tained from run 1 at 900° F. using recycle gas for entrainment is the least aromatic. The oil from run 2 at the same temperature but using air for entrainment is somewhat more aromatic. The air decreased the over-all oil yield by 20 to 25% and this decrease may have been differential according to hydrocarbon type. The oil obtained at the higher temperature of 950° F. and also using air, is the most aromatic, showing the combined effects of these two variables. The oil yield on this last run was equivalent to the run using recycle gas. The aniline points of the individual fractions obtained in the vacuum distillations of these oils, plotted in Figure 6, show that the differences in composition of the oils are also evident in the higher-boiling fractions where hydrocarbon group determinations could not be made.

Figure 6 includes aniline points for the entrained solids oil and an average curve that is taken as representative of oils produced in the Fischer assay, Gas Combustion, Union, and Otto retorts. The curve for the entrained solids oil approximates that for the medium aromaticity oil from the Parry retort, although the entrained solids oil was from a run having a nominal retorting temperature about 200° F. higher. Although retorting temperature is an important variable that may be correlated with composition for a given retort, other factors such as residence time affect composition. Oils from retorts in which the products are removed by a sweep gas and from the Fischer assay retort have much higher aniline points, as indicated by the upper curve in Figure 6.

As the Brazilian and Colorado shales differ with respect to nitrogen content, the hydrocarbon compositions of several oils were compared to see if differences were indicated. The Fischer assay, entrained solids, and Gas Combustion retorts were used on shales from both sources. Hydrocarbon analyses of the combined naphtha and light distillate fractions after removal of tar acids and tar bases are shown in Table III. The saturates for the Colorado oils are consistently higher and the aromatics correspondingly lower, with only small differences in the olefin contents. This trend is apparent even if the tar acids and tar bases, which are generally higher for the Colorado oils, are considered as aromatics.

SUMMARY

Oils obtained from Brazilian and Colorado shale by several different experimental retorting methods have been analyzed by the Bureau of Mines method for crude shale oil. The proportion of lower-boiling distillates was primarily a function of the retorting method, but the Colorado oils always contained larger amounts of residuum. The retorting method caused a variation in the total nitrogen and sulfur contents of the oils. The average nitrogen content of the Colorado oils was about twice that of the Brazilian oils. This difference apparently results from variations in structure of organic matter, as total nitrogen contents were about the same. Most of the Brazilian oils had a different distribution of nitrogen with respect to boiling range than the Colorado oils. Oils produced from the two shales by the same retorting method showed regular differences in hydrocarbon composition, the Colorado oils having a greater content of saturates and a lower content of aromatics.

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Distribution of Nitrogen Compounds in Wilmington, Calif., Petroleum

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Nitrogen compounds in petroleum are known to have deleterious effects on cracking catalysts in refining operations (*6, 8, 12, 16*) and on the stability of petroleum products (*5, 15*). Knowledge of the occurrence, types, and properties of nitrogen compounds in petroleum is important in combating these undesirable effects. To procure fundamental data on the structure and properties of these compounds, the American Petroleum Institute Research Project 52 on nitrogen constituents in petroleum was established July 1, 1954. The initial studies of one phase of Project

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52 have been concerned with the nitrogen compounds in a crude oil from the Wilmington field in California.

A concentrate of nitrogen compounds was prepared by a combination of deasphaltening and adsorption techniques. The removal of asphaltenes by pentane precipitation increases the fluidity of the oil, making it more convenient to handle. The nitrogen compounds were then segregated from the deasphaltened oil by an adsorption technique, using Florisil. Control tests of the two procedures gave considerable information on the distribution of the nitrogen compounds in the crude oil.

This report describes the distribution of nitrogen in the crude oil as a function of molecular weight, divides this nitrogen into basic and nonbasic categories, and describes some of the precautions necessary to prevent changes in the nitrogen compounds during processing. The major portion of the nitrogen compounds present in Wilmington crude oil have molecular weights above 320. The ratio of basic to total nitrogen is fairly constant throughout the crude oil with a value of 0.28. The nitrogen compounds have high sensitivity toward oxygen, and careful blanketing of the material with oxygen-free nitrogen during the various phases of processing was employed. A procedure for obtaining a concentrate of nitrogen compounds for further separation work is also given.

SELECTION OF CRUDE OIL

Wilmington crude oil was selected because it represents a large source of production and has a high nitrogen content, which facilitates the study of nitrogen compounds. For comparison, Table I shows the nitrogen contents of crude oils from the ten largest fields in the United States in 1953.

Table I. Nitrogen Contents of Crude Oils from Ten Largest Producing Fields in the United States

Field	State	Nitrogen, Wt. %
East Texas	Texas	0.085
Wilmington	California	0.65
Ventura Avenue	California	0.42
Coalinga	California	0.52
Rangely	Colorado	0.063
Huntington Beach	California	0.83
Wasson	Texas	0.10
Hawkins	Texas	0.13
Goldsmith	Texas	0.086
Velma	Oklahoma	0.27

The California Research Corp. supplied a 21-barrel sample of crude oil from the Wilmington, Calif., field. This sample was collected and stored under nitrogen in 1954. Twelve barrels of this sample were received by API Research Project 52 for studies of nitrogen compounds, 8 barrels were received by API Research Project 48 for studies of sulfur compounds, and 1 barrel was received by A. H. Corwin at Johns Hopkins University for studies of porphyrin content. The general properties of this crude oil, as determined by the Bureau of Mines routine crude-oil analysis (*14*), are listed in Table II.

EXPERIMENTAL

A concentrate of nitrogen compounds was prepared by deasphaltening the crude oil with *n*-pentane and segregating the nitrogen compounds of the deasphaltened oil by Florisil adsorption.

As some organic nitrogen compounds are sensitive to oxygen as well as to heat and light, materials were protected during all operations. The nitrogen used as an inert blanket gas was the commercial water-pumped grade subsequently purified by passage with 5% hydrogen over a platinum catalyst in a Baker & Co. Puridryer unit. After purification and drying, the nitrogen contained less than 2 p.p.m. of oxygen and up to 150 p.p.m. of water. All equipment was No. 7740 Pyrex glass or stainless steel to minimize contamination or decomposition of the nitrogen compounds. Solutions and solvents were transferred by stainless steel microbellows pumps.

Total nitrogen was determined on the fractions from these studies by the macro-Kjeldahl method using the modification of Lake and others (*4*). Basic nitrogen was determined on the fractions by potentiometric titration using the method of Moore, McCutchan, and Young (*10*). No determination of total or basic nitrogen was made below 0.001%. Molecular weights were calculated on the fractions from the distillations by the method of Mills, Hirschler, and Kurtz (*9*). Molecular weights of the residue from the distillation of the deasphaltened oil and of the asphaltenes were determined by the ebullioscopic method (*3*, *7*).

Deasphaltening. The crude oil was deasphaltened in stainless steel pressure vessels by diluting with 15 volumes of *n*-pentane. The selection of 15 volumes of *n*-pentane was based on results obtained in small-scale studies, which indicated that fewer asphaltenes were precipitated by either more or less dilution with *n*-pentane. After precipitation of the asphaltenes, the pentane solution was separated from them by pressure filtration, and the asphaltenes were washed with *n*-pentane. The *n*-pentane was removed from the oil by isothermal stripping at 50° in the Pyrex-glass apparatus shown in Figure 1. This isothermal stripping unit provides for evaporation of the solvent from a thin film of oil while sweeping with a countercurrent stream of purified nitrogen gas.

Distillation. Comparative fractions of the crude oil and deasphaltened oil were prepared by a distillation procedure similar to that employed in the Bureau of Mines routine analysis method. These distillations yielded, for each oil,

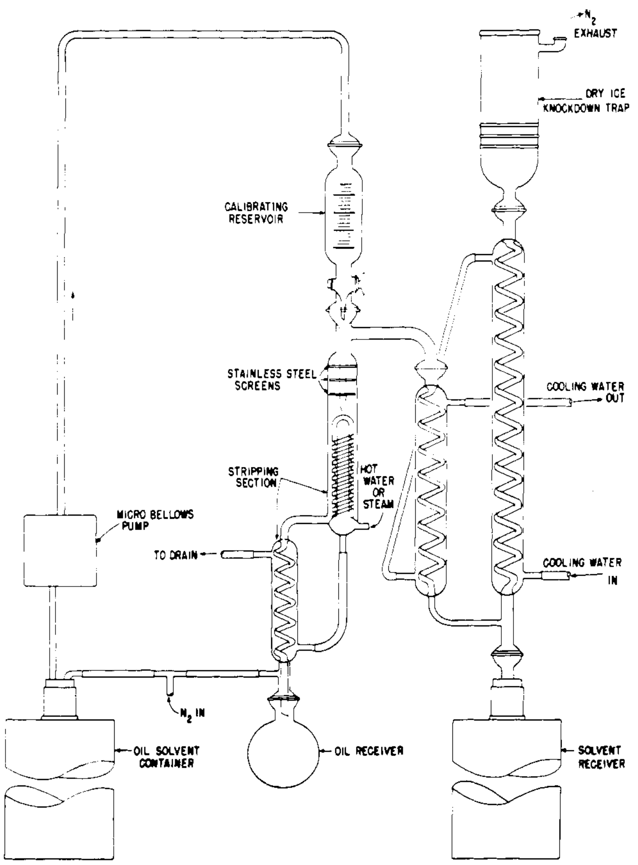

Figure 1. Isothermal stripping unit

Table II. Analysis of Wilmington, Calif., Crude Oil

General Characteristics

Specific gravity, 0.939. A. P. I. gravity 19.2°. Pour point, °F. Below 5
Sulfur, %, 1.59. Nitrogen, % 0.65. Color, brownish black
Saybolt Universal viscosity at 100°F., 480 sec.; at 130°F., 190 sec.

Fraction Cut at °C.	%	Sum, %	Sp. Gr., 60/60°F.	°A. P. I., 60°F.	C. I.	Aniline Point, °C.	S. U. Visc., 100°F.	Cloud Test, °F.
Stage 1. Distillation at atmospheric pressure, 760 mm. Hg. First drop, 58°C.								
50	...	...	...	...	...	...		
75	0.8	0.8	...	...	...	...		
100	0.8	1.6	0.715	66.4	...	51.6		
125	2.4	4.0	0.750	57.2	27	51.1		
150	2.5	6.5	0.771	52.0	29	51.9		
175	2.3	8.8	0.793	46.9	32	51.2		
200	2.6	11.4	0.814	42.3	36	51.0		
225	3.7	15.1	0.834	38.2	40	52.8		
250	4.7	19.8	0.853	34.4	44	54.2		
275	6.9	26.7	0.871	31.0	48	54.0		
Stage 2. Distillation continued at 40 mm. Hg.								
200	0.6	27.3	...	...	...	...	...	...
225	4.8	32.1	0.902	25.4	...	55.2	51	Below 5
250	6.4	38.5	0.914	23.3	57	56.2	72	20
275	5.7	44.2	0.933	20.2	63	56.8	145	40
300	7.2	51.4	0.947	17.9	66	58.2	450	55
Residuum	47.2	98.6	1.013	8.2		Too dark		

Carbon residue of residuum, 12.7%
Carbon residue of crude, 6.5%

Approximate Summary

	%	Sp. Gr.	°A. P. I.	Viscosity
Light gasoline	1.6	0.715	66.4	
Total gasoline and naphtha	11.4	0.773	51.6	
Kerosine distillate	...	...	...	
Gas oil	17.7	0.862	32.7	
Nonviscous lubricating distillate	8.5	0.902-0.922	25.4-22.0	50-100
Medium lubricating distillate	4.8	0.922-0.935	22.0-19.8	100-200
Viscous lubricating distillate	9.0	0.935-0.955	19.8-16.7	Above 200
Residuum	47.2	1.013	8.2	
Distillation loss	1.4	...	...	

nine fractions distilling up to 275° at 760 mm. of mercury pressure, five fractions distilling up to 300° at 40 mm. of mercury pressure, and a residue.

Florisil Adsorption. A concentrate of the nitrogen compounds was prepared from the deasphaltened oil, using Florisil (synthetic magnesium silicate), 30-60 mesh, as the adsorbent. Smith, Smith, and Dinneen (*13*) have shown this material to be superior to other adsorbents in the concentration of nitrogen compounds present in shale oil. Small-scale studies of the deasphaltened oil in all-glass systems indicated that, in eluting the hydrocarbon portion of the oil with pentane, optimum retention of the nitrogen compounds was obtained with a column height-to-diameter ratio of 60 and a ratio of 1 gram of Florisil to 1 mg. of nitrogen. Methanol, acetone, benzene, and mixtures of these materials were tested for desorptive properties, and benzene followed by acetone was found to give nearly quantitative recovery of the adsorbed nitrogen compounds. This combination was used in the subsequent studies described below.

The nitrogen compounds present in the deasphaltened oil were concentrated in a stainless steel column 1.75 x 105 inches, shown in Figure 2. The column was packed with 2 kg. of Florisil, heated to 150°, and purged 24 hours with purified nitrogen. The nitrogen flow was maintained while the column cooled to room temperature. *n*-Pentane was charged to the reservoir tank and the column was filled from the bottom with pentane to displace the nitrogen. About 7 liters of pentane then were passed downward through the Florisil to remove soluble materials from the adsorbent. Approximately 450 grams of the deasphaltened oil containing 0.53% of nitrogen were used. The deasphaltened oil was diluted with pentane, placed on the adsorbent, and eluted with approximately 15 liters of *n*-pentane to remove the nonnitrogenous portion of the oil. The nitrogen compounds were removed by consecutive application of approximately 15 liters each of benzene and acetone. The solvents were recovered for re-use by stripping in the isothermal unit previously described.

RESULTS

Nitrogen Distribution from Deasphaltening. Solvent extraction of the crude oil with 15 volumes of *n*-pentane gave two fractions—the asphaltenes and the deasphaltened oil. Table III lists the distribution of the nitrogen in these materials, together with the ratio of basic to total nitrogen. The deasphaltened oil contains three fourths of the nitrogen, and, as it contains the lowest boiling materials, is the most convenient and practicable for use in identification work. The asphaltenes, which have the highest molecular weights, represent approximately one fifteenth of the oil, and contain about one fourth of the nitrogen. This asphaltene material is of such complexity that detailed study of it will be postponed.

Some consideration was given to the stability of the asphaltenes, from the standpoint of both crude-oil distillation and storage of asphaltenes. Separate samples of the asphaltenes heated at 200° and 300° for 24 hours at atmospheric pressure showed only a slight increase in basicity and were somewhat less soluble in benzene than the untreated asphaltenes. No distillate was obtained at either temperature, although a small amount of hydrogen sulfide was formed at 300°. Exposure of the original asphaltenes to air at room temperature changed the N_B/N_T ratio from 0.24 to 0.17, indicating that oxidation or polymerization reactions had occurred.

To compare propane deasphaltening with pentane deasphaltening, a sample of the *n*-pentane–deasphaltened oil was deasphaltened further with propane by The Texas Co. This treatment precipitated additional asphaltenes equivalent to 14% of the crude oil. The resultant oil and asphaltenes contained, respectively, 0.33% and 1.7% of total nitrogen. Thus, deasphaltening with pentane followed by propane results in the removal of 21% of the crude oil or about three times as much as the pentane procedure alone.

Nitrogen Distribution According to Boiling Range. Table IV shows the nitrogen content of fractions from the distillation of both Wilmington crude oil and the deasphaltened oil. Nitrogen does not reach the 0.001% level in the distillates until the fraction distilling at a vapor temperature of 225° to 250° is reached. Both oils have high N_B/N_T ratios in the boiling range of 250° to 306° (306° corresponds to 225° at 40 mm. of mercury pressure). High ratios in this boiling range also were observed by Richter and others (*11*). A somewhat higher N_B/N_T ratio occurs in the crude oil fraction boiling in the range of 250° to 275° than in the corresponding fraction from the deasphaltened oil. The weight-per cents of the distillation fractions of the two oils agree within the limits of experimental error, except for the fractions boiling at 250° to 275°. This suggests that cracking of the crude oil occurs within this temperature range, causing the high N_B/N_T ratio. Above 275° the N_B/N_T ratios are almost the same for both oils. These ratios decrease in the higher boiling fractions to essentially the same ratios observed in the undistilled oils. The distillation residues have lower ratios than the corresponding undistilled oils.

Nitrogen Distribution from Adsorption Separations. The *n*-pentane–deasphaltened oil was subjected to adsorption on Florisil to produce a nitrogen-compound concentrate containing 1.5% of nitrogen. The concentrate, as shown in Table III, is approximately 25% of the crude oil, and has a N_B/N_T ratio of 0.27. The pentane eluate, or nonnitrogenous portion of the deasphaltened oil, contained only 0.01% of total nitrogen, and the basic nitrogen was too low to determine.

The adsorption experiments revealed the sensitivity of the nitrogen compounds to small amounts of oxygen. Table V presents data for a series of runs in which increasingly effective steps were taken to keep oxygen away from the oil. In run A, the Florisil column was washed with pentane by filling it from the top. The recovery of basic nitrogen, as shown in the table, was only 88%. Basic nitrogen determinations were more useful, as they show changes in basicity of nitrogen compounds as well as recovery. In run B the column was filled with pentane from the bottom in order to displace the air, and a recovery of 93% was obtained. Run C, which used the conditions finally adopted—namely, purging of the column with purified nitrogen at 150° followed by filling the column from the

Table III. Results of Deasphaltening and Adsorption

Sample	Wt. % of Crude Oil	Per Cent of Total Nitrogen	N_T Total Nitrogen, Wt. %	N_B Basic Nitrogen, Wt. %	N_B/N_T
Crude Oil	100	100	0.65	0.18	0.28[a]
		Deasphaltening			
Asphaltenes	7	26	2.28	0.54	0.24
Deasphaltened oil	93	74	0.53	0.16	0.30
		Adsorption of Deasphaltened Oil			
Florisil eluate	68	1	0.01	0.00	0.00
Florisil concentrate	25	73	1.50	0.41	0.27

[a] This ratio falls in range of 0.30 ±0.05 found for 14 crude oils by Richter and others (*11*). Ratio is higher for pentane-soluble material than for asphaltenes.

Table IV. Nitrogen Distribution According to Boiling Range

	Crude Oil			Deasphaltened Oil		
Fraction Temp. °C.	Fraction, Wt. %	Total nitrogen, %	N_B/N_T	Fraction[a], Wt. %	Total nitrogen, %	N_B/N_T
		Distillation at 760 Mm. of Mercury				
Up to 75	0.3	0.000	...	0.4	0.000	...
75–100	0.8	0.000	...	0.7	0.000	...
100–125	2.0	0.000	...	1.7	0.000	...
125–150	2.2	0.000	...	1.9	0.000	...
150–175	2.0	0.000	...	2.1	0.000	...
175–200	2.4	0.000	...	2.5	0.000	...
200–225	3.4	0.000	...	3.1	0.000	...
225–250	5.2	0.013	0.21	4.8	0.006	0.30
250–275	9.6	0.038	0.60	8.1	0.036	0.44
		Distillation Continued at 40 Mm. of Mercury				
Up to 200	0.6	0.084	0.44	0.9	0.087	0.47
200–225	4.7	0.114	0.47	4.6	0.109	0.46
225–250	6.1	0.213	0.35	5.8	0.183	0.38
250–275	5.9	0.320	0.30	5.8	0.293	0.31
275–300	8.4	0.427	0.28	9.3	0.397	0.28
Residue	46.4	1.20	0.27	40.8	1.03	0.25

[a] Calculated to crude-oil basis.

Table V. Effect of Air in Concentrating Nitrogen Compounds on Florisil

	Adsorption Run		
	A	B	C
Benzene fraction			
% of N_B	14.2	76.4	88.7
N_B/N_T	0.13	0.32	0.27
Acetone fraction			
% of N_B	74.0	16.6	14.1
N_B/N_T	0.55	0.35	0.23
Recovery			
% of N_B	88.2	93.0	102.8
% of N_T	90	91	99

Run A. Column filled with pentane from top before introduction of oil.
Run B. Column filled with pentane from bottom before introduction of oil.
Run C. Column purged with purified nitrogen at 150° and filled with pentane from bottom before introduction of oil.

bottom—gave quantitative recovery within experimental limits. Table V also shows that the proportion of the basic nitrogen removed from the Florisil by the benzene increased, and the amount removed by acetone decreased.

To determine the heat stability of the nitrogen concentrate, samples were heated at 200° and 300° for 24 hours under an atmosphere of purified nitrogen. No changes were noted at the lower temperature, but at 300° a decrease in N_B/N_T occurred with some evolution of ammonia. Distillation of the nitrogen concentrate to a temperature of 150° at 0.1 mm. produced only 3% of distillate. The concentrate was soluble in pentane; however, on exposure of the pentane solution to air, a granular precipitate was formed that was soluble in benzene.

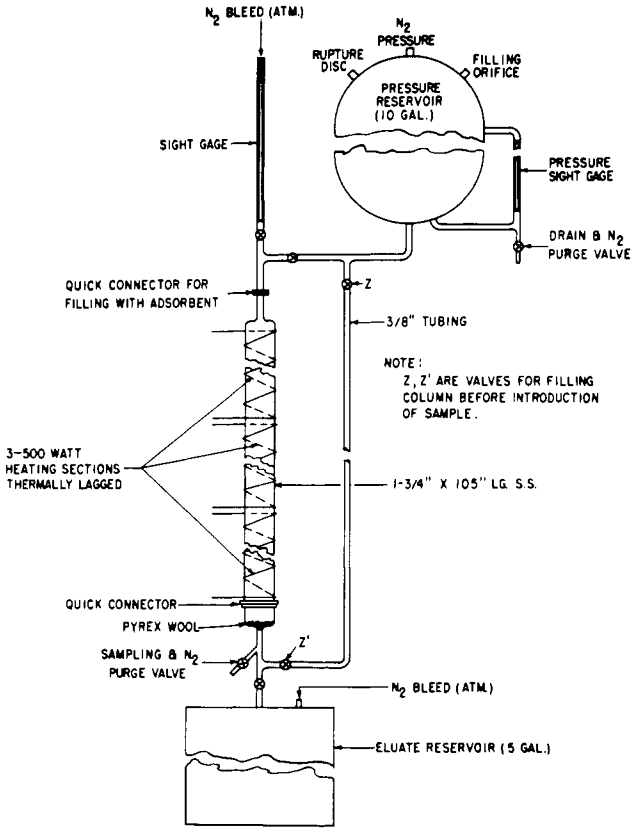

Figure 2. Florisil adsorption column

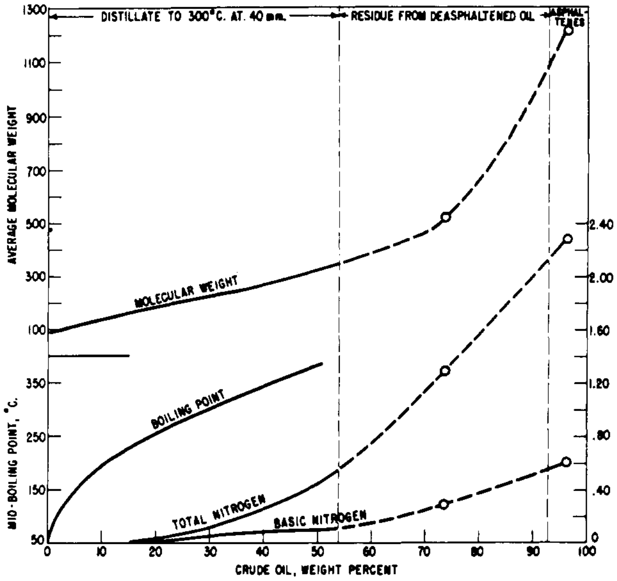

Figure 3. Properties of fractions from Wilmington crude oil

DISCUSSION

Figure 3 shows selected properties of fractions of Wilmington crude oil, including the average molecular weights, basic and total nitrogen contents, and mid-boiling points. The curves are derived from data obtained for the distillate fractions of the deasphaltened oil, the residue from the same oil, and the asphaltenes from the crude oil. Inasmuch as only two data points are available for the residue and asphaltenes, the curves are dotted in these regions.

Approximately 53% of the crude oil is distillable with the last fraction having a mid-boiling point of 380° at 760 mm. of mercury pressure. Calculation indicates that the lowest boiling fraction in which nitrogen compounds become appreciable has an average molecular weight of 180. The nitrogen content increases through the last fraction that contains 0.42% of nitrogen and has an average molecular weight of 325. If it is assumed that those nitrogen compounds present contain only 1 atom of nitrogen per molecule, this fraction contains about 10% of nitrogen compounds. Figure 4, based on the above assumption, shows per cent nitrogen compounds present in the fractions from Wilmington crude oil. The distillate contains only 13% of the total nitrogen in the crude oil and therefore represents only a small portion of the nitrogen compounds present in the crude oil. This is typical of nitrogen-containing crude oils as shown by the work of Ball, Whisman, and Wenger (*1*, *2*).

The residue from the distillation of deasphaltened Wilmington crude oil has an average molecular weight of 475. The molecular weight curve in Figure 3 indicates a molecular weight range of 320 to 1100 for this residue. The composition of the residue in terms of nitrogen compounds is shown in Figure 4. Based on the average molecular weight of 475, the residue contains 35% of nitrogen compounds, assuming one atom of nitrogen per molecule. This residue contains approximately 60% of the nitrogen present in the crude oil.

The asphaltenes from the crude oil have an average molecular weight of 1225. This material contains 26% of the nitrogen present in the crude oil. The assumption of one atom of nitrogen per molecule leads to the absurdity of 200% of nitrogen compounds, as shown in Figure 4. Consequently, most of these asphaltene molecules must contain more than one nitrogen atom.

The relationship between basic and total nitrogen is shown in Figure 3. The differentiation between basic and nonbasic nitrogen is probably significant in the lower molecular weight range as a measure of types of nitrogen compounds present. In the higher molecular weight range, however, this may not be the case. Substitution increases the basicity of pyrroles (*11*), and tetramethylpyrazine is only 50% titratable as basic nitrogen.

Results of the studies on asphaltenes indicate a decrease in the basic nitrogen content of these materials when they are exposed to air. The nitrogen concentrate from the deasphaltened oil, while originally soluble in pentane, will react when exposed to air to form a pentane-insoluble material. Florisil adsorption studies have shown that small amounts of air present on the adsorbent will cause low recovery of both total and basic nitrogen. In addition, a difference in ease of removal of the nitrogen compounds from the adsorbent by benzene and acetone is indicated by runs where various quantities of oxygen are present on the Florisil. The adsorption results show that nitrogen compounds from Wilmington crude oil will react with small concentrations of oxygen at room temperature. Both basic and nonbasic types of compounds are reactive.

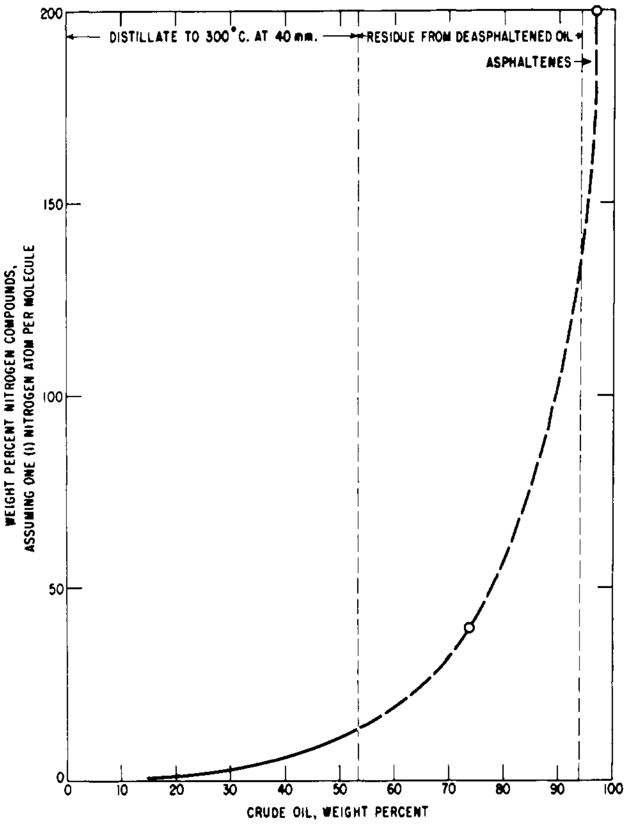

Figure 4. Quantity of nitrogen compounds in Wilmington crude oil fractions

A procedure by which a concentrate of nitrogen compounds may be obtained for future investigations of API Research Project 52 consists of a preliminary deasphaltening step followed by concentration of the nitrogen compounds by adsorption on Florisil. This results in a concentrate with one fourth the volume and more than twice the nitrogen content of the original oil. The remainder of the nitrogen is present in the high-molecular-weight asphaltenes. Calculations indicate that the nitrogen-containing molecules (assuming one nitrogen atom to the molecule and a molecular weight of 600) constitute about 65% of the concentrate. Further concentration and separation is planned to identify types of compounds and some individual compounds.

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