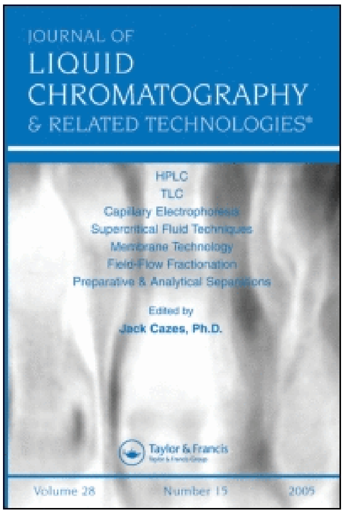

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Preparative Liquid Chromatographic Method for the Characterization of Minor Constituents of Lubricating Base Oils

P. Pei[a]; S. M. Hsu[a]
[a] National Bureau of Standards, Gaithersburg, Maryland

To cite this Article Pei, P. and Hsu, S. M.(1986) 'Preparative Liquid Chromatographic Method for the Characterization of Minor Constituents of Lubricating Base Oils', Journal of Liquid Chromatography & Related Technologies, 9: 15, 3311 — 3345

To link to this Article: DOI: 10.1080/01483918608074184

URL: http://dx.doi.org/10.1080/01483918608074184

JOURNAL OF LIQUID CHROMATOGRAPHY, 9(15), 3311-3345 (1986)

PREPARATIVE LIQUID CHROMATOGRAPHIC METHOD FOR THE CHARACTERIZATION OF MINOR CONSTITUENTS OF LUBRICATING BASE OILS

P. Pei and S. M. Hsu
National Bureau of Standards
Gaithersburg, Maryland

Abstract

In an effort to isolate, identify, and measure the properties of the active ingredients in a lubricating base oil, a high performance liquid chromatography (HPLC) separation scheme has been developed. The preparative mode of production is necessary to yield sufficient amounts of minor constituents for property measurements in terms of friction, wear, and oxidation characteristics.

In friction and wear control, the polarity of the molecular species is more important than the function groups in the species. Therefore the design of the separation scheme is based on the relative polarity of various functional groupings. Because the effort is directed towards identifying key components rather than analysis of the major compositions, mass recovery requirement is critical.

CONTRIBUTION OF THE NATIONAL BUREAU OF STANDARDS. NOT SUBJECT TO COPYRIGHT.

0148-3919/86/0915-3311$3.50/0

The separation scheme is divided into two stages. The base oil first undergoes a clay-gel separation to yield the saturates, aromatics, and the polar fractions. The polar fraction then is separated further using a neutral alumina column and the sequential solvent extractions into molecular compound classes of varying polarity. This paper describes the separation scheme and the detailed chemical characterization of the fractions.

1. Introduction

Lubricants generally consist of base oils and additives. Additives usually control the initial friction and wear characteristics of the lubricants, while base oils control the breakdown and failure mechanism of the lubricants, as well as additive response. It has been reported that different base oils with the same additives may perform significantly differently in engine performance tests (1). The two different responses from the same additive indicate possibly there are base oil-additive interactions. Lubricating base oils are generally composed of straight chain paraffins, cyclic hydrocarbons, aromatics, and a small amount of polar heteroatoms (nitrogen, sulfur, and oxygen). Typically, the composition of a base oil has 70 to 80 % by wt. of saturated hydrocarbons, 15 to 30 % aromatics, and 0.5 to 2 % by wt. of the polar heteroatom species (as defined by clay-gel separation method such as ASTM D2007) (2). For most base oils, there are few nitrogen and oxygen containing molecules (100-500 ppm), but sulfur containing molecules could be found as high as 1.2 % or 12,000 ppm and distributed among various structures as alkyl sulfides, cyclic sulfur and thiophenes. The response of base oils towards friction, wear, and oxidation stability are dependent on both the total concentration of the heteroatoms and the distribution of the heteroatom in various molecular forms (3). Therefore, if these heteroatoms were isolated and identified, the causes of different lubricant responses may be understood. One way to achieve this is to develop a separation method to isolate these minor species in sufficient amount for direct performance assessment in oxidation, wear, and additive response measurements using differential scanning calorimetry and thin film oxygen uptake tests (4-6).

A variety of separation schemes were reported in the literature with the purpose of studying compound types in high-boiling petroleum distillates. In 1968 Snyder and Buel (7) developed a separation scheme for separating nitrogen and oxygen compounds in petroleum. The column adsorbents used in the separation were alumina, cation exchange resin, silica gel, and charcoal. Altogether more than 20 subfractions were collected. This separation scheme, however, was relatively time-consuming. In 1972 Hirsch, et al., (8) used a dual-packed column (silica gel/alumina gel) and a gradient elution scheme to separate high boiling distillates into compound types such as saturates, monoaromatic, diaromatic and polyaromatic polar compounds. However, the polar compounds were not separated further into compound types for characterization. In 1972, Jewell, et al., (9) developed a separation scheme to isolate acid, base, neutral nitrogen, saturate, and aromatic fractions from heavy-end petroleum distillate with a variety of column chromatography methods, including ion-exchange, coordination and adsorption chromatography. Holme (13) later attributed to this method certain artifacts and molecular rearrangements of materials. In 1981, Later, et al., (10) reported the use of neutral alumina and silicic acid to separate organic compounds in synthetic fuel into chemical compound classes. Capillary column gas chromatography was used to achieve high resolution separation at the final stage. The characterization was done on the basis of the retention time of known standards and by gas chromatography/mass spectrometer analyses. This method is mainly designed for analytical characterization.

Previous separation methods (7-10) were designed mainly for analytical characterization. As a result, only major components in milligram quantities were isolated. The separation schemes were usually complex and time-consuming. In this study the effort was directed at developing a separation method which would isolate multi-gram quantities of minor components with good resolution and mass recovery.

The objective of the separation is to isolate those molecules that interact with the additives. Previous studies (3,11,12) have suggested that polar molecules with nitrogen, sulfur, or oxygen functional groups are important. Since polarity of the molecules plays a crucial role in polar species aggregation/interaction in hydrocarbon solvents (3), the separation is designed to achieve isolation of species based on polarity rather than purely functional group separation.

Several liquid chromatographic column methods were examined: an activated alumina column, clay-silica gel combination columns, an ion exchange column, and preparative High Performance Liquid Chromatography (HPLC) using various combination of columns.

Detailed discussion of the advantages and disadvantages of each of the separation techniques was presented elsewhere (11,12). The difficulty of using liquid chromatography for multi-gram sample separation is the long period of time (3-4 weeks) required to separate one oil into its compound classes. During this period, undesirable oxidation of the base oil constituents may occur. Therefore, a rapid high pressure liquid chromatographic method is required. The ion-exchange chromatographic method reported by Jewell, et al., (9) has also been evaluated. Holme's finding that some artifacts and molecular rearrangements of materials separated by this method may occur was confirmed (13). The method was not studied further.

The separation scheme finally selected uses a high performance preparative liquid chromatographic apparatus and consists of three stages: (1) a clay column to separate the oil into polar and saturate/aromatic fractions, (2) a silica-gel/activated alumina combination column to separate the saturate/aromatic fraction into its respective fractions, and (3) a neutral alumina column to separate the polar fractions further into four major subfractions designated as P-2, P-3, P-5, and P-6. The first two stages are the separation of the base oil into major constituents by functional groups and the last stage is the separation of the polar heteroatom polars into components of varying polarities. The detailed experimental procedure for the first two stages, the separation of the base oil into major constituents by functional groups, has been reported earlier (12).

2. Experimental

2.1 Chemicals and Instrumentation (14)

All solvents used in this study were glass distilled solvents. The clay adsorbent, attapulgus clay, conforms to ASTM D2007 clay specifications. The silica gel used was Davidson's silica gel 621 (60/200 mesh). Two types of alumina were used. For the separation of the saturates/aromatics into individual saturates and aromatics, basic alumina was used. For the separation of the polars into compound classes, neutral alumina adsorbents was used. The basic alumina adsorbent was chromatographic grade obtained from Fisher Scientific Corp. with a mesh size of 100 to 200 mesh. The neutral alumina adsorbent was Woelm's Alumina, with Activity 1 for column chromatography. The preparative High Performance Liquid Chromatography unit used was Waters Associates Model # Prep LC/System 500A. The columns were packed in our laboratory using the "tap and fill" method described previously (11).

The following instrumentation and methods were used to characterize the fractions. A Perkin-Elmer IR spectrograph (Model 283B) with data station was used to obtain IR spectrograms. For Gel Permeation Chromatography (GPC), a modular GPC unit was used. It consists of an LDC Constametric Pump (Model III); a Waters Differential Refractometer (Model R401); and a Rheodyne Injection Valve (Model 7125) with a 2 ml sample loop. A series of five ultramicro Styragel columns (30 cm x 4.5 mm) from Waters Associates was used to provide the separation. The columns were placed in the following series: two columns of 60 Å pore size, one each of 10^3, 10^4, and 10^5 Å pore size. An HPLC grade of tetrahydrofuran was used throughout the GPC experiments. The samples were dissolved in tetrahydrofuran before the injection.

2.2 Lubricating Base Oil Samples

Three conventional base oils were used for this study. They are of different viscosities and represent typical base oils used in the production of engine lubricants. Table 1 lists the physical properties of these oils. The 150N and 600N base oils were obtained as different distillates from the same source of crude oil. The 300N base oil came from a second source of crude oil.

2.3 Chromatographic Procedure

The separation scheme developed is shown in Figure 1. The process is divided into three steps: (1) the polar fraction is separated from the base oil on an attapulgus clay column, which separates the base oil into a polar fraction and a saturate/aromatic hydrocarbon fraction; (2) the saturate/aromatic hydrocarbon fraction is then separated into pure saturate and aromatic hydrocarbon fractions on a dual packed alumina/silica gel column; and (3) the polar fraction is further separated on a neutral alumina

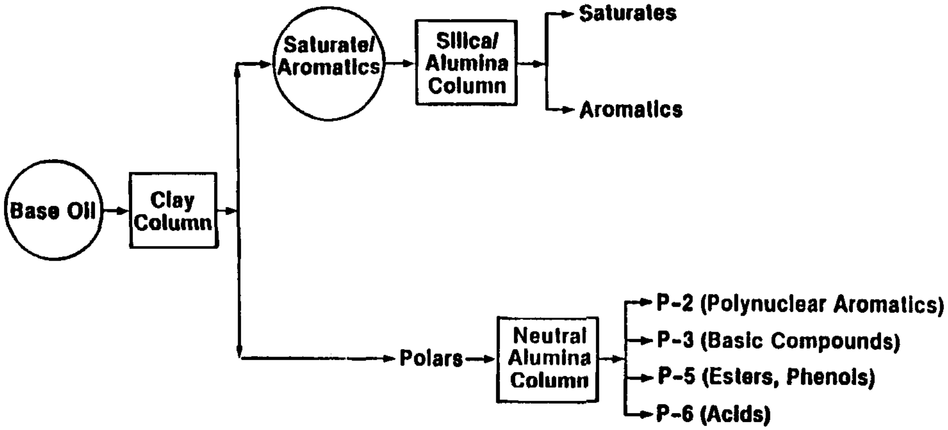

Figure 1. Separation Scheme of the Base Oil into Fractions and Compound Classes

Table 1

Chemical and Physical Properties of the Base Oils

	150N Mid-East	300N Mid-East	600N Mid-East
Kinematic Viscosity 40°C	30.25	53.16	107.65
Kinematic Viscosity 100°C	5.23	7.48	11.53
Refractive Index (n_D20)	1.4819	1.4814	1.4904
Density (gm/cm^{-3})	0.86990	0.87151	0.88749
Pour Point (°C)	-15	- 7	-10
Flash Point (°C)	235	241	244
Sulfur (wt. %)	0.49	0.36	0.67
TAN (mg KOH/g)	0	0	0.022
TBN (mg KOH/g)	----	----	0.343
Moisture (ppm)	95	139	65
Chlorine (ppm)	0.16	2.9	2.9
Bromine (ppm)	0	0	0.02
Sulfated Ash (wt. %)	0	0	0
Carbon Residue	0.03	0.03	0.16
Total Nitrogen (ppm)	42	58	114
Boiling Point, °C IBP	286	343	313
5% off	349	410	405
10% off	375	426	434
50% off	451	477	498
90% off	498	532	552
Hydrocarbon Types			
Saturates, wt. %	67.0	78.0	63.0
Aromatics, wt. %	32.5	21.4	35.3
Polars, wt. %	0.5	0.6	1.7

adsorbent column to obtain four subfractions containing mainly four different compound classes such as (1) polynuclear aromatic compounds, (2) nitrogen containing compounds, (3) esters and phenol type of compounds, and (4) carboxylic acid type of compounds.

2.3.1 Polar Fraction Separation from the Base Oil

The packed clay column was placed in a stainless steel chromatographic chamber, and the chamber was pressurized to 3.0 MPa (435 psi). After flushing the column with 1 liter of n-pentane, the sample solution (50:50 oil and pentane) was pumped onto the column at the rate of 50 mL/min. After the sample had been placed onto the column, four liters of n-pentane were used to sweep the clay column at the same flow rate. The fraction eluted by the n-pentane was designated the saturate/aromatic fraction. One liter of acetone/toluene (1 to 1 by volume) was then used to elute the polar fraction. Both fractions were evaporated to dryness using a rotary evaporator. When the fractions approached dryness, evaporation was completed under a nitrogen atmosphere. The fractions were then dried to a constant weight and their weights recorded. To determine mass balance, the sample at the detector outlet of the instrument was also collected and weighed.

2.3.2 Separation of the Saturate/Aromatic Fraction

After flushing the preparative unit with one liter of n-pentane, a freshly packed column containing alumina and silica gel was oriented in the chamber so the eluent first passed through the alumina, then through the silica gel. Approximately 75 g of the saturate/aromatic fraction obtained from the first separation was dissolved in 500 mL of n-pentane. This solution was pumped onto the column. An additional 1000 mL of n-pentane was pumped through the column to elute the fractions. The first 500 mL of eluent collected was designated the saturate fraction. After the elution with n-pentane, one liter of methylene chloride in toluene (50 %), followed by one liter of 10 % ethanol in tetrahydrofuran, were eluted through the column. The fractions were again evaporated to dryness on a Rotavap under nitrogen atmosphere. The final two elution volumes were combined for the aromatic fraction as shown in Figure 1.

2.3.3 Separation of the Polar Fraction on Neutral Alumina Column

A preparative HPLC method based on the neutral alumina column method was developed to separate the components in the polar fraction according to their polarity. The separation scheme is shown schematically in Figure 1. The procedure is described below.

> About 770 grams of neutral alumina was used to pack a column 33 cm long by 5 cm I.D. The packed column was placed in the chromatographic chamber of the preparative HPLC unit. After the chamber had been radially compressed to 3.0 MPa (435 psi), 100 mL of n-hexane was pumped onto the column. Then a sample of 5 g of polar fraction dissolved in 100 m of n-hexane was pumped onto the column at the rate of 50 mL/min. After the sample has been pumped onto the column, 400 mL of n-hexane was pumped through at the same rate. One liter of toluene followed. After the toluene, the following solvent systems were sequentially pumped onto the column at the 50 mL/min rate: one liter of 0.75 % ethanol in methylene chloride; 2 % ethanol in methylene chloride; 10 % ethanol in tetrahydrofuran; and finally two liters of methanol. A total of six subfractions were collected. The first was the 600 mL n-hexane

subfraction, designated the P-1 subfraction. This subfraction was found to contain only an insignificant quantity of saturate compounds and therefore was not studied. The second subfraction, designated P-2, was the one liter of toluene eluent. The third and fourth were the two methylene chloride subfractions, each one liter containing respectively, 0.75 % and 2 % ethanol. These two subfractions were combined to produce the P-3 subfraction. One liter of 10 % ethanol in tetrahydrofuran was collected as the P-5 subfraction. The remaining 1.5 liters of methanol were collected as the P-6 subfraction. All five subfractions were separately evaporated to dryness using a Rotavap.

When the fraction approached dryness, evaporation was completed under a nitrogen atmosphere. The fractions were dried to a constant weight and their weights recorded. To determine mass balance, the sample from the detector was also collected, evaporated, and weighed.

Three base oils of 150N, 300N, and 600N from mid-eastern crude were separated using the HPLC method described above. The separated saturated, aromatic, polar and polar subfractions were then characterized. Chemical characterization of these fractions is described below.

3. *Analytical Characterization of Fractions*

The weight percent data of each fraction of the original base oil are shown in Table 2. It can be seen that the polar molecules generally constitute less than one percent of the base oils, yet they are found to exert significant influence on oxidation stability and friction performance of the base oils (15).

Table 2

Weight Percentage Distribution of Three Principle Fractions and of Polar Subfractions

Oil Sample	Saturates	Aromatics	Polars	Polar Subfractions P2	P3	P5	P6
150N	65.8	32.8	0.32	0.04	0.14	0.09	0.03
300N	74.8	24.5	0.40	0.08	0.08	0.19	0.02
600N	64.5	34.5	0.80	0.17	0.45	0.04	0.01

Each major fraction and compound class was characterized chemically by analytical methods such as IR, mass spectroscopy, and gel permeation chromatography. In addition to analytical characterization, performance evaluation tests were performed on these fraction and compound classes. The results of the performance evaluation tests are being processed for later publication (15).

3.1 Physical Properties Characterization

The physical properties of the separated saturates and aromatics of the three base oils are shown in Table 3. As the viscosities of the base oils increase from 150N to 600N, the average molecular weights of the oils and fractions, as well as the molecular weight distributions, shift to the higher values. The average molecular weight of the saturates and aromatics derived from the viscosity data shown in Table 3 reflect this trend.

For hydrocarbons, the molecular structures are reflected by the change in refractive index (RI). Generally for petroleum products of equivalent molecular weight, the RI of paraffins have relatively low RI

Table 3

Physical Properties of the Base Oils and the Base Oil Fractions

	Viscosity cSt 40°C	Viscosity cSt 100°C	Viscosity Index	Avg. Molecular Weight	Refractive Index
150N					
Base Oil	30.3	5.2	103	402	1.4830
Saturate	25.1	4.8	116	404	1.4693
Aromatic	60.0	7.0	58	396	1.5134
300N					
Base Oil	53.2	7.5	102	459	1.4816
Saturate	46.1	7.0	109	457	1.4749
Aromatic	162.4	11.7	34	436	1.5214
600N					
Base Oil	107.7	11.5	93	520	1.4907
Saturate	73.4	9.7	109	520	1.4769
Aromatic	95.5	11.0	99	524	1.5039

(~ 0.14) and the RI of the aromatics have relative high RI (~ 1.5) (16). Compared with the base oils and the aromatics, the decrease in RI of the saturates of the three oils indicates that the saturates are predominantly paraffins. For the aromatics, the increase in RI when compared with that of the base oils and saturates suggests the increase in the amount of phenylic ring structures in the aromatic fractions.

Measurements of viscosity index (VI) are also very important, because of the relationship between VI and compsoition (16). The VI compares the rate of change of viscosity with temperature of the sample with the rates of change of two types of oil having the highest and the lowest VI at the time (1929) when VI scale was first introduced. A standard paraffinic oil was given a VI of 100 and a standard naphthenic oil, a VI of 0. Equations were developed for the relationships of kinematic viscosities at two temperatures and the VI scale for oils with VI between 0 and 100. In 1964, ASTM adopted an extension of the tables, and an equation for oils with VI's greater than 100. The increase in VI of the saturates when compared to the base oils suggests again that the saturates are predominately paraffins. For the aromatics, the VI behave differently for each oil. For the 150N oil, the decrease in VI suggests the increase of phenylic ring structures in the aromatics as expected. In the case of the 300N aromatics, the kinematic viscosity of this fraction at 40 °C is the highest of the three base oils but the VI is the lowest of all three aromatic fractions, which suggests that the aromatic compounds in this fraction have much stronger intermolecular attraction forces. This may be due to the presence of more polar functional groups such as sulfur groups, for the 300N aromatic has the highest sulfur content (2.26 wt. %, Table 4). In the 600N aromatics, the VI of the aromatics is higher than that of the base oil. This may be due to the increases in size of the aliphatic side chains attached to the aromatic or other ring structures as the molecular weight increases. The IR spectrum of 600N aromatics (discussed in the following Section 3.2) confirms this observation. The aromatic peak at 1600 cm^{-1} is very distinct but the rest of the IR spectrum looks like the saturate fraction. This indicates there are many mixed molecular structures where the aromatic ring structures are often attached by the aliphatic chain. The polar fractions of all three base oils were dark, and viscous. Therefore, kinematic viscosities and refractive indices measurements were not made.

Sometimes the molecular weight distribution provides a key piece of information about a base oil, because the alkyl chain length or the molecular weight affects the polarity of a macromolecule. The polarity in turn may affect the performance characteristics of the macromolecule in the base oil. The molecular weight scale for the gel permeation chromatography was calibrated with polystyrene and hydrocarbon standards of known molecular

Table 4

Elemental Analyses of the Base Oils and the Base Oil Fractions

	Weight %				
150N	C	H	N	S	O
Base Oil	86.2	13.2	<0.01	0.42	<0.3
Saturate	85.9	14.0	<0.01	0.01	<0.3
Aromatic	86.7	11.8	<0.01	1.54	<0.3
Polar	82.6	11.3	1.8	2.83	1.6
300N					
Base Oil	86.2	13.2	<0.01	0.33	0.34
Saturate	86.3	13.8	<0.01	0.01	<0.3
Aromatic	86.3	11.8	<0.01	2.26	<0.3
Polar	83.2	11.5	1.4	1.68	1.5
600N					
Base Oil	86.1	13.2	0.02	0.69	<0.3
Saturate	86.4	13.5	<0.01	0.09	<0.3
Aromatic	85.9	13.0	0.01	1.24	<0.3
Polar	84.3	11.5	1.2	2.19	0.8

weights. The molecular weight profiles of the separated fractions of all three base oils are shown in Figures 2, 3, and 4. The peak of the molecular weight distribution of the saturated fraction of 150N (Figure 2) occurs at a high molecular weight than does the distribution of the 150N base oil. The distribution of the saturates of 600N (Figure 4), on the contrary, has a peak value at a lower molecular weight than does the 600N base oil. The 300N saturates (Figure 3) have the same molecular weight distribution as the 300N base oil. The molecular weight profile of the aromatics of the three base oils as shown in Figures 2, 3, and 4 indicate the presence of smaller molecules than other separated fractions. However, the polars in both 300N and 600N (Figures 3 and 4) contain higher molecular weight compounds than the 300N and 600N base oil, while the 150N polars (Figure 2) have the same molecular weight profile as the 150N base oil.

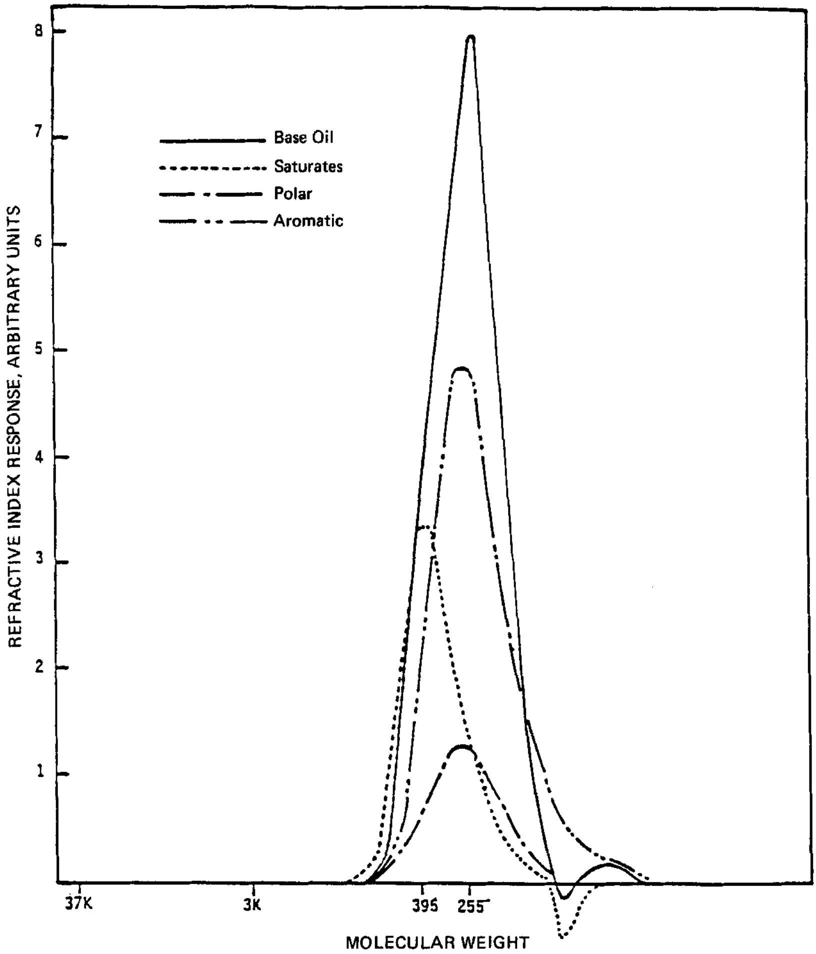

Figure 2. Molecular Weight Distribution of 150N Base Oil and Base Oil Fractions

3.2 Chemical Structural Characterization of the Fractions

The saturates, as separated, were found to be relatively free of aromatic and heteroatom compounds. The infrared spectra of the saturates (shown in Figures 5b, 6b, and 7b) showed no sign of aromatic band at 1600 cm^{-1} or the carboxyl and hydroxyl bands at 1700 and 3400 cm^{-1} regions. A

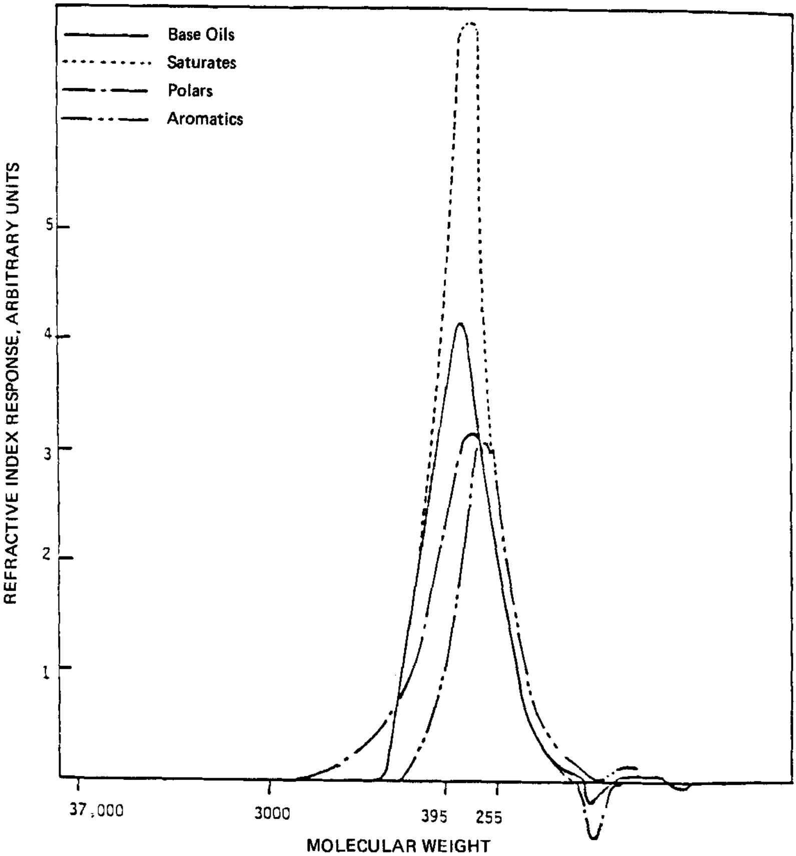

Figure 3. Molecular Weight Profile of the 300N Base Oil and its Fractions

strong methylene (CH_2) band at 720 cm^{-1} was evident in all three oils. The purity of the saturates was again confirmed by the elemental analysis results shown in Table 4. The carbon and hydrogen content of the fraction accounted for about 99.9 % of the material in all three cases, indicating the absence of no heteroatom compounds in the saturates.

For the aromatic fractions of all three base oils, the elemental analysis results (Table 4) showed a large concentration of sulfur compounds

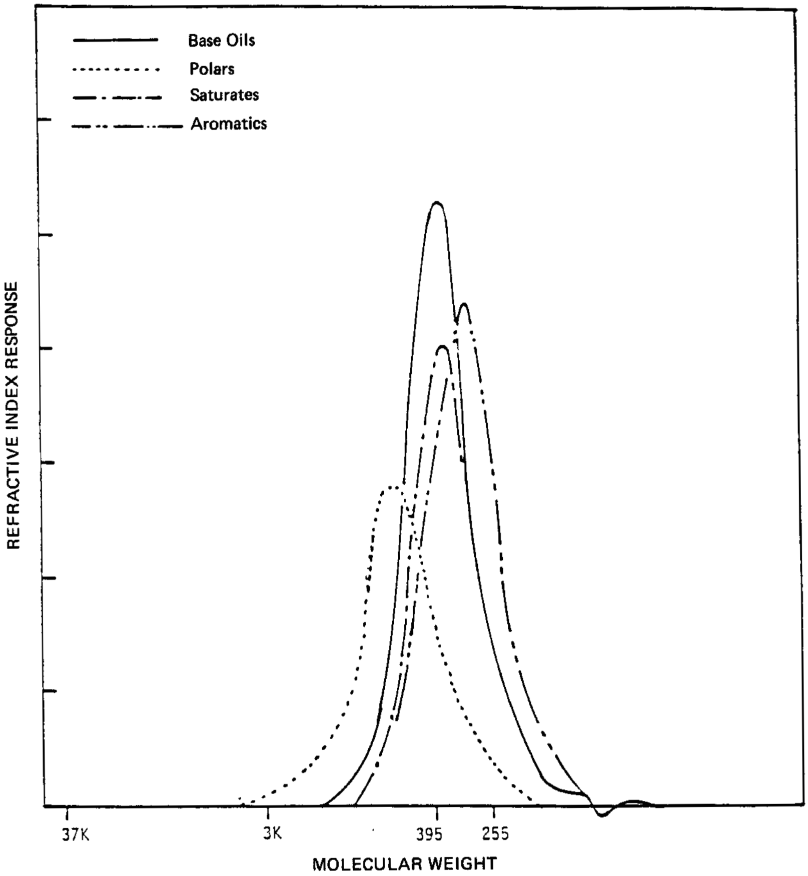

Figure 4. Molecular Weight Profile of the 600N Base Oil and its Fractions

associated with the aromatic structures. They are probably thiophenes (17). The aromatics were relatively free of nitrogen and oxygen compounds. The absence of the hydroxyl (3400 cm^{-1}) and carbonyl (1700 cm^{-1}) bands in the IR spectra (Figures 5c, 6c, and 7c) again confirmed this observation. According to elemental analysis, the polars contained large amounts of sulfur-, nitrogen-, and oxygen-containing molecules relative to other fractions (Table 4). Of the three base oils, the 600N polar fraction had the lowest nitrogen

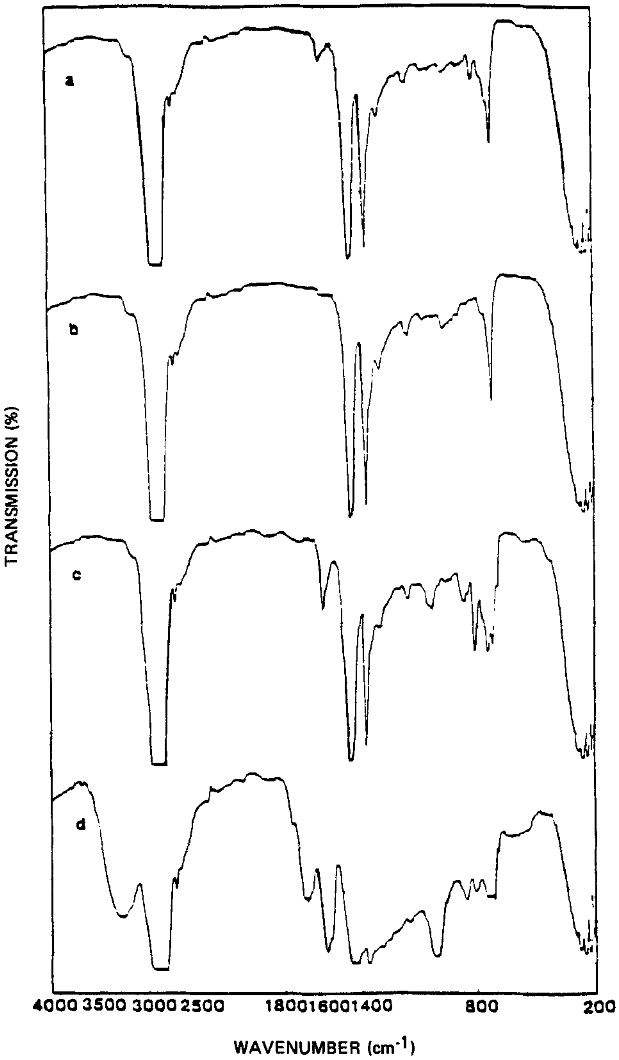

Figure 5. Infrared Spectra of Hydrocarbon Fractions of the 150N Base Oil:
a) Base Oil;
b) Saturate Fraction;
c) Aromatic Fraction;
d) Polar Fraction

and oxygen content and an intermediate sulfur content. The infrared spectra of the polars (Figures 5d, 6d, and 7d) showed the presence of very strong hydroxyl, carbonyl, aromatic, sulfur-oxygen and amide bands. The IR band at 1775 cm^{-1} (Figure 7d) was unique to the 600N polars. This may be due to the presence of γ-lactone and/or acetyl chloride. HRMS results of the three polars suggested the probable presence of nitrogen compounds as homologs of quinoline, sulfur compounds as homologs of thiophenes and oxygenated compounds such as esters, phenols and acids.

3.3 Chemical Structural Characterization of the Polar Subfractions

The polar fractions were very complex, as shown in the above chemical characterization study, so further separation was required. The separation scheme in Figure 1 was used. Four subfractions were obtained, designated P-2, P-3, P-5, and P-6. The chromatographic separation of the polar fraction was achieved on a neutral alumina column. Various molecular compounds were eluted off the column with solvents of different polarity. The P-2 subfraction was the least polar and the P-6 subfraction the most polar compounds. Each subfraction was in turn characterized by elemental analyses (Table 5), high resolution mass spectrometry (HRMS), Infrared Spectrometry (IR) and gel permeation chromatography (GPC).

3.3.1 150N Polar Subfractions

Molecular weight distribution profiles of the polar subfractions in the 150N polars are shown in Figure 8. The P-6 fraction contains compounds with the highest molecular weight. Elemental analysis results shown in Table 5 suggest the P-2 subfraction contains the least amount of oxygen while the P-6 subfraction contains the most. Sulfur and

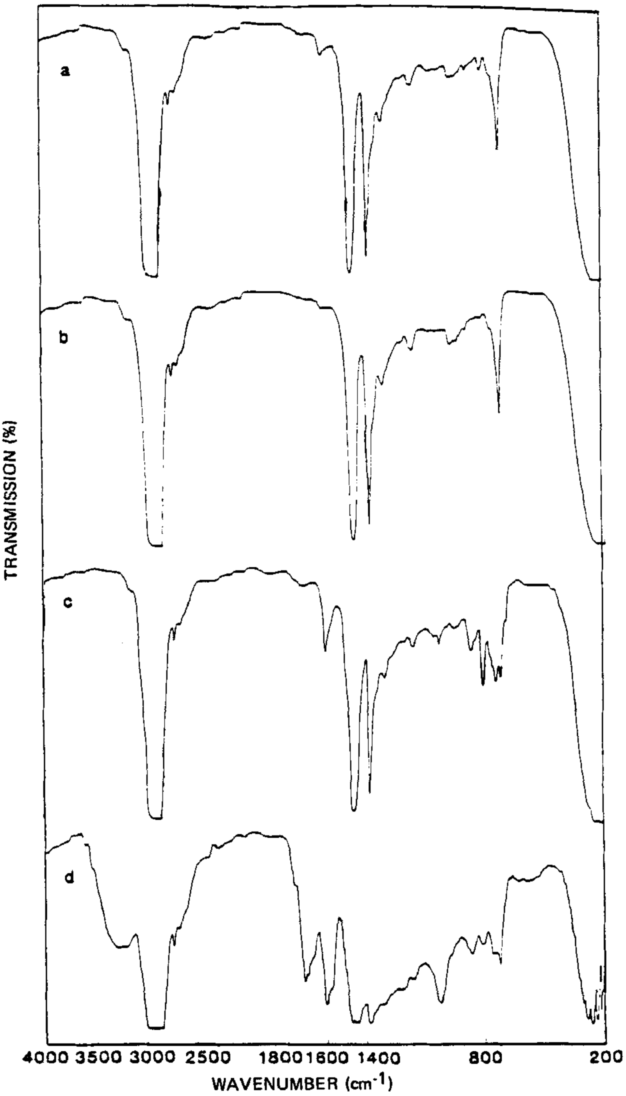

Figure 6. Infrared Spectra of Hydrocarbon Fractions of the 300N Base Oil:
a) Base Oil;
b) Saturate Fraction;
c) Aromatic Fraction;
d) Polar Fraction

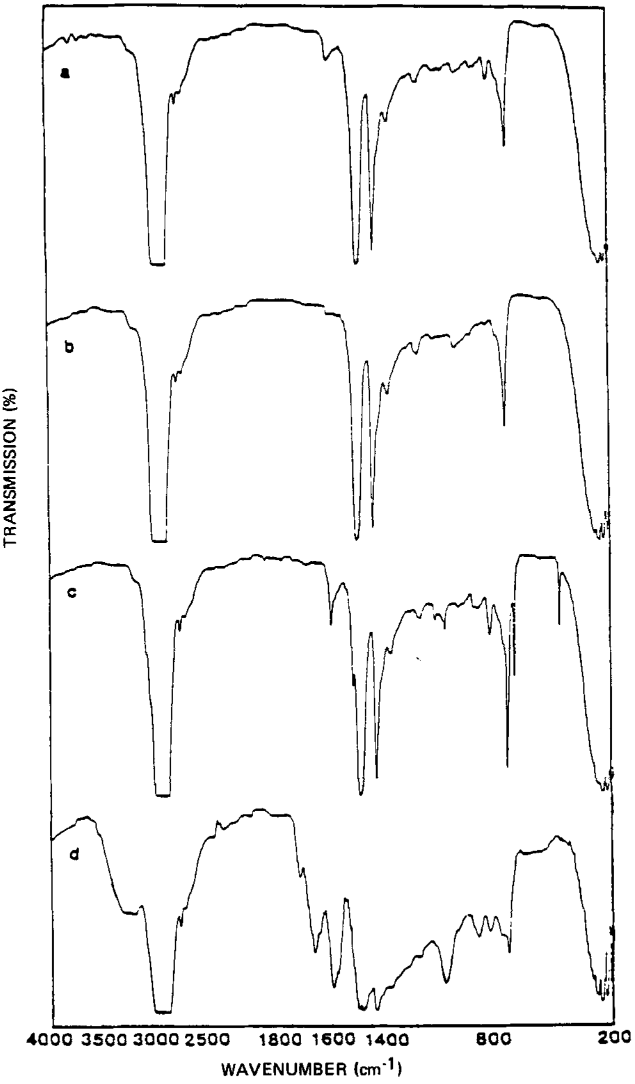

Figure 7. Infrared Spectra of Hydrocarbons Fractions of 600N Base Oil:
a) Base Oil;
b) Saturate Fraction;
c) Aromatic Fraction;
d) Polar Fraction

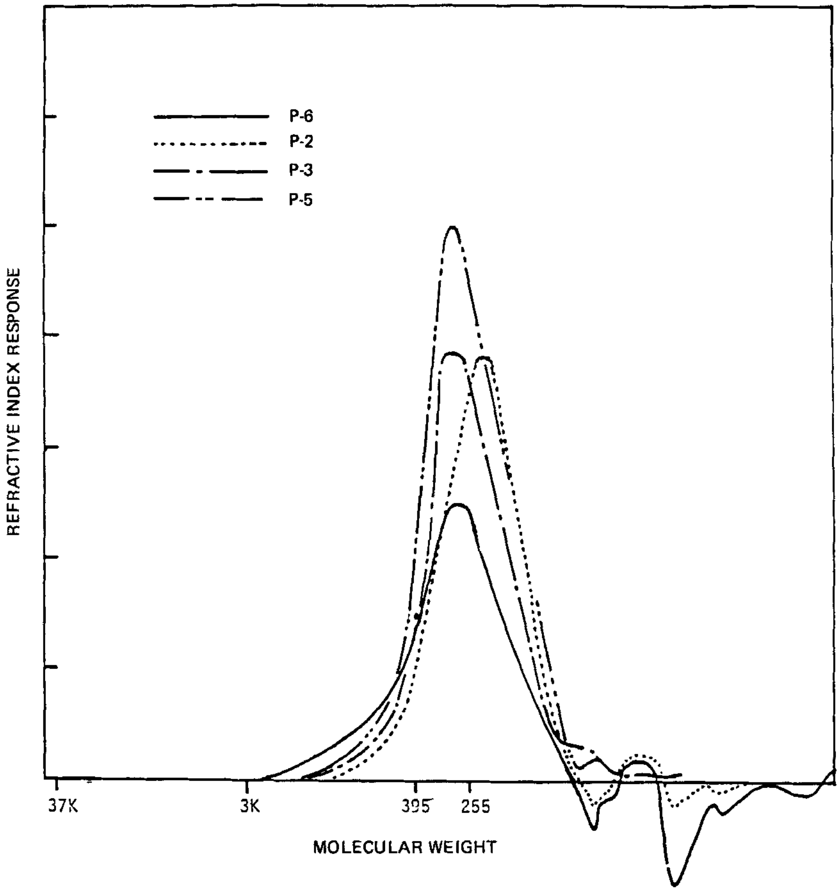

Figure 8. Molecular Weight Distribution of the Polar Subfractions of the 150N Base Oil

nitrogen molecules are distributed evenly among the four subfractions. Infrared spectra shown in Figure 9 suggests that the P-2 subfraction contains predominantly aromatic compounds(1600 cm^{-1}); the P-3 and P-5 subfractions contain amides (3300 and 1690 cm^{-1}), sulfoxides (1030 cm^{-1}), and esters (1700 cm^{-1}); and the P-6 subfraction contains phenols (3350 cm^{-1}), and esters (1735 cm^{-1}). High resolution mass spectroscopy data indicate the probable presence of the following compounds in each subfraction:

1. P-2, aromatic compounds;
2. P-3, thiophenes, amides, and sulfoxides;
3. P-5, carbazoles, quinolines, amides, and sulfoxides; and
4. P-6, phenols, esters, acids, and sulfoxides.

3.3.2 300N Polar Subfractions

The polarity of compounds in the 300N polar subfractions are in the increasing order of the P-2, P-3, P-5, and P-6. Elemental analysis results shown in Table 5 show that the P-2 subfraction contains the lowest amount of oxygen compounds while the P-6 subfraction has the highest

Table 5

Elemental Analysis of the Polars and the Polar Subfractions

	Weight %				
150N	C	H	N	S	O
Polar	82.6	11.3	1.8	2.83	1.6
P-2	84.1	11.2	1.6	2.71	0.7
P-3	82.4	11.4	1.6	2.66	2.1
P-5	81.0	11.3	1.2	3.52	3.2
P-6	75.3	10.0	1.0	3.11	7.3
300N					
Polar	83.2	11.5	1.4	1.68	1.5
P-2	85.0	11.4	<0.01	1.60	0.4
P-3	83.9	10.9	1.9	2.28	1.2
P-5	83.7	11.5	1.3	1.65	1.8
P-6	82.5	12.7	0.2	0.47	4.3
600N					
Polar	84.3	11.5	1.2	2.19	0.8
P-2	84.5	11.6	1.1	2.53	0.6
P-3	84.0	11.7	1.3	1.78	1.1
P-5	82.1	11.4	0.8	2.53	2.9
P-6	67.9	9.8	0.8	1.21	17.0

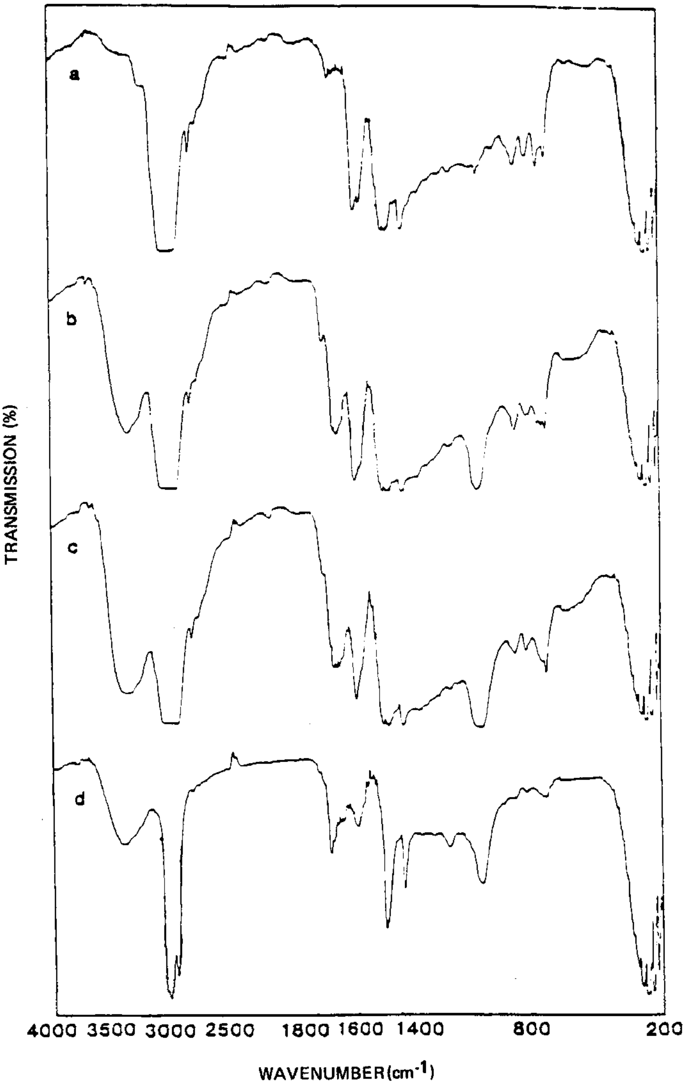

Figure 9. Infrared Spectra of Polar Subfractions of the 150N Base Oils

a) P-2 Subfraction;
b) P-3 Subfraction;
c) P-5 Subfraction;
d) P-6 Subfraction

oxygen content. Molecular weight distributions shown in Figure 10 suggest P-2, P-3, and P-6 subfractions contain relatively low molecular weight compounds while P-5 contains the highest molecular weight compounds. The infrared spectra in Figure 11 show the variation of the wavenumber of the carbonyl peaks in each subfraction. The carbon-oxygen bond in P-2 is possibly due to esters (1800 cm^{-1}), while in P-3 (1690 & 1710 cm^{-1}) and P-5 (1700 cm^{-1}) it is due to aromatic carboxylic acids and amides. The carbon-oxygen bond in P-6 is due to esters and acids. High resolution mass spectroscopy data suggest the presence of the following compounds:

1. P-2, aromatic hydrocarbons, phthalates, quinolines,carbazoles;
2. P-3, phthalates, quinolines, carbazoles;
3. P-5, phthalates, phenol, quinolines, carbazoles, indoles; and
4. P-6, phenols and carboxylic acids.

3.3.3 600N Polar Subfractions

Elemental analysis data of the four polar subfractions of the 600N polars (Table 5) demonstrate that more sulfur compounds are present in the P-2 and P-5 subfractions, but nitrogen compounds are evenly distributed among the subfractions. However, oxygen-containing compounds are concentrated in the P-6 subfraction (to as high as 17 %). The molecular weight distribution of the subfractions shown in Figure 12 shows that the P-6 subfraction contains the lowest amount of high molecular weight molecules among the subfractions. The carbon-oxygen bond in the infrared spectra (Figure 13) at 1775 cm^{-1} in P-3 and P-6 may be due to the presence of cyclic structures (such as γ-lactones) or acetyl chloride. The oxygen-hydrogen bond at 3300 cm^{-1} is observed in P-3, P-5, and P-6, but is absent in P-2. The

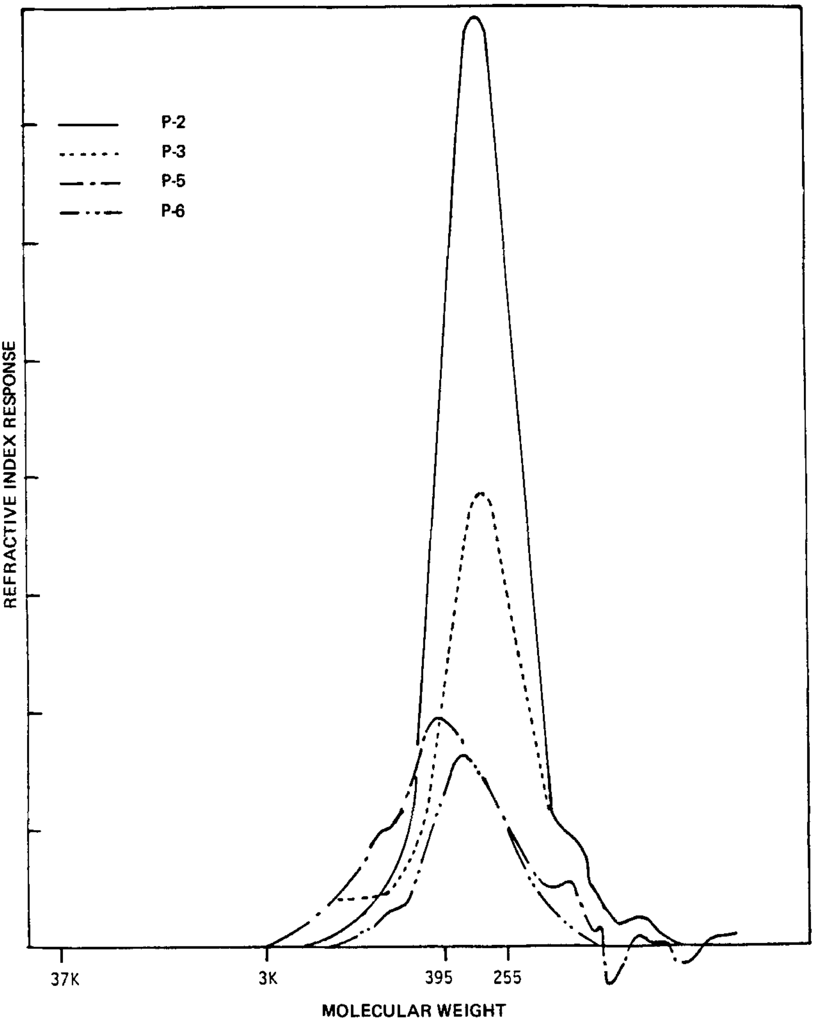

Figure 10. Molecular Weight Profile of the Polar Subfractions of the 300N Oil Base

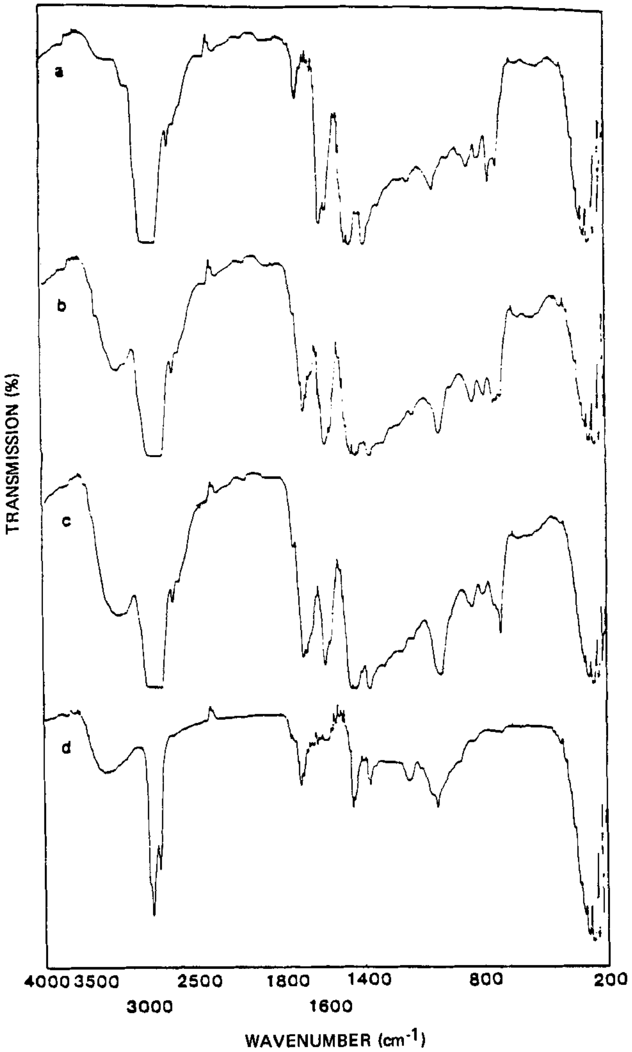

Figure 11. Infrared Spectra of Polar Subfractions of the 300N Base Oil
a) P-2 Subfraction;
b) P-3 Subfraction;
c) P-5 Subfraction;
d) P-6 Subfraction

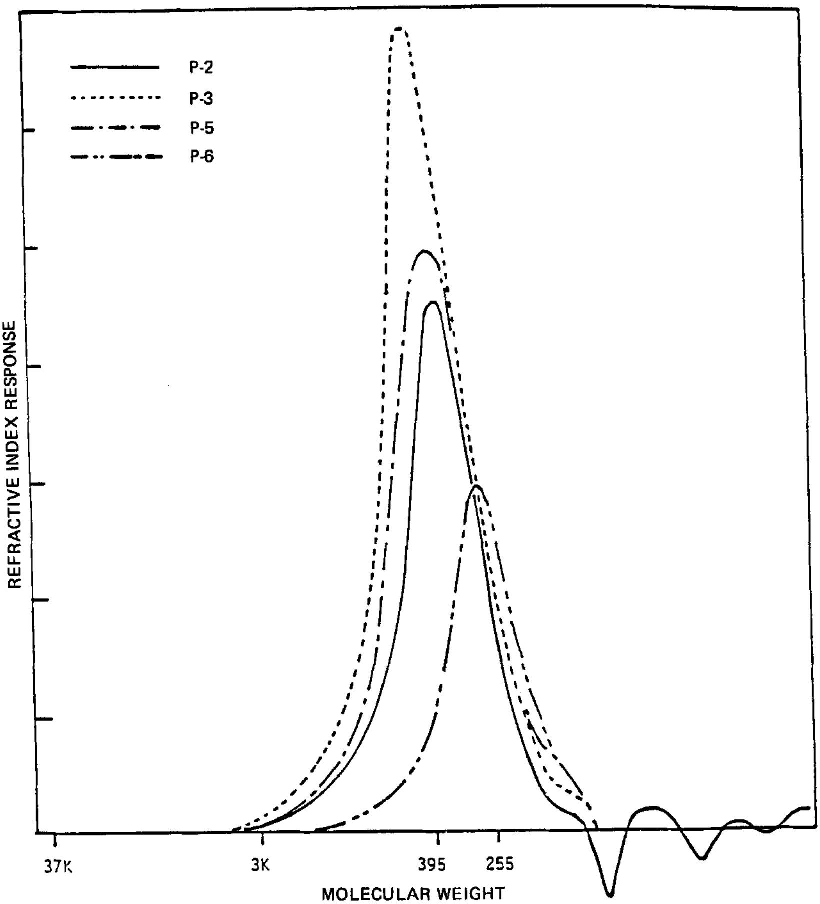

Figure 12. Molecular Weight Profile of the Polar Subfractions of the 600N Base Oil

carbonyl bond attributable to ester linkage at 1735 cm^{-1} is observed in all subfractions. The sulfur-oxygen bond at 1030 cm^{-1} is observed in P-3, P-5, and P-6. High resolution mass spectroscopy results suggest the presence of the following structures.

1. P-2, aromatic hydrocarbons, phthalates, quinolines, carbazoles, and thiophenes.

2. P-3, phthalates, quinolines, carbazoles, indoles, and thiophenes.
3. P-5, phthalates, phenols, carboxylic acids, indoles, quinolines, and carbazoles.
4. P-6, phenols, carboxylic acids, phthalates, and thiophenes.

3.4 Summary of Chemical Characterization

The detailed analytical characterization of each individual fraction and subfraction has been described and compared within each base oil. The effectiveness and the extent of the separation of the base oils into narrow compound classes have been demonstrated. The data are summarized in Table 6 for easy comparison of the separated compound classes of the three base oils. The 150N and the 600N were refined from the same crude source. The 300N was refined from another crude source in the Middle East. Overall, there are similarities among the separated fractions of these three oils, showing the effectiveness of the separation method. There are also differences among the fractions, suggesting different initial compositions, hence different compounds in the fractions.

Table 6 lists the most probable molecular structures present in each fraction and subfractions, based on infrared spectroscopy, elemental analysis and high resolution mass spectroscopy. Molecular information in C_{20} plus compounds is usually diffused and complex. Definitive structural determination will require further separations.

Overall, the separation of the base oils into saturates, aromatics, and polars is very clean. The separation of the polars into molecular compounds classes of varying polarity necessitates overlapping molecular

Table 6

Comparison of Base Oil Fractions in Terms of Elemental Analysis and Molecular Structrues

		Induction		
Saturate	N	S	O	Most Probable Molecular Structures
150N	<0.01	0.01	<0.3	paraffins, naphthenes
300N	<0.01	0.01	<0.3	paraffins, naphthenes
600N	<0.01	0.09	<0.3	paraffins, naphthenes, alkyl sulfides
Aromatic				
150N	<0.01	1.54	<0.3	mono-, di-aromatics, thiophenes
300N	<0.01	2.26	<0.3	mono-, di-aromatics, thiophenes
600N	<0.01	1.24	<0.3	alklated aromatics, thiophenes
Polar				
150N	1.8	2.83	1.6	heteroatom compounds
300N	1.4	1.68	1.5	heteroatom compounds
600N	1.2	2.19	0.8	heteroatom compounds
P-2				
150N	1.6	2.71	0.7	thiophenes, amides, polynuclear aromatics
300N	<0.01	1.60	0.4	phthalates, indoles, mono- and polynuclear aromatics
600N	1.1	2.53	0.6	phthalates, carbazoles, thiophenes, polyaromatics
P-3				
150N	1.6	2.66	2.1	quinolines, amides, sulfoxides, thiophenes
300N	1.9	2.28	1.2	quinolines, carbazoles, carboxylic acids, thiophenes
600N	1.3	1.78	1.1	phthalates, carbazoles, thiophenes, polyaromatics
P-5				
150N	1.2	3.52	3.2	phenols, carboxylic acids, quinolines, indoles, thiophenes
300N	1.3	1.65	1.8	phthalates, carboxylic acids, phenols
600N	0.8	2.53	2.9	esters, indoles, carboxylic acids
P-6				
150N	1.0	3.11	7.3	phenolic, alcohols, sulfoxides, thiophenes
300N	0.2	0.47	4.3	phenols, carboxylic acids
600N	0.8	1.21	17.0	esters, acids, sulfoxides (lactone or chloride)

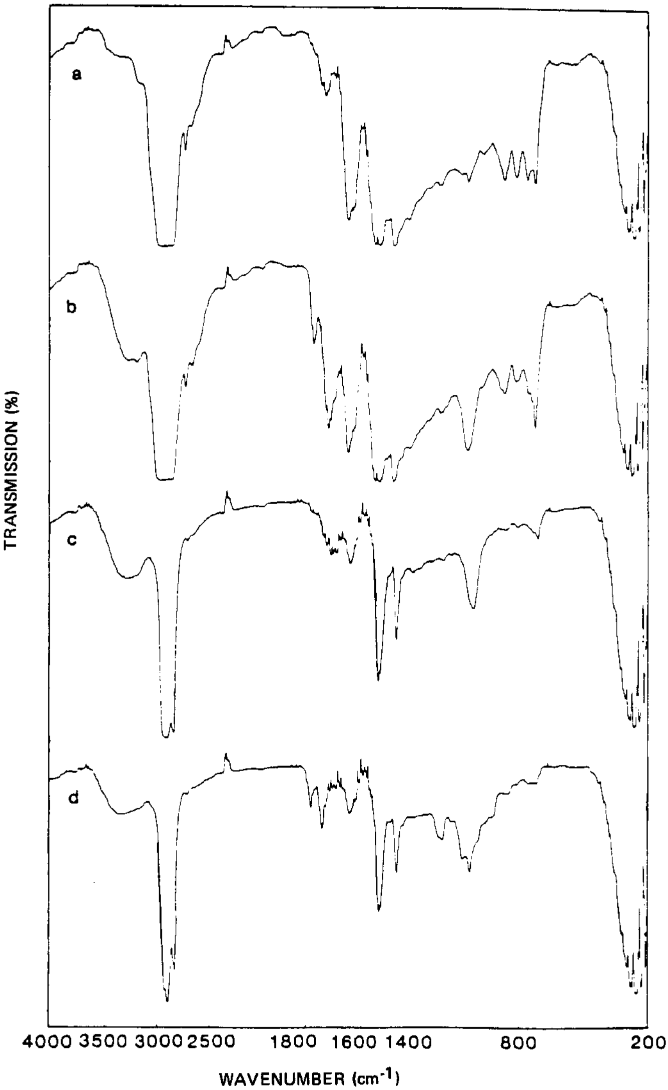

Figure 13. Infrared Spectra of Polar Subfractions of 600N Base Oil
a) P-2 Subfraction;
b) P-3 Subfraction;
c) P-5 Subfraction;
d) P-6 Subfraction

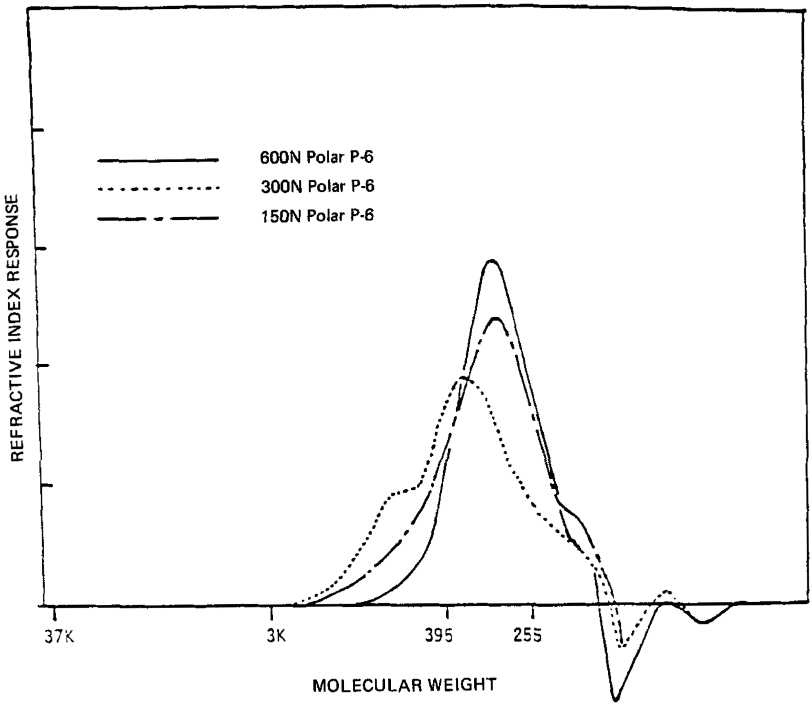

Figure 14. Comparison of the Molecular Weight Profiles of P-6 Subfractions of Base Oils

structures (but different polarity). One of the key pieces of information is the molecular weight distribution since frequently the alkyl chain length, or the molecular weight affects the polarity of a macromolecule. Generally, the molecular weight increases from the 150N fractions to the 600N fractions, but there are a few exceptions in the P-6 polar subfractions, as shown in Figure 14.

In the polar subfraction separation, the data in Table 6 suggests that the differences between the P-2 and P-6 subfraction are the most. P-2 fractions are generally mostly polynuclear aromatics but contain few or no oxygenated compounds. P-6 fractions are mostly oxygenated compounds with few aromatics. The P-3 and P-5 fractions have overlapping structures between these two extremes.

4. Summary and Conclusion

A preparative liquid chromatographic separation scheme to characterize minor constituents of base oils has been developed. The separation scheme separates lubricating base oil into compounds according to their polarity, but the chemical analyses indicate that to a limited extent; some separation of molecular compound classes also occurred. Multigram quantities of minor components are isolated, characterized, and tested with performance evaluations. The separated fractions of the three base oils of different viscosities show different chemical characteristics, as well as interesting performance characteristics (15). Extensive performance evaluation of the separated molecular compound classes has confirmed the success of the separation, i.e., each of the compound classes has its characteristic oxidation and wear performance and interaction patterns with additives. Detailed discussion of the performance results will be presented elsewhere. Therefore, the preparative separation method has successfully isolated the minor components which can affect the performance of a lubricating base oil.

This study has illustrated a rapid, high volume characterization technique for complex hydrocarbon mixtures in the lubricating base oils. With the same approach, this characterization technique can be applied to toxic industrial waste, chemical feed stocks, environmental research, and other areas. The preparative HPLC technique has been developed as a direct means of characterization technique coupling not only to analytical tools but also to material performance tests.

Acknowledgement

The geneous support of the Energy Conversion and Utilization Program (ECUT), Department of Energy is gratefully acknowledged.

References

1. Sands, T.P., "Comments on Additive Response to Different Base Oils," NBS SP 488, National Bureau of Standards, Gaithersburg, MD, August 1977.

2. ASTM D2007, 1985 Annual Book of ASTM Standards, "Characteristic Groups in Rubber Extender and Processing Oils by Clay-Gel Adsorption Chromatographic Method;" ASTM, Philadelphia, PA, V.05-02, 155-163 (1985).

3. Hsu, S.M., Pei, P., Ku, C.S., Lin, R.S., and Hsu, S.T., "Mechanisms of Additive Effectiveness," 5th International Colloquium on Additives for Lubricants and Operational Fluids, Federal Republic of Germany, January 1986. Proceedings of the colloquium are in press.

4. Gates, R.S. and Hsu, S.M., "Development of An Oxidation-Wear Coupled Test for the Evaluation of Lubricants," Lubrication Engineering, 40, 1, 27-33 (1984).

5. Hsu, S.M., Cummings, A.L., and Clark, D.B., "Evaluation of Automotive Crankcase Lubricants by Differential Scanning Calorimetry," SAE SP 526, 127-138, Society of Automotive Engineers, Warrendale, PA, October 1982.

6. Ku, C.S. and Hsu, S.M., "A Thin Film Oxygen Uptake Test for the Evaluation of Automotive Crankcase Lubricants," Lubrication Engineering, 40, 2, 75-83 (1984).

7. Snyder, L.R., Buell, B.E., "Nitrogen and Oxygen Compound Types in Petroleum, A General Separation Scheme", Anal. Chem. 40, 1295, 1968.

8. Hirsch, D.E., Hopkins, R.L., Coleman, H.J., Cotton, F.O. and Thompson, C.J., "Separation of High-Boiling Petroleum Distillates Using Gradient Elution Through Dual-Packed (Silica Gel-Alumina Gel) Adsorption Columns," Anal. Chem. 44, 915, 1972.

9. Jewell, D.M., Weber, J.H., Bunger, J.W., Plancher, H., and Latham, D.R., "Ion-Exchange, Coordination and Adsorption Chromatographic Separation of Heavy-End Petroleum Distillate," Anal. Chem., 44, 1391, 1972.

10. Later, D.W., Lee, M.L., Bartle, K.D., Kong, R.C. and Vassllaros, D.L., "Chemical Class Separation and Characterization of Organic Compounds in Synthetic Fuels", Anal Chem. 53, 1612-1620, 1981.

11. Hsu, S.M., Pei, P.T. and Gates, R.S., "Friction and Wear Characteristics of Molecular Compound Classes from Lubricating Base Oils", Part 1, Separation and Chemical Characterization," NBSIR 84-2821, National Bureau of Standards, Gaithersburg, MD, February 1984.

12. Pei, P., Britton, J. Jr., and Hsu, S.M., "Hydrocarbon Type Separation of Lubricating Base Oil in Multigram Quantity by Preparative HPLC," J. Liquid Chromatography, 6 (4), 627-645, 1983.

13. Holmes, S.A., "Artifacts from Ion-Exchange and Coordination-Complex Chromatography: Effect Upon Characterization of Nitrogen Compounds in Shale Oil", Paper #172, 1982 Pittsburgh Conference, Atlantic City, NJ, March 1982.

14. Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards nor does it imply that materials or equipment identified are necessarily the best available for the purpose.

15. Hsu, S.M., et al., "Friction and Wear Characteristics of Molecular Compound Classes from Lubricating Base Oils" Part 2, Performance Characterization. National Bureau of Standards, Gaithersburg, MD. In preparation.

16. Weeks, S. and Hsu, S.M., "Evaluation of Test Method for Physical Properties of Re-refined Lubricating Base Oils," National Bureau of Standards (U.S.), Special Publication 674, 109, 1984.

17. Snyder, L. R., Sounders, D. L., "Chromatography in Petroleum Analysis," Altgelt, K. H., and Gouw, T. H., Eds., Marcel Dekker, New York, NY, 1979, Chapter 10.