volatile materials since his data cover a temperature range (119° to 152° C.) at which the vapor pressure of terephthalic acid should be essentially zero. After the completion of the work reported in this paper, it was learned that a value of 33.3 ± 0.4 was obtained by other workers by means of a thermal gradient strip technique (*9*).

A value of ΔH_s = 33.1 kcal. per mole can be calculated from data obtained for benzoic acid and benzene (*3*). The contribution to the heat of sublimation per six benzenoid carbons is taken as 10.5 kcal. per mole, and the contribution of each carboxyl group is taken as 11.3 kcal. per mole.

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Spectroscopic Identification of Basic Nitrogen Compounds in Wilmington Petroleum

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A study of the basic nitrogen compounds in Wilmington (Calif.) petroleum fractions has produced considerable information on their composition. Characterization of the classes of basic nitrogen compounds in the 130° to 350° C. distillate fractions was made by low-voltage mass spectral analyses. Two individual compounds—an alkyl-substituted cyclopentapyrindan and an alkylcycloalkyl-substituted pyridine—were separated and identified. Procedures used to separate the compounds from the oil included distillation, mineral acid extraction, and gas-liquid chromatography. The identifications were made by a combination of mass, infrared, ultraviolet, and nuclear magnetic resonance spectrometry.

NITROGEN compounds are an important, minor constituent of petroleum. Even in trace amounts, they cause serious problems in processing and in the stability of products. They cause catalyst poisoning and are involved in the formation of gums, lacquers, and precipitates.

The nitrogen present in petroleum is usually divided into two broad types: basic nitrogen, defined as that which is titratable with perchloric acid in acetic acid solution, and nonbasic nitrogen which is not titratable.

Numerous studies have been made on the nature of the basic nitrogen compounds in petroleum fractions. Bratton and Bailey (*1*) found several pyridines and quinolines in a cracked gasoline. Hackman, Wilbant, and Gitsel (*4*), studying a cracked California gasoline, identified pyridines, quinolines, isoquinolines, and a tetrahydroquinoline or pyrindan. Nixon and Thorpe (*15*) reported quinolines, pyrindines, and anilines present in catalytically cracked jet fuel. LaLau (*8*), who investigated unspecified fractions, found pyridines, quinolines, and their naphtheno-substituted homologs. Jewell and Hartung (*7*) identified quinolines, benzoquinolines, indolo- and carbazoloquinolines, hydroxybenzoquinolines, and 1,10-phenanthroline in a straight run heavy gas oil although some of these identifications have been questioned (*19*). Drushel and Sommers (*2*) studied a catalytic cycle oil and found pyridines, quinolines, pyrindines, and cyclopentaquinolines present. An American Petroleum Institute-sponsored project at the University of Texas extensively studied the composition of the basic nitrogen compounds in a California petroleum. As a result of this study, 10 pyridines, 22 quinolines, one tetrahydroquinoline, and two dihydropyrindines were identified (*9-11*).

This paper describes a characterization of the classes of basic nitrogen compounds present in distillate fractions of Wilmington crude oil (*6*) and includes the identification of two individual compounds. Distribution of the classes of compounds was determined by low-voltage mass spectral analyses. The individual compounds were identified by a combination of mass, infrared, ultraviolet, and nuclear magnetic resonance spectral techniques. The work was carried out as part of American Petroleum Institute Research Project 52, which was concerned with the study of nitrogen compounds in petroleum. The project was discontinued June 30, 1966.

EXPERIMENTAL

The separation procedure used in this study is outlined in Figure 1. The investigations reported in this paper were carried out on the fractions indicated by the solid-lined

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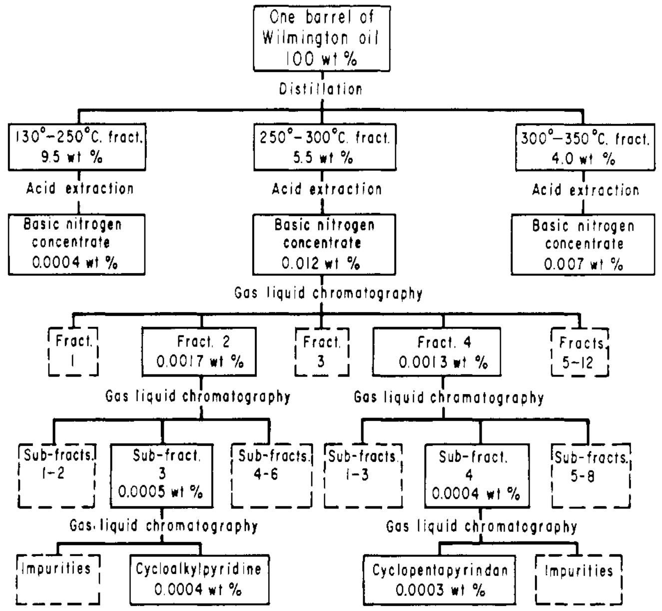

Figure 1. Separation procedure

boxes. The percentage figure given in each box refers to the weight per cent of the original crude oil present in the fraction.

One barrel of Wilmington crude oil was distilled in a specially designed inclined-plane still (*5*). Three fractions with boiling ranges at atmospheric pressure of 130° to 250°, 250° to 300°, and 300° to 350° C. were collected. These three fractions were extracted with 0.1*N* HCl to give concentrates of the basic nitrogen compounds. Each of these concentrates was analyzed by low-voltage mass spectrometry (~9 v.), using a Consolidated Mass Spectrometer, Model 21-103, to characterize the basic nitrogen compounds according to types.

The concentrate from the 250° to 300° C. fraction was separated by gas-liquid chromatography (GLC), using Aerograph Model A-700 and Model 1520 chromatographs equipped with thermal conductivity detectors. Twelve fractions were obtained from the initial GLC separation of the basic nitrogen concentrate, using a 30-foot by 3/8-inch aluminum column packed with 15% of the polar liquid substrate Carbowax 20M on Gas Chrom-P maintained at 200° C. Low-voltage mass spectral analyses of the 12 fractions showed that the Carbowax 20M substrate had made a compound-type separation of the concentrate. The alkyl-substituted pyridines were eluted first, followed by the cycloalkyl-substituted pyridines, the alkyl-substituted cyclopentapyrindans, and the alkyl-substituted quinolines.

Mass spectral analyses showed that fraction 2 contained a concentration of cycloalkylpyridines and that fraction 4 contained a concentration of cyclopentapyrindans. These two fractions were each separated on a 30-foot by 3/8-inch aluminum column packed with 15% of the nonpolar liquid substrate silicone rubber SE-30 on Gas Chrom-P and maintained at 150° C. Fraction 2 was separated into six subfractions and fraction 4 into eight subfractions. Low-voltage mass spectral analyses of the subfractions from these separations showed that each subfraction contained five, or less, major components. However, individual compounds could not be identified from any of the subfractions, indicating that additional separation was required.

The choice of liquid phase to be used for further separation of each of the subfractions was made by the trial and error method. The sample was run on a large number of both polar and nonpolar liquid phases. As a result of these tests, Triton X-305 was the best liquid phase for the separation of cycloalkyl-substituted pyridines and Tween-20 the best for separating cyclopentapyrindans.

Subfraction 3 of fraction 2 was separated on a 50-foot by 1/4-inch aluminum column packed with 15% of the polar liquid substrate Triton X-305 and maintained at 175° C. The material under the major peak of the chromatogram was trapped and analyzed by low-voltage mass spectrometry. One compound of the cycloalkylpyridine type was the only component present.

Subfraction 4 of fraction 4 was separated on a 50-foot by 1/4-inch aluminum column packed with 15% of the polar liquid substrate Tween-20 on Gas Chrom-P and maintained at 175° C. The material under the major peak of the chromatogram was trapped and analyzed by low-voltage mass spectrometry. One compound of the cyclopentapyrindan type was the only component present.

The identification of the two individual compounds was made by mass, infrared, ultraviolet, and nuclear magnetic resonance spectroscopy. The instruments used were as follows: mass, Consolidated Electrodynamics Corp., Model 21-103; infrared, Perkin-Elmer, Model 521; ultraviolet, Cary, Model MS-11; nuclear magnetic resonance, Varian Associates, Model HA-100.

RESULTS AND DISCUSSION

Characterization of the Basic Nitrogen Compounds in the 130° to 350° C. Boiling Range. Characterization of the basic nitrogen compounds in petroleum, using mass spectrometry, has been made by several investigators (*2, 7, 8, 17*). These characterizations have been made by assigning specific compound types to *Z*-number mass series with the *Z*-number corresponding to the hydrogens in the compound according to the formula $C_nH_{2n+z}N$. The assignment of a compound type to a *Z*-series requires some knowledge of the composition of the compounds present, since more than one type often meets the requirements. The *Z*-5 and *Z*-11 series are usually assigned to alkylpyridines and alkylquinolines, respectively, because these compound types are known to be present in petroleum (*9*). The *Z*-7 series can be assigned to cycloalkylpyridines, dihydropyrindines, or tetrahydroquinolines. The authors have assigned this series to cycloalkylpyridines, because, as reported later in this paper, an individual compound of this type is identified. The *Z*-9 series can be assigned to dinaphthenopyridines (cyclopentapyrindans) or alkylpyrindines. The authors have assigned this series to the cyclopentapyrindan type because of the identification of an individual compound. The *Z*-13 series can be assigned to cycloalkylquinolines or mononaphthenoquinolines and the *Z*-17 series to benzoquinolines or acridines. Individual compounds in these two series were not identified in this work, so a single type is not listed for these two series.

The basic nitrogen compound concentrates from the 130° to 250°, 250° to 300°, and 300° to 350° C. fractions were analyzed by low-voltage mass spectrometry to determine the amounts of the various types of compounds in each fraction (Table I). The amounts of the various compound types were calculated as per cent of the total ionization of the low-voltage spectra.

The 130° to 250° C. fraction contains mostly cycloalkylpyridines with the C_1-substituted compound (m.w. 175) the most predominant member of the series present. The alkylpyridines in this fraction contain from C_2- to C_8-substituent groups, while the quinolines contain from one to three alkyl groups.

In the 250° to 300° C. fraction, the cycloalkylpyridines are also the predominant compound type. The C_5-substituted members of the series are present in the highest concentration with lesser amounts of C_1- through C_7-substituted cycloalkylpyridines. The cyclopentapyrindans contain from four to eight substituent groups,

Table I. Composition of Basic Nitrogen Compounds in Fractions of Wilmington Crude Oil

Z Number	Possible Compound Type	Total Ionization, %[a] 130° to 250° C. fraction	250° to 300° C. fraction	300° to 350° C. fraction
5	Alkylpyridines	36.9	4.8	...
7	Cycloalkylpyridines	55.4	44.8	17.6
9	Cyclopentapyrindans	...	19.1	4.7
11	Alkylquinolines	7.8	31.7	60.6
13	Cycloalkylquinolines and/or mononaphtheno-quinolines	...	...	10.1
17	Benzoquinolines and/or acridines	...	...	6.8

[a] Calculated from low-voltage mass spectra.

while the alkylquinolines have from three to six substituent groups. The alkylpyridines have almost disappeared in this fraction.

In the 300° to 350° C. fraction, the alkylquinolines are the most prevalent type and make up almost two-thirds of the compounds present. The C_6-quinoline is present in the greatest concentration. Compounds with Z-numbers corresponding to cycloalkylquinolines and benzoquinolines make their appearance in this fraction, while the cyclopentapyrindans have almost disappeared.

Identification of 2,4-Dimethyl-6-(2,2,6-trimethylcyclohexyl)-pyridine. A low-voltage mass spectrum showed that the compound has a molecular weight of 231 and, from measurement of the isotope abundance ratios of the molecular ions, an empirical formula of $C_{16}H_{25}N$. A compound with this molecular weight and empirical formula could be a cycloalkylpyridine, and the spectral data presented will show that the compound is a cyclohexylpyridine. The ultraviolet spectrum showed maxima at 264, 268, and 271 mμ with extinctions of 3950, 3600, and 3470, respectively, which is highly indicative of the pyridine ring chromophore. The infrared spectrum contained bands at 1600 and 1575 cm.$^{-1}$ which are attributed to pyridine ring vibrations. Doublet bands at 1385 to 1370 and 1162 to 1152 cm.$^{-1}$ correspond to a *gem*-dimethyl group attached to a quaternary carbon (*14*).

The major portion of the information needed for the identification of the compound was obtained from its NMR spectrum. The 100-megacycles per second NMR spectrum of purified subfraction 3 is shown in Figure 2. Chemical shifts are given in parts per million relative to tetramethylsilane, which was used as an internal standard. The assignment of the pyridine ring protons and the protons on a carbon α to a pyridine ring are based on the extensive correlation study of McDonald and Cook (*13*). The signals at 6.74 and 6.66 p.p.m. (*a*), each equivalent to one hydrogen, are assigned to two hydrogens attached to a pyridine ring at the 3 and 5 positions. The signal at 2.46 p.p.m. (*b*), equivalent to three hydrogens, is assigned to a methyl group at the 2 position of the pyridine ring, while the signal at 2.24 p.p.m. (*c*), equivalent to three hydrogens, is assigned to a methyl group at the 4 position of the pyridine ring. The assignment of hydrogens or methyl groups at the 2, 3, 4, and 5 positions means that the cyclohexyl group is attached to the pyridine ring at the 6 position. This conclusion is verified by the absence of a signal in the 8.3 p.p.m. region which is assigned to hydrogens at the 2 or 6 position. The area from 2.2 to 1.0 p.p.m. (*d*), equivalent to eight hydrogens, has been assigned to the ring hydrogens of the cyclohexyl ring. The two singlets at 0.91 (*e*) and 0.73 (*f*) p.p.m., each equivalent to three hydrogens, are assigned to unsplit methyl groups (*gem*-dimethyl) on the cyclohexyl ring. The doublet centered at 0.62 p.p.m. (*g*), equivalent to three hydrogens, is due to a methyl group on the cyclohexyl ring. This methyl group is split by an adjacent hydrogen.

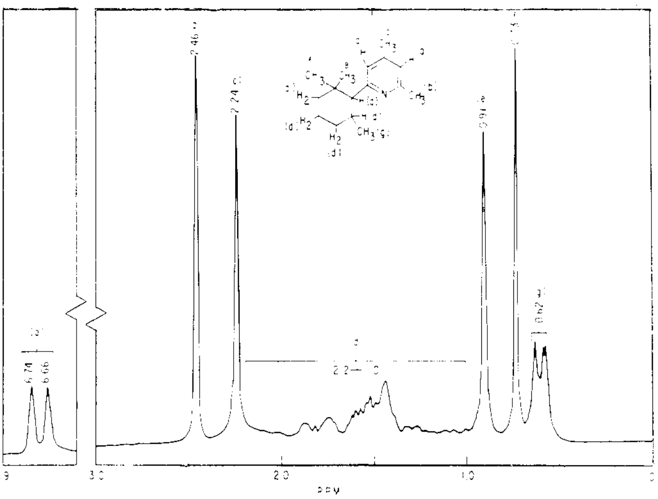

Figure 2. NMR spectrum of purified subfraction 3

The spectral data presented are consistent with that postulated for 2,4-dimethyl-6-(2,2,6-trimethylcyclohexyl) pyridine. This compound was first isolated from petroleum in 1931 by Thompson and Bailey (*20*), and was not identified until 10 years later by Shive and co-workers (*18*).

Identification of 2,4,7a,8,8-Pentamethylcyclopentapyrindan. A low-voltage mass spectrum showed that the compound has a molecular weight of 229. Measurement of the isotope abundance ratios of the molecular ions showed the empirical formula of $C_{16}H_{23}N$, which corresponds to a C_5-substituted cyclopentapyrindan. The ultraviolet spectrum showed maxima at 266, 271, and 274 mμ with extinctions of 4266, 4165, and 3809, which is indicative of an alkyl-substituted pyridine ring. The infrared spectrum showed two strong bands at 1590 and 1570 cm.$^{-1}$ that are due to the vibrations of a pyridine ring. Doublets at 1380 to 1375 and 1165 to 1160 cm.$^{-1}$ indicate a *gem*-dimethyl group attached to a quaternary carbon atom.

The NMR spectrum of purified subfraction 4 is shown in Figure 3. The signal at 6.78 p.p.m. (*a*) is assigned to a single hydrogen at the 3 position of the pyridine ring. The triplet at 2.72 p.p.m. (*b*) is assigned to a hydrogen at the junction of the two five-membered rings. The signals at 2.46 (*c*) and 2.21 p.p.m. (*d*), each equivalent to three

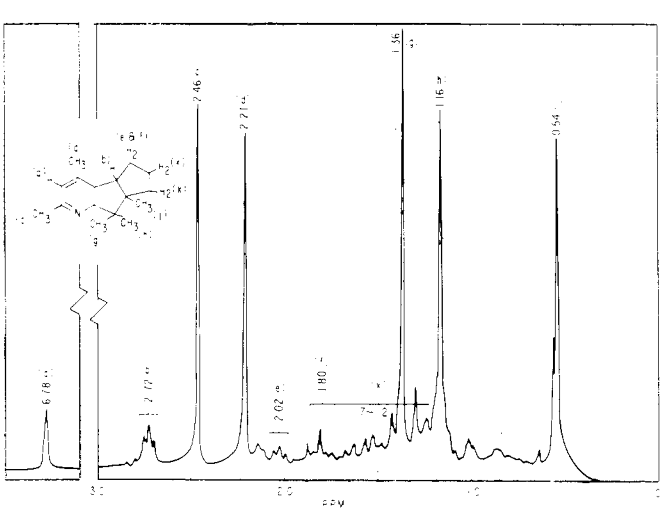

Figure 3. NMR spectrum of purified subfraction 4

hydrogens, are assigned to methyl groups at the 2 and 4 positions on the pyridine ring. The triplet centered at 2.02 p.p.m. (*e*) and the multiplet centered at 1.80 p.p.m. (*f*) are assigned to the two methylene hydrogens (*e*) and (*f*) on the basis of double and triple resonance experiments. When either of the signals (*e*) or (*f*) are externally irradiated, the signal at 2.72 p.p.m. (*b*) simplifies to a doublet, and when (*e*) and (*f*) are simultaneously irradiated, (*b*) coalesces to a sharp singlet. Hence, (*b*) is coupled to both hydrogens (*e*) and (*f*) by the same value of 5 cps. These effects are reciprocal, for when (*b*) is irradiated (*e*) simplifies to a doublet, and (*f*) becomes sharper. The signals at 1.36 (*g*) and 1.16 p.p.m. (*h*), each equivalent to three hydrogens, are due to the *gem*-dimethyl groups at the 8 position. The signal at the unusually high field of 0.54 p.p.m. (*j*) is assigned to the methyl group at position 7a. The four other methylene hydrogens on the five-membered ring give signals in the area from 1.7 to 1.2 p.p.m. (*k*). The signals for the *gem*-dimethyl hydrogens are also in this area and partially obscure the signals of the four methylene hydrogens.

The spectral data presented are consistent with that postulated for 2,4,7a,8,8-pentamethylcyclopentapyrindan. This is the first compound of this type to be identified in petroleum.

Optical Activity of the Identified Compounds. A number of workers (*3, 12, 16*) have observed optical activity in petroleum fractions. Fenske *et al.* (*3*) studied the distribution of optical activity in distillation fractions of a number of crude oils. They reported that optical activity appears in petroleum distillates at molecular weights of approximately 220 and reaches a maximum at about 400 molecular weight. This optical activity is taken as supporting evidence that petroleum is formed from the remains of plants and, to a lesser extent perhaps, animals. The two compounds isolated from petroleum are optically active. The cyclohexylpyridine has a specific rotation of $(\alpha)^{27}_{\mathrm{D}}$ −3.8°, and the specific rotation of the cyclopentapyrindan is $(\alpha)^{27}_{\mathrm{D}}$ −2.0. The optical activity of these compounds is additional evidence in support of the theory that natural products, such as terpenoid-type compounds, are the source material of petroleum.

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Hydrolysis of Oil-Soluble Organic Amine Salts in the Two-Phase Water-Benzene System

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SMALL CONCENTRATIONS of high molecular weight organic salts are added to bulk-refined petroleum products to protect against the corrosive action of fresh or salt water generally found as subnascent phases in storage, transport, and handling facilities. These additives are preferentially adsorbed on ferrous metals or their oxide films to form a barrier that retards corrosion. Rust inhibitors for fuels should be of the ashless type exemplified by the ammonium or organic substituted ammonium salts of the high molecular weight sulfonic or carboxylic acids. Normally, only minor losses of the additive from the fuel should occur by processes other than adsorption on corrosion-susceptible surfaces. Field performance of commercially available salts has been erratic. Fuels rendered rust-inhibitive at their points of origin have rapidly lost that property through contact with the aqueous phase. The carbon dioxide concentration or the pH of the aqueous phase also affects the susceptibility of the inhibitor to water extraction.

The cations and anions of these ammonium salts in solution in an organic phase are, respectively, Brönsted acids and bases that are susceptible to attack by other bases or acids located in a contacting immiscible phase such as water. The stability and the retention of an ammonium salt in the organic phase depend on such factors as the intrinsic acid and base strengths of the proton donors and receptors in each phase, the effect of the phase dielectric constant on ionic activity, and the stability conferred on