydrolysis with hydrochloric acid, treatment with aqueous and alcoholic solutions of potassium hydroxide and by fusion with potassium hydroxide, extraction with organic solvents and by destructive distillation or heating. The types of the degradation products are summarized in table 36.

TABLE 35. - Distribution of organic carbon in products obtained by oxidation of materials with alkaline potassium permanganate

	Percent of total organic carbon					
	CO ₂	Volatile acids	Oxalic acids	Nonvolatile, nonoxalic acids	Unoxidized organic carbon	Oxidation period, hr.
Oil shale:						
Colorado (kerogen)	62	2	33	1	1	100
Volga (Russia) ^{1/}	88	4	5	4	0	500
Kimeridge (England) ^{2/}	50	8	31	10	1	57
Ermelo (South Africa) ^{2/}	31	5	13	17	34	145
Pumpherstons (Scotland) ^{2/}	21	4	11	13	51	125
Carbohydrates ^{3/}	58	5	35	0	-	1/3 to 3
Aliphatic acids ^{3/}	48	0	51	0	-	1/6 to 115
Terpene compounds:						
Low molecular weight	48	1	28	2	21	20 to 28
C ₂₀ and C ₃₀ compounds	71	5	7	15	2	-
Natural gums, oils, balsam	71	3	0	17	9	47 to 67
Aromatic hydrocarbons	16	0	7	75	-	6 to 104

1/ Lenin, V. A., and Pronina, M. V., Bull. acad. sci. U.R.S.S., Classes sci. tech., 1944, pp. 745-751.

2/ Down, A. L., and Himus, G. W., Jour. Inst. Petrol., vol. 27, 1941, pp. 419-445.

3/ Randall, R. B., Benger, M., and Grocock, C. M., Proc. Royal Soc. (London), vol. A165, 1938, pp. 432-452.

TABLE 36. - Degradation products from Colorado kerogen

Degradation method	Type of product
Extensive oxidation with alkaline potassium permanganate solution (1.6 to 3.0 percent KmnO ₄)	Aliphatic acids (carbonic and oxalic) with 1 percent, or less, of high-molecular-weight acids.
Nitric acid (60 percent)	Acids: 1st fraction (72 percent) consisted of aliphatic acids with some benzenoid acids; 2d fraction (27 percent) consisted of amphoteric acids, principally compounds of nitrogen.
Hydrochloric acid (30 percent)	p-Menthane Carbohydrate-type humin, sugars, furane compounds, cyclic terpene alcohols, and ethyl mercaptan.
Potassium hydroxide (aqueous and alcoholic solutions and by fusion)	Aliphatic acids, with some benzenoid acids. Derivatives of pyridine and pyrrole. Indication of alkaline-earth salts of kerogen acids.
Treatments involving heat (solvent extraction and destructive distillation)	Pyrrole, alkyl pyridines, alkyl benzene, cresols, furfural, dipentene, and sulfur compounds (mercaptans, sulfides, and disulfides).

Partial oxidation of Colorado kerogen with 60-percent nitric acid at 60° to 70° C. yielded two fractions of mixed acids (table 36). The first fraction, an amorphous, yellowish-brown solid that resembled the regenerated humic acids obtained by alkaline permanganate oxidation of kerogen, consisted of aliphatic acids with some benzenoid acids. The second fraction, a bright-yellow, two-phase liquid product, consisted preponderately of nitrogenous amphoteric acids. Oxidation of kerogen with dilute nitric acid, similar to partial oxidation by alkaline permanganate, provided a means of obtaining considerable quantities of soluble products from kerogen (approximately 70 to 80 percent of the kerogen) that contained little or no mineral matter from the shale. These mineral-free products then could be used further in kerogen-constitution studies.

Hydrolysis of kerogen with hydrochloric acid yielded a carbohydrate-type humin, sugars, furan compounds, and ethyl mercaptan, while treatment of kerogen with solutions of potassium hydroxide, or by fusion, yielded aliphatic and some benzenoid acids, various nitrogen compounds, and an indication of alkaline earth salts of kerogen. Extraction of kerogen with dimethylformamide and tetralin, and destructive distillation of kerogen, yielded pyrrole, alkyl pyridines, cresols, furfural, and various sulfur compounds. Except for products resulting from the potassium hydroxide treatments, these degradation products contained only trace amounts of terpene compounds. The total yields of identified products by each of these treatments represented less than 5 percent of the kerogen.

In general, these degradation studies indicated that Colorado kerogen consists preponderantly of nonbenzenoid structures. Aromatic and terpene structures appeared to be present in small amounts, but they were either of low molecular weight or readily susceptible to oxidation. The presence of considerable quantities of highly condensed benzenoid or aromatic structures in Colorado kerogen was not indicated. By virtue of their basic character, compounds of nitrogen may play an important part, possibly by combination with the acidic kerogen constituents, to form the relatively stable, condensed kerogen.

Two other methods for degradation of kerogen are being investigated. An ozonization apparatus (fig. 57) was constructed and should be useful for preparing soluble products from kerogen and for determining the structures of these products. Also, a benzene-soluble product was prepared by the hydrogenation of kerogen in the presence of stannous chloride catalyst. No analytical data on these methods or products are available at this time.

Shale-Oil Research and Analysis

Knowledge of the composition of shale oil is still sketchy, but it is vastly greater than that available a few years ago. This knowledge has been augmented during the past year by publications on pyrroles identified in shale-oil naphtha, on gum formation in shale-oil naphtha, and on the determination of nitrogen in shale oil. Presentations before technical societies included papers on mass spectral correlations in composition studies, crude-oil composition, and oils from high-temperature retorting.

Analytical research during the past year has been directed primarily toward composition studies on three types of shale-oil products. These are oils from high-temperature retorting and two fractions - primary naphtha and heavy gas oil - from N-T-U crude oil. In addition, some work has been done on the development of analytical methods.

Oils from High-Temperature Retorting

Shale oils produced by high-temperature retorting at 1,200°, 1,500°, and 1,700° F. were analyzed. The purpose of the investigation was to determine the effect on oil composition of retorting at these temperatures which are substantially higher than those normally employed. Analyses of these oils were made, utilizing previous experience obtained in studying various fractions of shale oil and employing such techniques as fractional distillation; silica-gel adsorption; infrared spectra, ultraviolet spectra, and mass-spectrometer data; refractive index; density; and boiling point. The outstanding characteristics shown by the 1,500° and 1,700° F. oils are the aromaticity of their distillates, which contain virtually negligible quantities of saturates and olefins. The 1,200° F. oil, although much less aromatic than the oils produced at the higher temperatures, has an aromatic content of 54 percent in the distillate boiling below 600° F. This is about twice the aromatic content of oils produced by the usual retorting methods.

In addition to the general high aromatic content of these oils, the contents of individual aromatic hydrocarbons show an important relationship to the retorting temperature (table 37). For all three oils the simplest member of an aromatic homologous series (for example, benzene or naphthalene) is the predominant compound; and, in general, the quantity of material in a molecular-weight group decreases as the molecular weight increases. The contents of benzene and naphthalene increase with increasing temperature. Contents of toluene and the methylnaphthalenes reach a maximum in the 1,500° F. oil. The other benzene homologs are present to about the same extent in the 1,200° and 1,500° F. oils but are nearly absent in the 1,700° F. oil. Other hydrocarbons found include styrene, indene, and biphenyl.

Investigation of the nonhydrocarbon compounds in these oils was confined to the pyridines from the 1,500° F. oil and the phenols from the 1,200° and 1,500° F. oils. Determination of these types of compounds depended primarily on the infrared spectra of narrow-boiling fractions (see fig. 58). The pyridines qualitatively identified were 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2,4-dimethylpyridine, and 2,4,6-trimethylpyridine. As in shale oils from ordinary retorting methods, the 2,4,6-trimethylpyridine is the predominant compound. The 2,4-dimethylpyridine is also present in large amounts. The other dimethylpyridines appear to be absent or present only in small quantities.

A quantitative estimate was made of the individual phenols boiling below about 220° C. (table 38). Although the fractions from which the phenols were extracted had approximately the same boiling range (up to 280° C.), the great difference in the distribution of the phenols from the two oils is evident. In the 1,200° F. oil, about two-thirds of the material boiled above the xylenols, whereas, in the 1,500° F. oil, phenol, o-cresol, and m-cresol make up 75 percent of the phenols. As with hydrocarbons, these latter results indicate the tendency for higher retorting temperatures to produce the simpler members of a homologous series.

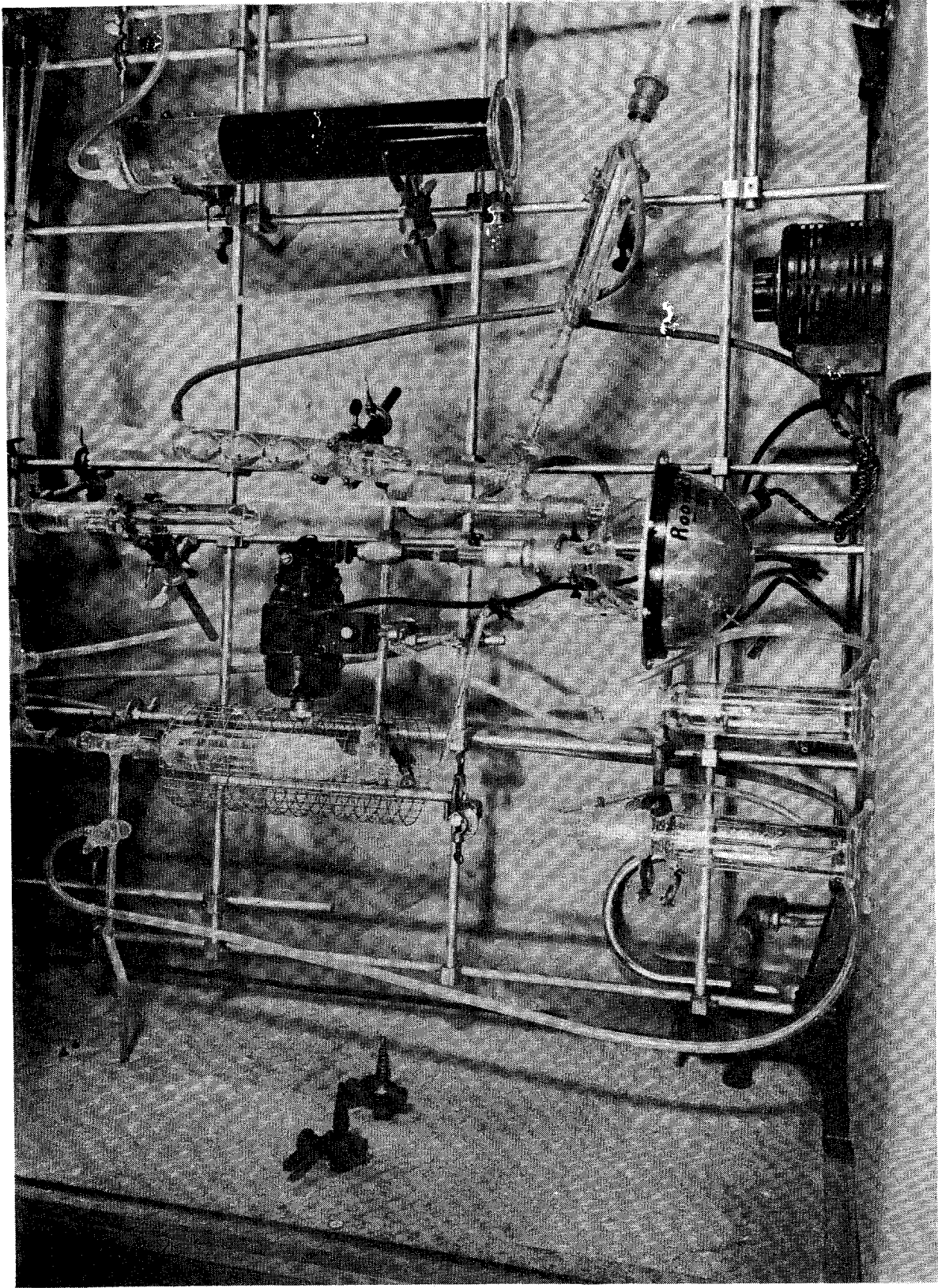


Figure 57. - Ozonization apparatus for study of constitution of Colorado oil-shale kerogen.

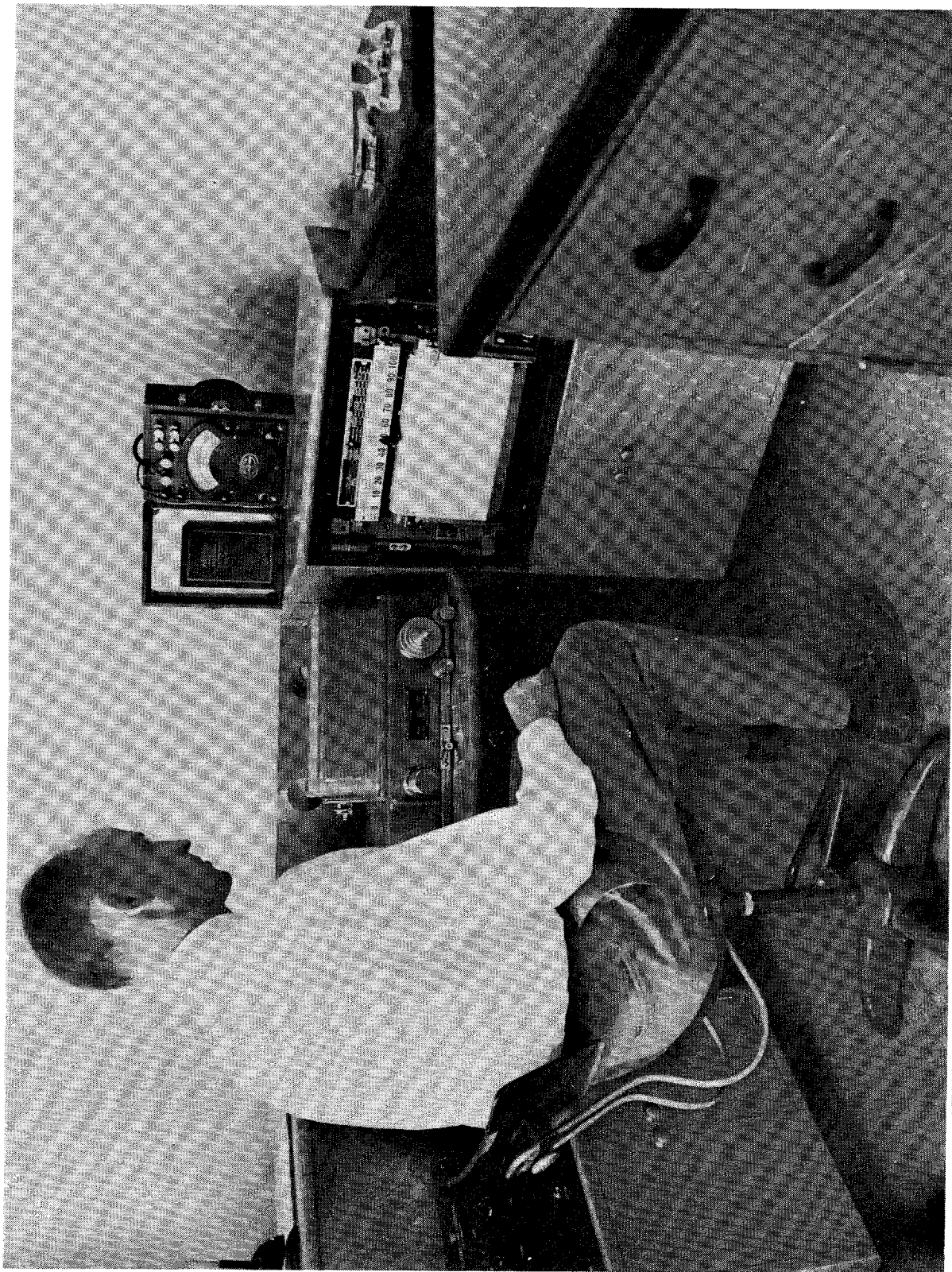


Figure 58. - Infrared spectrometer used for qualitative identification and quantitative estimation of certain compounds in shale oil.

TABLE 37. - Content of some aromatic compounds in crude shale oils produced at 1,200°, 1,500°, and 1,700° F.

Compounds	Volume percent of crude oil retorted at -		
	1,200° F.	1,500° F.	1,700° F.
Benzene.....	4.88	15.50	22.56
Toluene.....	4.41	7.26	.97
Ethylbenzene.....	2.11	.38	.19
Xylenes.....		2.15	
C ₉ -Benzenes.....	1.09	.66	.02
C ₁₀ -Benzenes.....	.19	.72	.02
C ₁₁ -Benzenes.....	.67	.80	.01
C ₁₂ -Benzenes.....	.89	.30	
Naphthalene.....	.47	3.60	8.69
1-methylnaphthalene.....	.33	.80	.25
2-methylnaphthalene.....	.42	1.80	
Dimethylnaphthalenes.....	-	1.60	-
Styrene.....	.52	.69	.04
α -and β -methylstyrene.....	.11	.39	-
Indene.....	.80	1.16	.07
Biphenyl.....	-	.10	-

TABLE 38. - Composition of phenols extracted from 1,200° and 1,500° F. oils

	Phenolics, volume percent	
	1,200° F. oil	1,500° F. oil
Phenol.....	1	35
o-Cresol.....	3	22
m-Cresol.....	3	19
o-Ethylphenol.....	1	2
2,3-Xylenol.....	3	3
2,4-Xylenol.....	15	11
2,5-Xylenol.....	-	3
3,4-Xylenol.....	2	-
3,5-Xylenol.....	4	-
Higher-boiling material.....	66	5

Primary N-T-U Naphtha

Basic studies have been conducted on primary naphtha from N-T-U crude oil. This material has been selected partly because of the availability of methods with which to investigate it. However, it seems logical that the pattern of types of compounds present in the naphtha may well provide clues as to the types of materials that will be present in higher-boiling fractions. Consequently, a rather thorough investigation has been made of the different types of compounds that may be found in this naphtha. The investigation has

included not only the hydrocarbons which are the predominant compounds but also the pyridines, pyrroles, phenols, and thiophenes.

The hydrocarbons in the naphtha consist of 32 percent saturates, 45 percent olefins, and 23 percent aromatics. The types of compounds within these groups fall into definite patterns. The saturates contain about 80 percent paraffins and 20 percent cycloparaffins. The paraffins in turn contain about two-thirds straight-chain compounds and about one-third branched-chain compounds. This ratio of about 2 for straight-chain to 1 for branched-chain paraffins is not constant throughout the boiling range of the naphtha but increases from about 1.5 in the C₆-range to about 3.0 in the C₁₁-range. The pattern for olefins is quite similar to that for saturates. In the olefins the content of aliphatic compounds is about twice that of the cyclic compounds. Of the aliphatic olefins about 80 percent are straight-chain compounds. The contents of the individual aromatic hydrocarbons boiling below about 180° C. were determined (table 39). The results indicate a very regular pattern as to the number and position of substituent alkyl groups. The content of monosubstituted benzenes decreases with increasing molecular weight so that the propylbenzenes are present only in very small quantities and no butylbenzenes could be detected. A large part of the polysubstituted benzenes have alkyl groups in at least the 1 and 4 positions.

TABLE 39. - Aromatics in N-T-U primary neutral naphtha

Compound or class	Naphtha, volume percent
Benzene.....	0.07
Toluene.....	.40
Ethylbenzene.....	.24
p-Xylene.....	.18
m-Xylene.....	.89
o-Xylene.....	.35
Styrene.....	.02
Isopropylbenzene.....	.08
n-propylbenzene.....	.09
1-methyl-3-ethylbenzene.....	.04
1-methyl-4-ethylbenzene.....	.96
1,3,5-trimethylbenzene.....	.33
1-methyl-2-ethylbenzene.....	
1,2,4-trimethylbenzene.....	.94
1-methyl-4-isopropylbenzene.....	2.47
Other C-10 alkyl benzenes.....	1.15

When the work on shale oil was first begun, it was believed that one of the major problems in processing would be removal of sulfur compounds, and considerable emphasis was given to studying them. This study has developed into a somewhat more difficult research problem than was at first anticipated. One of the difficulties is that the sulfur compounds are mostly thiophenes. However, the techniques necessary to identify these compounds finally have been developed, and their identification in primary N-T-U naphtha is well under way (see fig. 59). The method, parts of which have been mentioned in

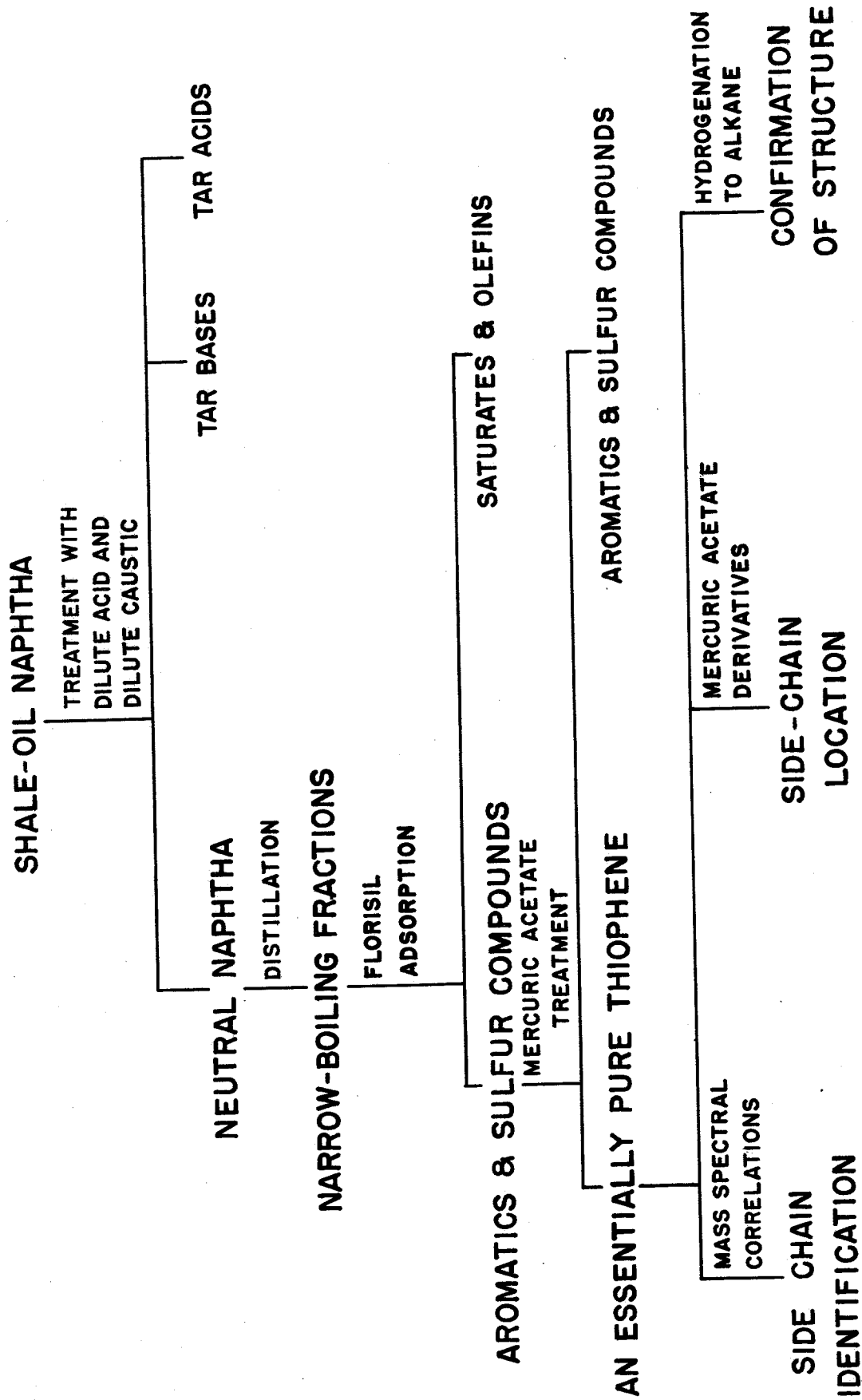


Figure 59. - Scheme for separation and identification of thiophenes in shale-oil naphtha.

previous reports, is in many respects quite original. Briefly it consists of removing the tar acids and tar bases from a shale-oil naphtha by treatment with dilute caustic and dilute acid, leaving a neutral naphtha that is distilled into fairly narrow boiling-range fractions. By adsorption of these on Florisil, a series of products consisting essentially of the aromatic and sulfur compounds in the naphtha is prepared. A treatment with mercuric acetate then forms derivatives with the thiophenes. The thiophenes are regenerated with dilute acid, reprecipitated with mercuric acetate, and again regenerated with acid. For the narrow-boiling-range fractions, this procedure often yields an essentially pure thiophene. Identification of the thiophene is then obtained by a judicious combination of the following techniques: Mass-spectrometer analysis to identify the particular side chains that are present on the thiophene nucleus; reaction with mercuric acetate to indicate the positions on the nucleus occupied by hydrogen; methylation combined with mass spectra to distinguish between the 2 and 5 substituted compounds and the 3 and 4 substituted compounds; and hydrogenation with Raney nickel to split out the sulfur and leave a saturated hydrocarbon that may be identified by mass spectra.

Using these techniques, 17 individual thiophenes have been identified so far in N-T-U naphtha (table 40). This is a larger number than the total found by all previous investigators in the field. The sulfur in these 17 thiophenes represents about two-thirds of the total sulfur in this particular 195° C. end point naphtha. The thiophenes show a definite tendency for substitution in the 2-, 2,3-, 2,5- and 2,3,5-positions.

TABLE 40. - Sulfur and nitrogen compounds identified in primary N-T-U naphtha

Thiophene	Pyridine
2-methylthiophene	2-methylpyridine
3-methylthiophene	3-methylpyridine
2,3-dimethylthiophene	4-methylpyridine
2,5-dimethylthiophene	2,3-dimethylpyridine
3,4-dimethylthiophene	2,4-dimethylpyridine
2-ethylthiophene	2,6-dimethylpyridine
3-ethylthiophene	3,4-dimethylpyridine
2-isopropylthiophene	2,3,5-trimethylpyridine
2-methyl-5-ethylthiophene	2,3,6-trimethylpyridine
2,3,5-trimethylthiophene	2,4,6-trimethylpyridine
2-methyl-5-isopropylthiophene	2-methyl-4-ethylpyridine
2-methyl-5-n-propylthiophene	4-methyl-2-ethylpyridine
2,3-dimethyl-5-ethylthiophene	Quinoline
2,4-dimethyl-5-ethylthiophene	2-methylquinoline
2-methyl-5-sec-butylthiophene	
2,3-benzothiophene	
Benzonitrile	Pyrrole
o-tolunitrile	2-methylpyrrole
m-tolunitrile	2,3,4,5-tetramethylpyrrole
	2,3,5-trimethyl-3-ethylpyrrole

In addition to the pyridines and pyrroles, whose presence in shale oil has been known for some time, individual members of another class of nitrogen compounds, the nitriles, were identified for the first time during the year. Thus, it has been shown that the nitrogen compounds of the naphtha fraction fall into at least three quite different classifications, with regard to chemical activity. As shown in table 40, several individual compounds from each of these classes have been identified. In general, the identifications involve the isolation of the compound from a narrow-boiling fraction by some technique such as derivative formation or adsorption. Properties such as melting point (fig. 60) or spectra are obtained on the isolated material and the results compared with an authentic sample, if possible, or with values in the technical literature.

The individual phenols boiling below about 220° C. were determined quantitatively. As the phenols were extracted from a 212° C. end-point naphtha, phenol and the three cresols made up 60 percent of the material. However, on the basis of the crude oil, these compounds were present in smaller quantities than in either of the high-temperature oils discussed previously.

N-T-U Gas-Oil Fraction

Interest in the composition of the gas-oil fraction from shale oil has increased because processing data show it does not crack in the same manner as does gas oil from petroleum. The determination of the composition of gas oil is quite difficult because the properties of the compounds boiling in that range are not available in the literature. Also the properties of any particular group of compounds may be modified by the additional side chains or functional groups that may be present. As has been reported previously, adsorption on Florisil (fig. 61) has been used to separate the gas oil into a nitrogen concentrate (43 percent) and a hydrocarbon concentrate (57 percent). Adsorption with silica gel has been used to separate an aromatic portion from the hydrocarbon concentrate. The aromatic portion, which comprises 22 percent of the gas oil, has been separated further by adsorption on activated alumina into three subfractions. From various ring structure correlations, ultimate analyses, and spectra on the fractions, the average structure of the compounds in each fraction was estimated. Apparently the three-subfractions consist essentially of one-ring, two-ring, and three-ring aromatic compounds, respectively. The quantity of each is about 9, 7, and 6 percent of the gas oil. The second sub-fraction seems to contain the naphthalene nucleus and the third contains the phenanthrene nucleus.

Development of Analytical Methods

Analytical methods have received only minor emphasis during the past year, as work has been primarily on composition studies involving application of previously developed methods. However, a series of four papers dealing with the determination of nitrogen resulted from a cooperative effort between the Bureau of Mines and Union Oil Co. of California. The first of these papers discusses the applicability of established methods of nitrogen determination to shale oils. This study was based on a cooperative testing program involving both industry and Government laboratories. The

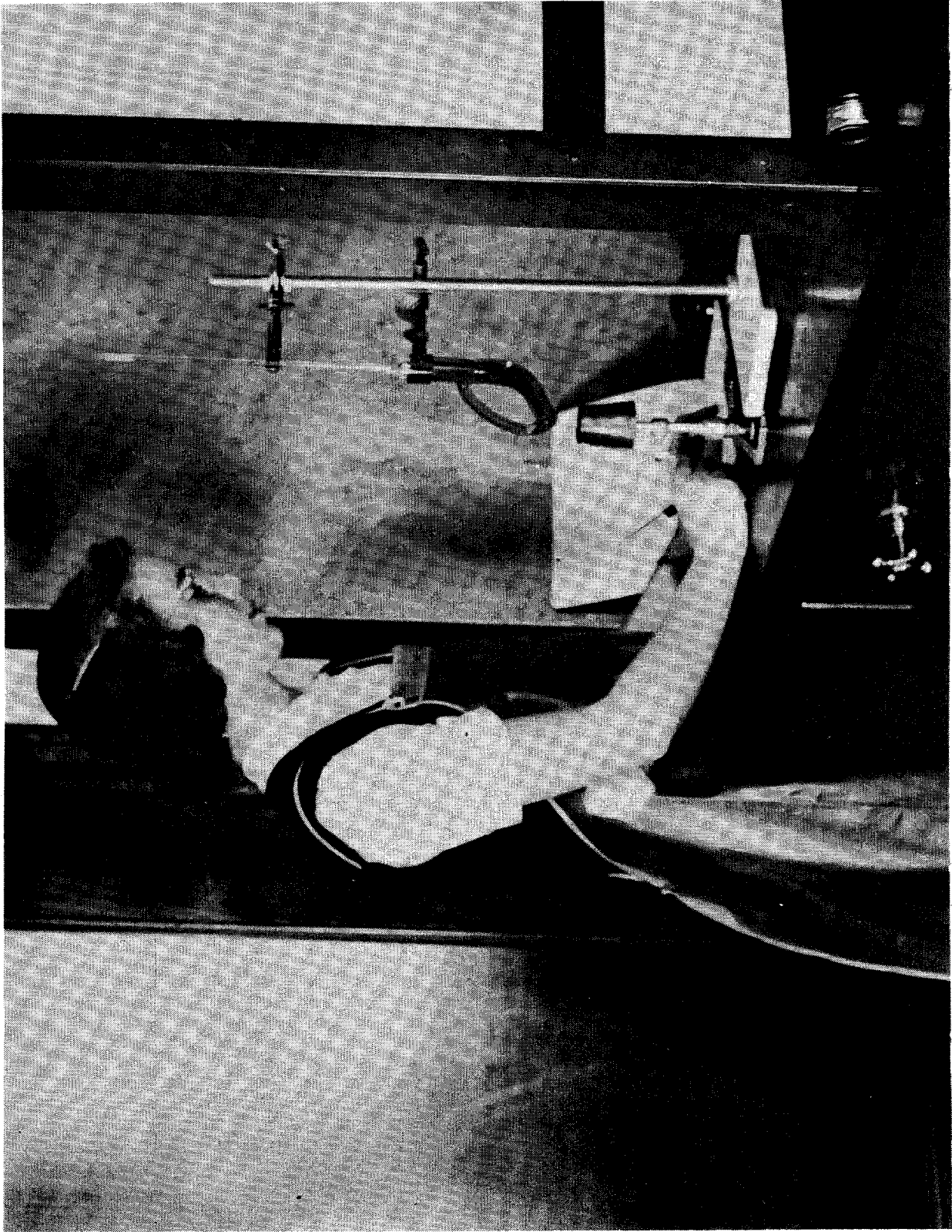


Figure 60. - Determination of melting point, one of properties used in establishing identity of unknown compounds.

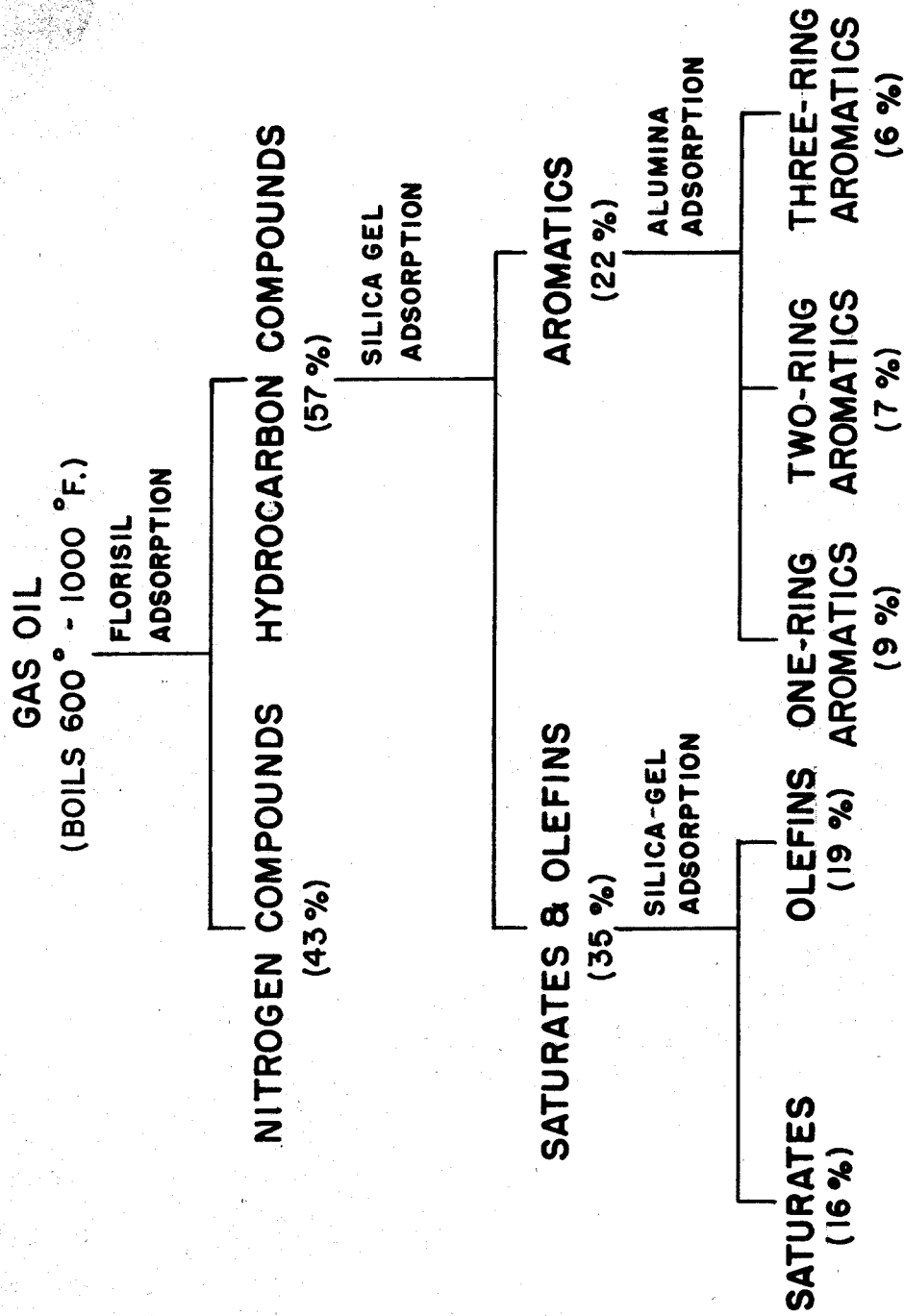


Figure 61. - Separation of shale-oil gas oil, with results in percentage of starting gas-oil fraction.

results showed that the ordinary use of either the Dumas or the Kjeldahl method does not give a satisfactory nitrogen determination on shale oil or its distillates. The second paper gives the conditions necessary for an accurate determination of nitrogen by the Kjeldahl method. The most-important of these is maintenance of digestion temperature within a rather narrow permissible range. The third paper describes the use of mass-spectrometer analysis of the gas produced during a Dumas microdetermination of nitrogen as an aid to obtaining accurate results by this latter method. The last paper gives a procedure for determining basic nitrogen by the perchloric acid titration method. This is a very useful method for shale oils which contain substantial quantities of both basic and non-basic nitrogen.

Byproduct-Utilization Research

Separation of Paraffin and Olefin Waxes

The separation of crystalline waxes from shale-oil wax distillate by the common methyl ethyl-ketone solvent extraction method^{5/} produces a wax containing approximately 18 percent olefins. Tests to determine the feasibility of separating the mixed, semirefined paraffin and olefin wax into fully refined paraffin and olefin waxes promised commercial application. The mixed waxes were percolated through a column of silica gel until the adsorptive capacity of the gel for the wax was reached. The waxes then were separated by eluting with a solvent. A fully refined paraffin wax was separated in this manner without acid treatment, and a high-purity olefinic wax was obtained by additional silica gel treatments.

Tar Acids

The caustic sludge from the refining of thermally cracked naphtha made by recycle cracking N-T-U crude oil contains recoverable tar acids. As the naphtha had a boiling range of 93° to 395° F., the tar acids were mainly phenol, cresols, and xylenols for which there is a large market demand. The crude tar acids that were sprung from the sludge had a foul odor, were reddish brown to black, and contained impurities, mainly nitrogen bases, dissolved hydrogen sulfide, organic sulfur compounds, neutral oils, carboxylic acids, water, and nondistillable material. The sulfur content was 2.3 percent and nitrogen 2.4 percent. Of these, the sulfur was the more difficult to eliminate.

The crude acids were purified in the laboratory in the following manner:

The crude tar acids were dehydrated at 5 mm. absolute pressure to avoid overheating. The distillation pressure was then increased to 40 mm. \pm 5 mm. absolute, and the tar acids were rapidly distilled leaving a pitch residue. Under these conditions the vapor temperature of the distillation did not exceed 311° F. Thus the lower-boiling phenols were recovered, and some of the higher alkylated phenol, as well as a considerable quantity of the nitrogen and sulfur-bearing compounds, remained as residue.

^{5/} Tisot, P. R., and Horne, Joseph W., Waxes from Shale-Oil Wax Distillate: Bureau of Mines Rept. of Investigations 4708, 1950, 21 pp.

The recovered phenols, after air blowing to remove hydrogen sulfide, were treated with sodium hydroxide to form the sodium cresylate, sodium salts of phenol, and alkyl phenols. The sodium cresylate was steamed at 392° F. to remove neutral oils and organic bases. Further removal of sulfur was attained by the addition of finely divided nickel sulfide to the cresylate and the introduction of air into the steam after the removal of the major portion of the steam distillable impurities. The treated cresylate was then filtered to remove the nickel sulfide. The filtered cresylate was acidified with carbon dioxide to a pH of 10, and the tar acids were separated. These acids then were washed with sodium carbonate to remove carboxylic acids and reblown with carbon dioxide.

The phenol, cresols, and xylenols purified by this treatment contained about 0.01 percent nitrogen and less than 0.1 percent sulfur. The recovery of purified acids was equivalent to 0.23 percent of the original cracked gasoline. An analytical distillation of these acids gave the following approximate composition:

<u>Constituent</u>	<u>Vol. percent of charge</u>	<u>Physical character</u>
phenol	4.4	Solid
o-cresol	10.0	Liquid
m,p-cresol	16.0	Do.
2,4- and 2,5-xyleneol	20.0	Do.
2-isopropyl phenol	5.0	Solid
2,3-xyleneol	3.0	Liquid
4-ethylphenol	3.0	Do.
3,5-xyleneol	8.0	Solid

Some small samples of acid- and base-catalyzed phenolic resins were made in the laboratory, using formaldehyde as the condensing agent to indicate the suitability of these phenolics for plastics manufacture. Natural colors of the resins were yellow, pink, and brown.

Tar Bases

Tar bases were extracted and purified from the dilute-acid sludge from refining the crude naphtha made by recycle cracking of N-T-U heavy gas oil. The impurities present in the tar bases, consisting essentially of neutral oils and tar acids, were removed by steam stripping. The bases then were sprung with 40-percent sodium hydroxide solution, their pH adjusted to 12, water-washed, and dehydrated. The bases then were blown with dry air at 350° F. for 12 hours under total reflux. A black, finely divided residue, formed by this treatment, was removed by filtration. The filtered bases were distilled at 80 mm. absolute pressure. Their initial boiling point was 167° F. and their end point 284° F.

This refined product was completely soluble in 10 percent hydrochloric acid, had a relatively stable light straw color and a sulfur content of less than 0.03 percent, and consisted only of basic nitrogen compounds possessing the characteristic odor of the pyridines. The purified bases may be added to the refined gasoline without detrimental effect to the stability of the fuel, and they increase the octane rating 1 to 1-1/2 octane numbers when added in essentially the same proportion as they were present in the raw gasoline. They have many other potential uses, such as in rust inhibitors, pharmaceuticals, and as the base stock for many nitrogen-bearing chemicals.