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SYNTHETIC OIL BASE STOCK AND ITS IMPACT ON NEW AND USED ENGINE OIL ANALYSES

INTERIM REPORT
AFLRL No. 100

By

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During the past decade synthetic oils have been introduced into engine test programs in the U.S. Army. These test programs have ranged from evaluation of vehicle fleet operation to engine test development for arctic engine oil specifications. Both performance and physico-chemical properties have been evaluated including the development of analytical schemes to identify lubricant base stock composition. It has been our experience that, in many respects, routine oil analyses have not been influenced by the nature of a lubricant's base stock (as to whether it is mineral oil or synthetic oil base stock). However, some laboratory tests have been rendered useless while others have been enhanced with respect to their applicability to synthetic-based lubricants

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as opposed to mineral oil-based lubricants. This report has as its objective to place in perspective the Army's experience primarily with ground vehicle engine lubricants so as to illustrate the impact synthetic and hybrid oil base stocks have had in the analysis of new and used engine oils.

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

I. INTRODUCTION AND BACKGROUND

The U.S. Government operates the largest single ground-vehicle fleet in the world, including materials handling and automotive support equipment. The U.S. Army has the custodial responsibility for the principal automotive engine lubricant specifications(1,2)* under which the Federal Government purchases engine oils for its civilian and military ground vehicle fleet. In addition to this enormous engine oil responsibility, the Army also develops and maintains specifications for the procurement of gear oils(3), arctic engine oils(4,5), and hydraulic oils(6,7) for use in DOD ground-powered military equipment, and in Army aircraft systems. Knowledge of lubricant nature, product quality, basic composition, and performance characteristics is essential for the Army to write the most meaningful specifications for government product procurement purposes. Product quality control, quality assurance, and used-lubricant analyses are three of the critical lubricant functional aspects in which state-of-the-art chemical analysis must be applied if the best interests of the government as a *lubricant end-user* are to be satisfied.

Many routine chemical analyses developed in industry and government are directly applicable to certain of the lubricants the government uses in *noncombat* ground-vehicle service or support equipment (i.e., purchased under specification MIL-L-46152(2)). However, the requirements and needs of the Army and DOD ground-powered combat/tactical fleet and support equipment are *entirely different* from those in the civilian and noncombat sector. For example, one specification(1) lubricant is designed to satisfy a wide variety of engine types operating under varying conditions, unique to the military. Specific severe operating conditions include: *frequent long* periods of engine idling, short vehicle trips, or engine shutdown; unintentional or inadvertent use of wrong specification products; mixing of several different suppliers' products and viscosity grades (qualified under the *same* specification) in many engines, such that when there is an unusual problem, it becomes difficult to identify the specific lubricant(s) being used; and the widest environmental temperature and climatic variations, including *frequent trips* into sandy, dusty and snowy areas.

Until the early 1960's, the U.S. Army procured and used relatively simple lubricants compared with those materials being offered as a result of the modern lubricant formulation technology of the 1970's. It was common for the Army to purchase single grade, *conventionally formulated* mineral oils of variable quality level, depending on the performance requirements of the equipment in which the lubricants were to be used.

In the mid-1960's the Army recognized the benefits of using multiviscosity grade engine oils and quickly adapted these oils(8) for noncombat-type vehicles (i.e., GSA Interagency motor pool sedans and pickup trucks; U.S. Postal Service trucks and sedans; and DOD commercial trucks and sedans). These multigrade oils, with their high molecular weight polymers added for high-temperature thickening purposes, introduced the first of a series of complex problems to the government. This was due to the nature of the polymeric thickening material (generally referred to as a *viscosity index improver*). While industry and the civilian sector had been using these multigraded oils for a *decade* or more, the fact

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*Superscript numbers in parentheses refer to references at the end of this report.

remained that the government was only beginning to purchase these types of oils in the mid-1960's. Viscosity index improvers are high molecular weight straight-chain/cross-linked polymeric materials which undergo varying degrees of shear degradation in service and lose some (or all) of the viscosity improvement capability they are intended to impart to the finished lubricant. From an analytical standpoint, these materials present problems of identification (i.e., polar and nonpolar blends) and separation, because of the critical solubility of the polymeric improvers, particularly if the lubricant is a used sample and possibly was mixed with another supplier's oil in the field.

Lubricant formulation technology has continued to advance (and become more complicated) since the mid-1960's, at which time the Army turned to synthetic-based arctic engine oils. The difficult requirement of low-temperature fluidity coupled with good high-temperature performance in modern high-output diesel engines necessitated the development(9,10) of a new arctic engine oil specification(4,5) designed around the use of synthetic lubricants as *problem solvers*. More recently, the 1973 Middle East oil embargo and the consequent advent of so-called *long-life* or *extended drain* and *no-drain* synthetic crankcase lubricants(11-14) has required the Army to intensify chemical analysis research and development for the purposes of lubricant characterization.

The properties and physical performance characteristics of many synthetic and mineral-based lubricants have been presented and discussed.(15-17) It is the intention of the current report to place in perspective a part of the Army's experience primarily with ground vehicle engine lubricants so as to illustrate the *impact* synthetic and hybrid oil base stock has had on the analysis of new and used engine oils.

II. SPECTROMETRIC OIL ANALYSIS PROGRAM

A. Fleet Tests

During the mid-1960's, interest in the analysis of used engine oils from military ground equipment (that is, trucks, tanks, generators, and so forth) had been in large part due to the application of the Army Spectrometric Oil Analysis Program (ASOAP) to aircraft engine maintenance.(18)

During fleet tests sponsored by the U.S. Army Coating and Chemical Laboratory (this was disestablished in June 1974 and the function transferred to become part of the Energy and Water Resources Laboratory at MERADCOM) in 1967-1969, the engine and gear oils were sampled and analyzed in support of broadening the application of ASOAP to include ground vehicles.(19-21)

While ASOAP relied specifically on metals analysis of used lubricant samples for wear level evaluations of oil wetted engine and gear components, applications of ASOAP to diesel and gasoline engines required more comprehensive analysis.

Contamination and deterioration due to a combination of fuel dilution, blowby products, and engine operating parameters result in a complex analytical situation where many oil properties can change in service, some of which changes were more meaningful than others.

B. Standard Analytical Methods

Standard test procedures outlined in Table 1 were and are used to provide data from engine oil drain samples. A casual consideration of the tests contained in Table 1 would lead correctly to the conclusion that synthetic base stock would *not* impair these procedures whether the sample is new or used.

TABLE 1. TEST PROCEDURES

Test Description	ASTM Designation[22]
Viscosity	D-445
Flash Point	D-92
Pour Point	D-97
Total Acid Number	D-664 or D-2896
Total Base Number	D2896
Pentane & Benzene Insolubles	D-893
Carbon	D-524 or D-189
Sulfur	D-129
API Gravity	D-287
Copper Strip Corrosion	D-130
Steel Strip Corrosion	D-130
Sulfated Ash	D-874
Fuel Dilution	D-322

C. Modern Analytical Methods

Modern analytical techniques, which have not been standardized, have been used to measure metal concentrations, chemical reactions, diesel fuel dilution, and other characteristics in engine oils.

These nonstandard methods include infrared spectrometric analysis, gas chromatography, and various metal sensitive spectrophotometers and spectrometers. More than casual consideration as to *base stock impact* must be given to these test methods.

1. Infrared Spectrometric Analysis

Lubricants, both new and used, yield spectral absorption traces in the infrared (IR) region of the electromagnetic spectrum from 600 to 4000 cm^{-1}, which can be used both qualitatively and quantitatively to describe chemical differences and changes.

The most commonly utilized IR technique is referred to[23] as differential infrared (DIR) and has been applied to used oil analysis by Frassa and associates.[24,25] This technique involves the use of a dual beam infrared spectrometer and matched (of the same sample thickness) solution cells.

An alternative method, the direct absorption technique, eliminates the need for using matched solution cells. Demountable sample cells, utilizing lead spacers to form a sample cavity, are completely dismantled, cleaned, and polished between each run. Some variance in the thickness of lead spacers, as well as some difficulty in measuring the depth of the sample cavity, requires use of the interference method[26] to determine cell thickness. This cell thickness must be determined, since the spectral results are reported in absorbance per centimeter.

Figure 1 contains spectra obtained by both the differential and direct infrared techniques for a used oil, and illustrates the comparable results obtained by the two methods. Using the direct infrared absorption technique, the dashed line in spectrum A (Figure 1) is of the new oil, and the solid line is from the same oil after 5800 miles of service. In spectrum B, illustrating the differential technique, the dashed line is from the new oil in both reference and sample cells. The solid line in spectrum B is a differential of the new oil and the same oil after 5800 miles of service. Calculation of the oxidation products present in the used oil by the base line technique gives essentially the same result by both the differential and the direct infrared techniques.

Table 2 lists the frequencies assigned to particular molecular species found in new and used mineral oil-based lubricants. Interferences will be noted for some compounds, as indicated in column 6 of Table 2, which shows the overlapping frequencies that can occur. The sensitivities, as determined by using a 0.0025-cm cell, are tabulated in column 5. These calculations were based on calibration standards for water, glycol, and additives prepared in new oils, while the reaction products were calculated utilizing used lubricant.

Fuel contamination may in some cases be detected by infrared by the measurement of out-of-plane deformation vibrations due to aromatic C-H bonds. The considerations here are that the fuel has sufficient aromaticity and that the lubricant be primarily saturated. In actuality, however, this idealized situation is not realized.

A 1966 fuel survey[27] indicated that the range of aromaticity in 78 (No. 1 and No. 2) diesel fuels varied from 12 to 38 percent. A similarly large range in aromatic content also occurs in gasolines. This wide spread would cause difficulty in accurate dilution calculations utilizing aromatic absorptions. Also, aromatics have different absorption frequencies and different absorptivities, depending upon their structural arrangements.

Some correlation work has been done using 20-percent fuel bottoms. This was successful, but only to the extent that the fuel contained a high aromatic content and the same fuel and lubricant systems were maintained. This technique could be developed for a specific application where a fleet is utilizing a single fuel of high enough aromaticity and a single lubricant not containing synthetic base stock of the polyalkylated benzene type.

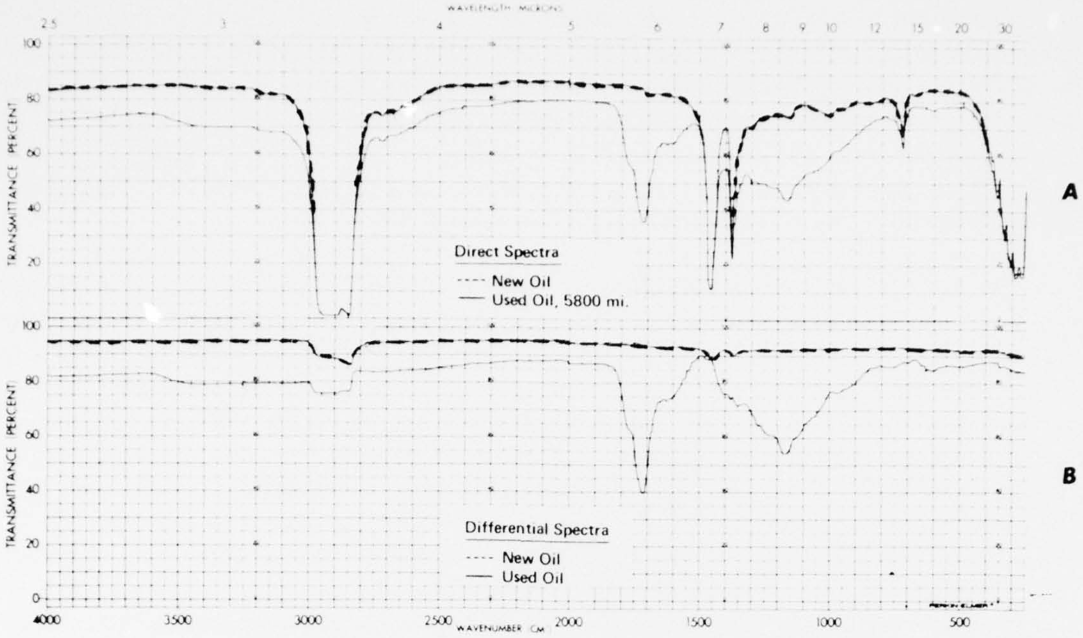

FIGURE 1. COMPARISON OF DIRECT AND DIFFERENTIAL INFRARED SPECTRA

TABLE 2. INFRARED SPECTROPHOTOMETRY OF LUBRICANTS–ABSORPTIONS AND INTERFERENCES

Primary Absorption (cm^{-1})	Secondary Adsorption (cm^{-1})	Type of Vibration	Diagnostic Significance	Sensitivity*	Interferences
3300-3500	1600	O-H stretch	Water	0.05% vol	Glycol, oxidation
1700-1750	1100-1200	C=O stretch	Viscosity improver	0.2% wt	Oxidation
1700-1750	1100-1200	C=O stretch	Oxidation	1 A/cm	Viscosity improver
1630	1270	N=O stretch	Organic nitrate	1 A/cm	Alkenes
1100-1200	-	SO_3 assymetric	Sulfonate detergent	0.2% wt	Oxidation
1040	3300-3500	C=O stretch	Glycol	0.2%** vol	Oxidation
1080	3300-3500	C-O stretch	Glycol	0.2% vol	Antioxidant
950-1050	-	P-O-C Asymmetric stretch	Zinc dithiophosphate	0.2% wt	Aromatics
500-1000	1600	C-H out of plane deformations of aromatics	Fuel dilution	Indeterminate	Unsaturation in lubricants

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* Based on a cell thickness of 0.0025 cm.

** When absorbances at 1040 cm^{-1} and 1080 cm^{-1} are added together.

Insoluble particulate material, commonly found in used diesel or light service spark ignition engine lubricants, adsorb and scatter the infrared radiation and thus effectively remove the energy from the sample beam. These particulate materials are primarily sludge and carbon particles from incomplete combustion, and may be separated by any of several techniques such as filtration, solvent dilution, and ultracentrifugation. Filtration has generally failed to give desired results, since either the fine pore size filters plugged immediately or the larger pore sizes failed to remove the insolubles.

By far the most promising approach has involved the centrifugation at speeds equivalent to forces in excess of 30 kgf. The centrifuged samples can then be analyzed by infrared as well as by other techniques. Figure 2, spectrum A, shows IR absorption spectra that were obtained before and after centrifuging a used lubricant which was high in insoluble particulate material. The dashed line in spectrum A is of the used lubricant before centrifugation, and the solid line is of the same sample after centrifuging for 1 hour in a Sorvall ultraspeed centrifuge at 30 kgf. The characteristic high absorption at 4000 cm^{-1} and background slope of the spectrum of the used oil have been eliminated in the spectrum of the oil after centrifuging. In spectrum B, the spectrum of the used oil after centrifugation (solid line) is compared to the spectrum (dashed line) from new oil, which allows inspection for additive bond changes, oxidation, and other changes without the problems imposed by the initially high particulate matter content.

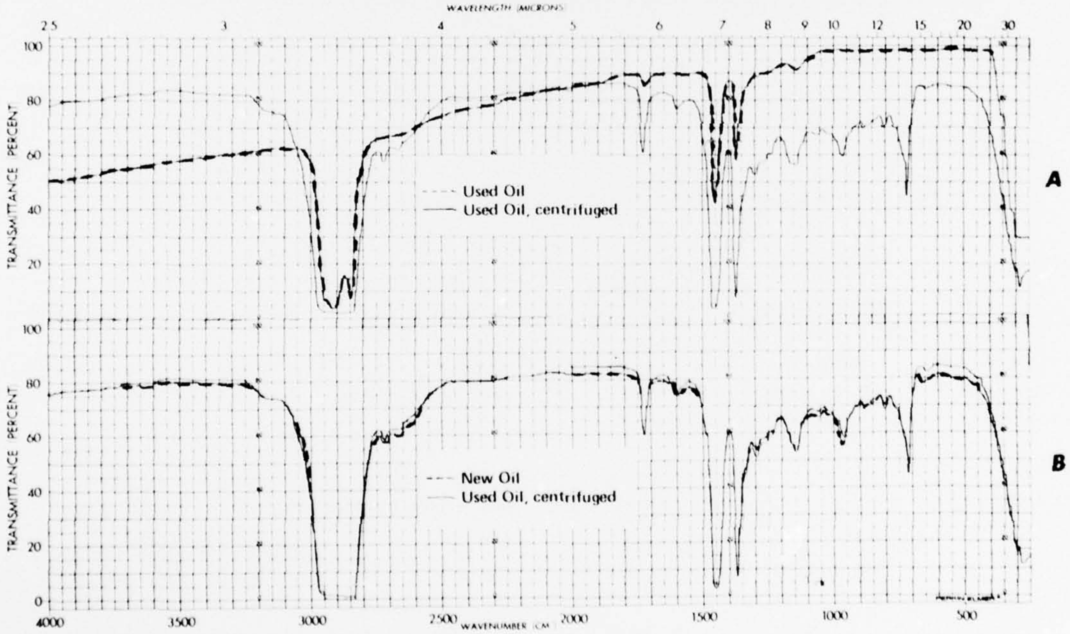
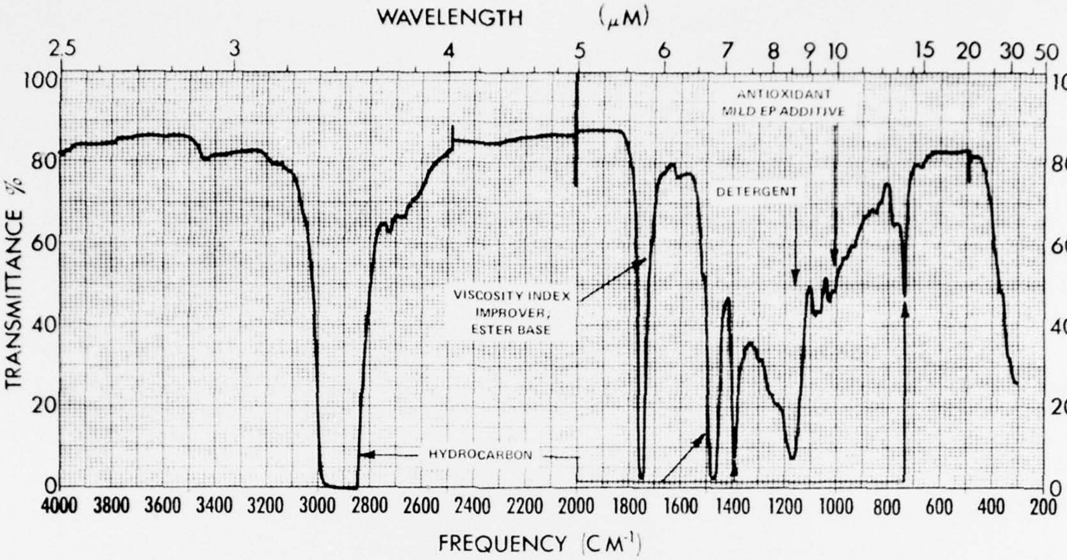


FIGURE 2. THE EFFECT OF ULTRA-CENTRIFUGATION ON A USED DIESEL LUBRICANT

Figure 3 is an infrared spectra of an ester-based engine oil (SAE viscosity grade: 10W-30) which clearly demonstrates the impact that this type of material has on the interpretation of used oil properties (particularly at 1200 and 1750 cm^{-1}). The only synthetic lubricant base stock which does not interfere with infrared interpretations is that made up of poly-alpha-olefins such as the oligomers of decene-1.



(Remarks: 0.05-mm cell, neat sample as received.)

FIGURE 3. INFRARED SPECTRUM OF AL-5851

2. Fuel Dilution By Gas Chromatography

As was discussed in an earlier section, infrared analysis does not provide for determining fuel dilution if the fuel does not contain sufficient aromatic hydrocarbons, which is true with many diesel fuels. A rapid gas chromatographic (GC) technique can be used to evaluate fuel dilution due to gasoline, diesel, or compression ignition-gas turbine fuels if the oil is sufficiently nonvolatile. Volatility measurement is independent of the chemical nature of the lubricant base stock. However, for a given viscosity grade, the volatility of ester-base stocks will be much lower than that for mineral oil-based stocks. Gas chromatographic operating conditions have been chosen for each type of fuel such that:

a. The instrument inlet, column, and detector are maintained at constant temperatures.

b. A single peak from the fuel in the oil is obtained with the area of the peak being measured and used as an index of the fuel dilution.

A distillation residue from the fuel used in the engines is used for calibration. Based on a 1957 ASTM survey(28) of gasoline engine crankcase oil dilution tests, it was concluded that a 20- to 25-percent distillation residue was commonly present in used gasoline engine oils. Similar data are not available for diesel engine used oils; however, Davis and Luntz(29) have reported that the 25-percent distillation residue from commercial "all year" railroad diesel fuel is characteristic of the diluent found in used diesel engine oils subjected to normal operation. Although use of a 25-vol % residue from DF-2 is probably much lower than is realistic, it can be used for semiquantitative analysis, which would allow monitoring of changes more than of absolute quantities.

More recently, GC methods incorporating internal standards have been used to determine fuel dilution and are discussed later in this report.

3. Metals By Instrumental Methods

To varying degrees, atomic absorption spectrophotometers, atomic emission spectrometers, and more recently X-ray fluorescence spectrometers have been employed for rapid metal analyses of oils.

Table 3 is a listing of the usual wear, contamination, and additive metals found in engine oils. The specific sources of the metals in Table 3 are dependent on engine component metallurgy, type of fuel, and lubricant formulation, such that some of the metals can be from multiple origins. To cite a few examples:

TABLE 3. METALS IN ENGINE OILS

Wear	Contamination	Additives
Fe	Si	P
Pb ←	→ Pb	Zn
Cu	B ←	→ B
Cr	Ca ←	→ Ca
Al ←	→ Al	Ba
Ni	Na ←	→ Na
Ag		Mg
Sn		

a. *Pb* is a "wear" metal from bearing inserts containing lead and is also a "contaminant" from leaded gasoline.

b. *Aluminum* is generally from aluminum piston and aluminum alloy wear, but is also present from dust and dirt contamination.

c. *Boron* is generally a contaminant from engine cooling liquids containing boron, but has also been used in some qualified engine lubricants as part of the additive package.

d. *Calcium* generally is present as an oil "additive" in the form of a detergent-dispersant, but can also be from coolant and external water contamination as well as from dust ingestion at some locations.

While the known physical and matrix differences (especially viscosity) between used oil samples *affect the accuracy* of metals analysis, no demonstrated effects due to base stock type (mineral versus synthetic) have been demonstrated except for X-ray fluorescence which is dependent on elemental matrix effects which would be present to differing degrees in esters but not poly-alpha-olefins which closely resemble the mineral oil containing metal standards.

D. Fleet Test Oil Analytical Data Results

A complete compilation of the large bulk of analytical data obtained for the engine and gear oil samples during the 1967-1968 fleet test program is contained in a special report.(30) Utilization of some of the nonstandardized test techniques employed in this study(19,30) included the following essential considerations:

(1) Comparison of metal concentration data from three laboratories indicated that accuracy of analysis was a problem from both procedural and interlaboratory standpoints, although precision within a laboratory permitted the monitoring of trend changes in metal concentrations for diagnostic purposes.

(2) The direct infrared absorption technique, employing a demountable cell, eliminated the necessity of maintaining cells in matched condition. High-speed centrifugation was used to clarify optically dense oil samples.

(3) A technique involving gas chromatographic single peak analysis of gasoline, diesel, and CITE(31) fuel dilution was developed to provide a rapid method of monitoring fuel dilution changes.

(4) Particulate matter size distribution was determined by a microfiltration procedure described by Frassa and associates(24,25) with the exception that the pentane-diluted sample was filtered through three consecutive filter pore sizes (5, 1.2, and 0.22 μ) to give four weight distributions: $> 5\ \mu$, > 1.2, but less than $5\ \mu$, > 0.22 but less than $1.2\ \mu$; and total weight percent, $>0.22\ \mu$.

(5) Dispersancy was determined by blotter spot test(32) using one drop of oil (at room temperature) on Whatman No. 40 filter paper (horizontally suspended).

Analyses of oils from 20,000-mile road tests of 24 Army general-purpose vehicles provided an evaluation of the significance of spectrometric oil analysis techniques.(19) The results of this evaluation allowed the following observations to be made:

(1) Bearing insert failures:

   a. Failures were more readily predicted than other types of component failures in diesel engines, on the basis of lead, copper, and iron concentrations in the oils.

   b. Failures were not readily predicted in two gasoline engines for the following reasons: contamination of the oil with lead from the fuel, lack of copper in the bearing overlays, and possibility of iron originating from other components.

(2) Wear rates were not directly related to wear metal concentrations because of variations in:

a. Oil consumption, drain period, and/or wear metal suspension properties.

b. Type of wear in that distinctions between normal wear and scuffing, scratching, and/or scoring could not be made.

(3) Coolant leaks and dust ingestion were readily detected through analysis for silicon, boron, and/or sodium. Concentrations greater than 0.05 vol % for water and greater than 0.2 vol % for glycol can be determined by infrared.

(4) Infrared provided a means of monitoring chemical changes involving additive bond depletions and oxidation, but the interpretation of such changes was found to be dependent on prior knowledge of lubricant properties.

(5) Poor oil dispersancy could not be determined by metal concentrations or infrared analysis, and was assessed through the use of microfiltration and blotter spot tests. The tests were shown to be qualitative in that their direct correlation to engine sludge ratings has not been demonstrated.

While many of these test techniques continue to be used, they have not been fully evaluated and standardized for all lubricant base stocks. Their use with synthetic-based oils such as dibasic acid esters and polyol esters must be questioned and not assumed to be equal to that of mineral oils. This has already been shown in the case of infrared spectrophotometry.

During a recent field test comparing mineral oil and ester-based lubricants under extended drain conditions,(33) direct visual comparison of blotter spot tests for the different oils suggested different compatibilities may exist with respect to the blotter spot test paper, perhaps due to the higher polarity of the esters. Knowing the variety of types of synthetic lubricant base stocks should provide the analytical chemist with an indication of what physical-chemical effects will be operational in a particular analytical technique.

III. CHARACTERIZATION OF LUBRICANT BASESTOCKS

To properly understand the nature of today's complex lubricants, it has become necessary for the Army to develop and use more extensive analytical methods. This has provided a basis for the characterization of the many different lubricants or combinations of lubricants used in fielded equipment.

A comprehensive analytical methodology has been made available to the petroleum chemist to provide desired lubricant characterization data through the use of the analytical approach outlined in Figure 4.(34,35) This approach proposes no new art, but places emphasis on the utilization of existing methods in a logical sequence as a guide to generate useful information about lubricant composition so that an end user may properly select a lubricant for his application. Figure 4 is not a "cookbook" line diagram to the analysis of all lubricants. It is a guide to suggesting methodology and instrumentation used to elucidate the structure and define the composition of synthetic and hybrid lubricants. Both instrumental analyses and chemical separations are used in characterizing lubricants. Instrumentation includes gas and liquid chromatography and spectrophotometry. Chemical processes include hydrolysis and derivatization of the hydrolysis products.

The logic of the major paths in Figure 4 is as follows: An infrared spectrum is obtained to indicate major chemical types present. Gel permeation chromatography is performed to determine molecular weight distribution and, if needed or desired, to obtain low molecular weight base stock and high molecular weight viscosity index (VI) improver fractions. Mixtures of polar and nonpolar base stocks are separated with adsorption or reversed phase chromatography or are analyzed directly, whichever is the more appropriate for a particular sample. Both polar and nonpolar base stock fractions are analyzed directly by gas chromatography (GC). The polar fractions are also hydrolyzed. Derivatives of the hydrolysis products are analyzed by GC for detailed characterization. The VI improver fraction is analyzed similarly, taking into consideration its chemical polarity and molecular weight.

The elements of Figure 4 have been used to characterize the base stocks of a variety of selected test lubricants which are described in Table 4. Table 4 identifies the types of lubricants and provides some of the physical and chemical properties usually supplied by the manufacturer or obtained by analysis. In addition to the typical data in Table 4, other composition data are generally obtained, including: sulfur, phosphorus, barium, calcium, zinc, sodium, sulfated ash, and carbon residue. No special techniques are required for these analyses due to base stock type (mineral versus synthetic). These lubricants have been categorized in Table 4 as Qualified/Candidate Military Lubricants and Commercial "Extended Drain" Lubricants. The arctic lubricants were purported to be dibasic acid esters (alternatively called dibasic esters), synthesized hydrocarbons, or hybrid blends of each which have demonstrated good performance in laboratory tests and Army arctic field operations since 1967.(9,10,16,17) Also included in Table 4 are synthetic-based lubricants already qualified to MIL-L-46152 and a collection of current-generation commercial synthetics intended for extended-drain operation in commercial fleet vehicles and private passenger cars for periods of roughly 25,000 to 50,000 miles.(15) The physical-chemical property data in Table 4 are not adequate to characterize base stock composition so as to define what is meant by the "synthetic" designations. Infrared spectra of these lubricants served to provide preliminary distinctions regarding lubricant base stock based on the presence or absence of aromatic, carbonyl, and other absorption bands. This information is usually not conclusive nor is it quantitative with regard to the specific type or quantity of synthetic material in a lubricant, but it does provide a preliminary classification. Based on this preliminary classification, further information must be obtained through the chromatographic and chemical techniques suggested in Figure 4.

A. Application of High Performance Liquid Chromatography

Gel permeation chromatography (GPC) was an analytical high-performance liquid chromatography (HPLC) method used to obtain information about molecular size distribution (molecular weight range) and to provide a method to isolate and quantitate the high molecular weight fraction of lubricants. Through preparative scale GPC, the high-

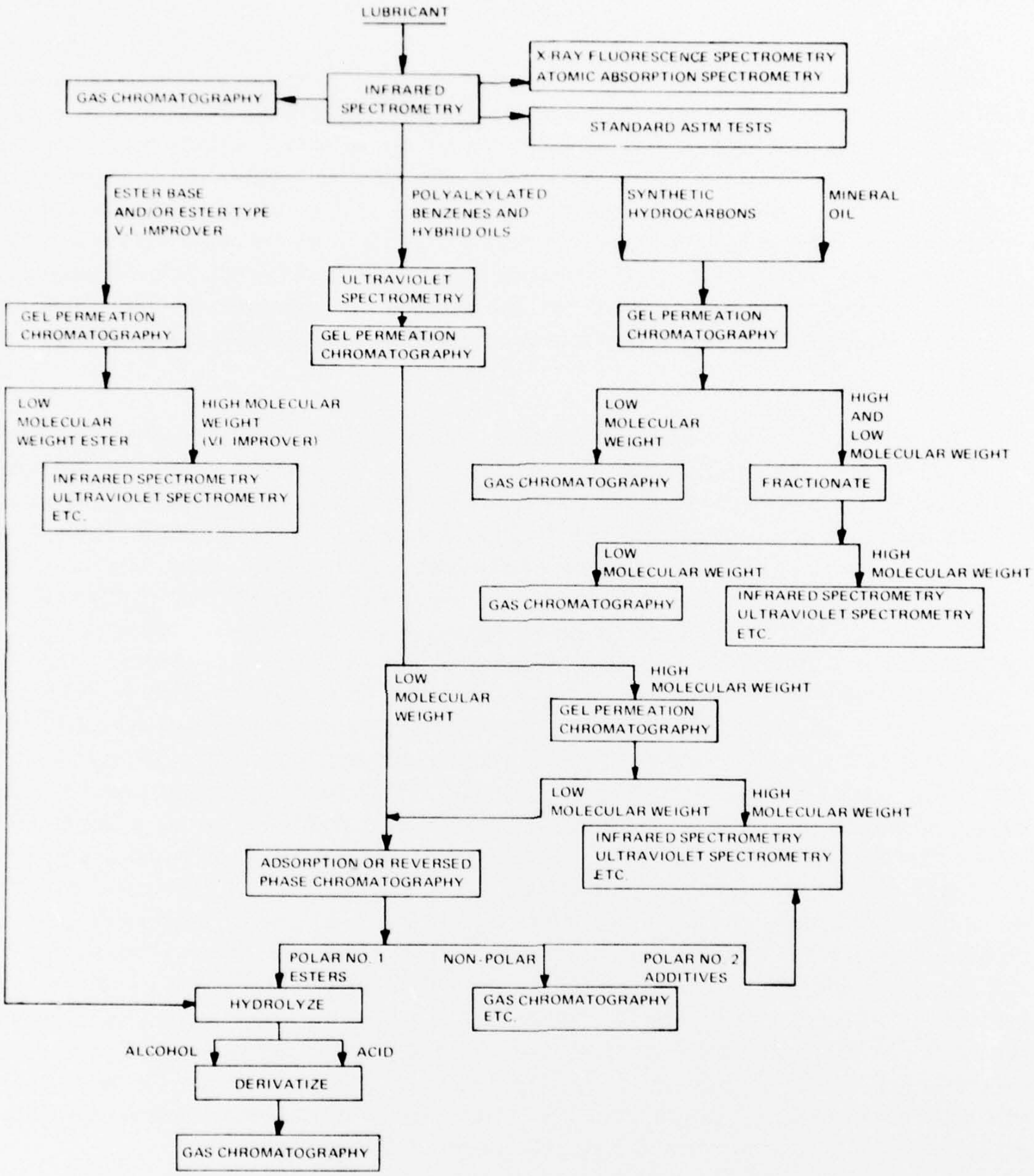


FIGURE 4. ANALYTICAL APPROACH TO THE CHARACTERIZATION OF LUBRICANTS

TABLE 4. PHYSICAL PROPERTIES OF TEST LUBRICANTS

Lubricant	Qualified/Candidate Military Lubricants							Commercial "Extended-Drain" Lubricants		
Code No	AL-3776	AL-5140	AL-5681	AL-5594	AL-5604	AL-5074	AL-6307	AL-5670	AL-5738	AL-6367
Type	Syn	Syn	Syn	Syn	Syn	Mineral	Syn	Syn	Syn	Syn
SAE viscosity grade	5W-20	5W-20	10W-50	N/A	N/A	N/A	10W-40	10W-50	10W-50	5W-20
Description										
SAE J183a	CC	CC	SE/CC	N/A	N/A	N/A	SE/CC	SE	SE	SE/CC
Military	Arctic	Arctic	MIL-L-46152	FA PD-5136*	FA PD-5136*	MIL-H-6083	MIL-L-46152	None	None	None
Properties										
Vis at 98.9°C, cSt	6.13	6.52	17.39	3.80	3.80	ND	14.29	20.99	18.85	7.94
Vis at 37.8°C, cSt	28.64	35.08	111.22	16.84	16.88	14.5	76.98	127.06	116.00	46.62
Viscosity index	214	153	178	131	ND	ND	207	203	142	157
Acid, meq/g	0.05	2.04	2.76	ND	ND	ND	1.74	1.40	3.25	2.68
Base, meq/g	6.40	8.04	8.32	ND	ND	ND	5.52	7.49	0.05	5.66
Flash point, °C	249	227	241	218	238	104	232	238	227	238
Pour point, °C	-65	-54	-40	ND	ND	ND	-55	-40	-35	-56
API gravity at 15.6°C	21.1	23.5	21.7	33.6	34.4	32.9	25.3	22.2	16.4	30.3

(Note: Refer to Reference No. 1 for analytical methods for properties and composition.)
*Frankford Arsenal Purchase Description 5136, Fire Resistant Hydraulic Fluid.
Syn–Synthetic
N/A–Not Applicable
ND–Not Determined

and low-molecular weight (MW) components were separated and gravimetrically measured to yield values (in weight percent) for the lubricant's high-molecular weight viscosity index improver. Results using this approach, as well as the other major analytical characterization data obtained for the synthetic-based lubricants in Table 4, are summarized in Table 5. The preparative scale GPC-separated lower molecular weight fractions were retained for further study using analytical GPC and adsorption chromatography.

Low-resolution preparative-scale adsorption chromatography was used to obtain first approximation concentrations such as 27 and 73 wt percent of ester and synthetic hydrocarbon, respectively, for AL-5594 as indicated in Table 5.

B. Application of Gas Chromatography

Gas chromatographic techniques were used to determine the boiling point distribution data in Table 5 and provide "fingerprints" for comparative analysis of lubricants. The volatility characteristics of four lubricants as determined by molecular distillation are shown in Figure 5. Two of these lubricants are mineral oils, and the other two are synthetic lubricants. These same lubricants were evaluated by GC, and the resulting boiling point distributions are shown in Figure 6. Comparison of the data in Figures 5 and 6 demonstrate some of the advantages of gas chromatography. Gas chromatography not only has higher resolution, but can be more accurate and less time consuming than the molecular distillation approach or other similar distillation techniques. The GC approach assumes that the hydrogen flame ionization detector (HFID) has an essentially equal response on a weight basis for all lubricant hydrocarbons. Molecular distillation was used to give a residue portion [approximately 566°C (1050°F) and greater] and a distillate portion for verification of quantitative GC analysis. This distillate by GC analysis showed essentially no residue based

TABLE 5. ANALYTICAL CHARACTERIZATION DATA FOR TEST LUBRICANTS

	Lubricant Code No.							
	AL-3776	AL-5140	AL-5681	AL-5594	AL-6307	AL-5670	AL-5738	AL-6367
Boiling point distribution[a] % off, °C								
0.5	352	266	264	325	282	329	275	337
5	418	373	368	400	378	385	376	391
10	438	401	400	416	416	412	415	413
20	453	424	435	422	430	455	445	423
30	458	429	458	424	443	461	456	431
40	462	434	464	426	445	466	467	446
50	464	440	468	428	451	470	471	480
60	467	445	472	431	475	474	484	485
70	469	450	475	432	487	477	488	489
80	472	458	479	435	510	483	500	494
90	480	473	492	451	87%/539	88%/539	85%/539	528
95	539	505	91%/539	487				93%/539
Last	95%/539	96%/539		99.5%/539				
Residue, wt %	5	4	9	0.5	13	12	15	7
High molecular weight fraction, wt %	ND[b]	4.1	8.7	ND	8.1	9.6	7.7	5.6
Lubricant base stock, wt %								
Dibasic Ester	100	40.3	100	27[c]	---	100	1	1
Polyol Ester	---	---	---	---	48.4	---	69.2	33.5
Polyalkylated Benzenes	---	59.7	---	---	---	---	---	---
Polyalpha Olefins	---	---	---	73[d]	51.6	---	---	65.5
Mineral oil	---	---	---	---	---	---	29.8	---
Other	---	---	---	---	---	---	---	---
Ester parent components								
Alcohols								
Mono-, wt %								
2-Ethylhexanol	---	100	---	100	---	---	---	---
Iso-octanol (c_8)	5	---	---	---	---	---	---	100
Isononanol (C_9)	---	---	---	---	---	---	---	---
Isodecanol (C_{10})	95	---	11.8	---	---	---	---	---
Isoundecanol (C_{11})	---	---	---	---	---	---	---	---
Isododecanol (C_{12})	---	---	---	---	---	---	---	---
Isotridecanol (C_{13})	---	---	88.2	---	---	100	100	---
Poly-, wt %								
Trimethylolpropane	---	---	---	---	93.5	---	6.7	40.0
Pentaerythritol	---	---	---	---	3.9	---	85.7	60.0
Dipentaerythritol	---	---	---	---	---	---	---	---
Other	---	---	---	---	2.5	---	7.6	---
Carboxylic Acids								
Mono-, wt %								
Butanoic (C_4)	---	---	---	---	1.3	---	---	---
3-Methyl-butanoic (C_5)	---	---	---	---	0.2	---	---	---
Pentanoic (C_5)	---	---	---	---	0.2	---	---	---
Hexanoic (C_6)	---	---	---	---	1.5	---	---	---
Heptanoic (C_7)	---	---	---	---	96.5	---	100	100
Octanoic (C_8)	---	---	---	---	0.3	---	---	---
Nonanoic (C_9)	---	---	---	---	<0.1	---	---	---
Decanoic (C_{10})	---	---	---	---	<0.1	---	---	---
Di-, wt %								
Succinic (C_4)	1.5	---	4.3	---	---	0.3	---	---
Glutaric (C_5)	0.6	0.2	14.0	---	---	3.1	---	14.5
Adipic (C_6)	1.4	1.7	78.3[e]	---	---	93.3	---	85.5
Pimelic (C_7)	1.8	2.2	---	1.9	---	---	7.9	---
Subaric (C_8)	4.9	4.6	2.0	4.1	---	0.5	5.1	---
Azelaic (C_9)	75.0	79.8	0.8	87.8	---	0.1	71.9	---
Sebacic (C_{10})	4.9	6.2	0.6	2.0	---	0.2	15.1	---
Other (C_{11} + C_{12})	9.9	5.3	---	4.2	---	2.5	---	---

---

[a] Last % off plus residue equals 100 wt %.

[b] ND–Not determined.

[c] HPLC determined value of 27 wt %, compared to 25 wt %, determined by method of additions using infrared spectrometry with iso-octane as a diluent.

[d] Composed of 3 wt % C_{20}, 85 wt % C_{30}, 9 wt % C_{40} and 2 wt % C_{50} oligomers of decene-1 determined by GC.

[e] Includes 15.2 wt % iso-C_6 acids.

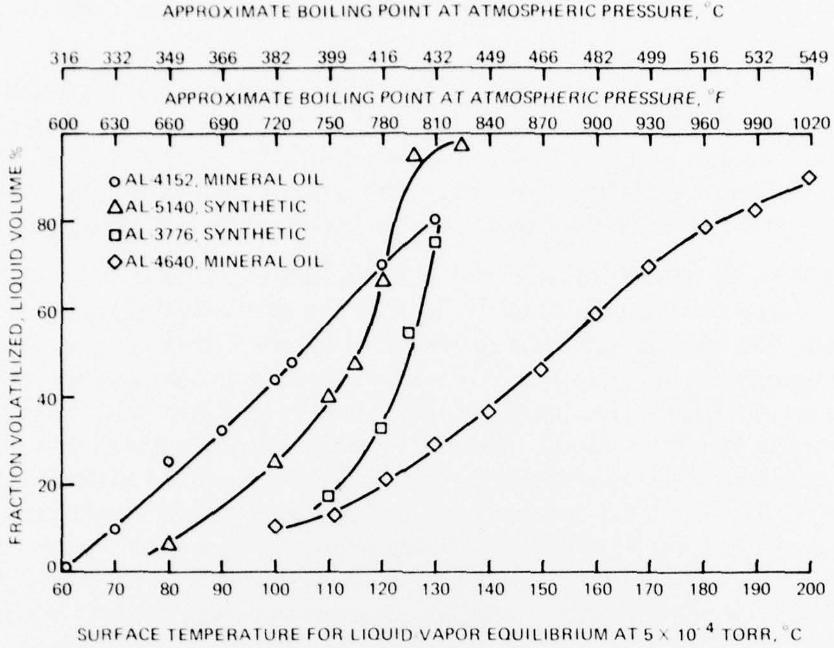


FIGURE 5. VOLATILITY CHARACTERISTICS OF LUBRICANTS AS DETERMINED BY MOLECULAR DISTILLATION

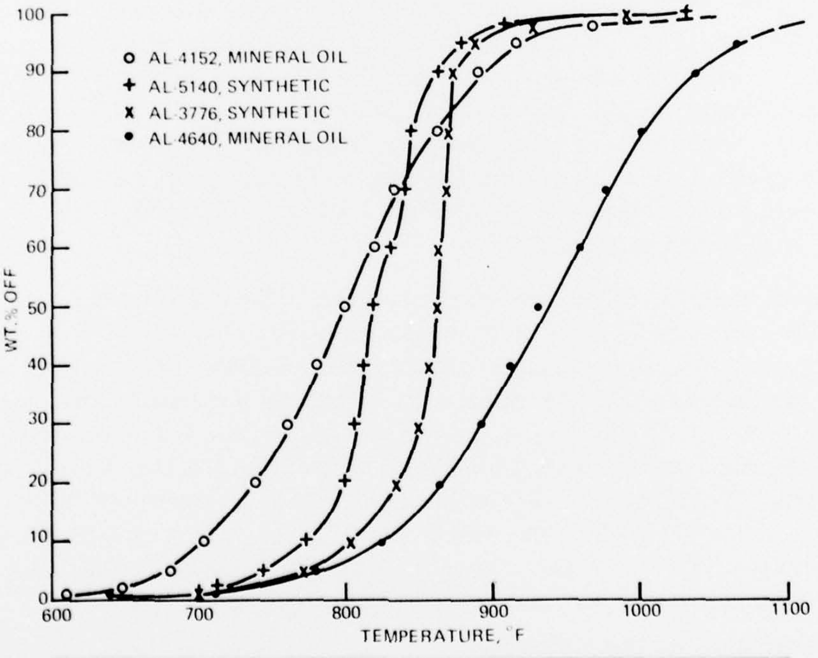


FIGURE 6. BOILING POINT DISTRIBUTION OF LUBRICANTS BY GAS CHROMATOGRAPHY

on a C_9-C_{11} internal standard and confirmed the assumption of equal detector response for the hydrocarbons present.

The gas chromatographic detector output recordings are computer reduced to form detailed boiling point distribution data in terms of wt percent off versus boiling point and the amount of residue boiling higher than the selected final boiling point. Any high molecular weight viscosity index improver, as well as other high boiling materials, will stay in the column and are accounted for as a "residue" in this analytical procedure.

When interest in petroleum-base and synthetic-base hydraulic oils and Army arctic engine oils required boiling point analysis by GC, the established procedures for mineral oils were used. The chromatograms reproduced in Figure 7 are examples of the "fingerprints" obtainable for lubricants by GC. In descending order, the first two lubricant chromatograms are of synthetic hydraulic oils AL-5594 and AL-5604, formulated to the same specification by two different suppliers. The GC chromatograms and data revealed differences between the two lubricants' compositions in spite of the major base stock boiling point similarity. The third chromatogram of Figure 7 vividly demonstrated the very high volatility of lubricant AL-5074, composed primarily of a *kerosene base stock*, compared to the other hydraulic fluids which were *synthetic*-based fire-resistant lubricants. The boiling point distribution data for AL-5074 gave a residue value of 15 wt percent, most of which was confirmed by liquid chromatography to be viscosity index improver.

While the mineral oil boiling point distribution procedure provides a final boiling point of 615 °C (equivalent to n-C_{60} in the standard), it was found that this extended range was not necessary for most synthetic-based lubricants. A simplified procedure was developed using a C_5-C_{40} normal saturate standard providing adequate calibration to 539 °C (1000 °F) for use with synthetic and most hybrid mineral oil-based lubricants except where very high ($>$ 10 percent) residues were encountered. This method provided the same resolution and "fingerprinting" capabilities exhibited in Figure 7. The lower column oven temperature also permitted the use of a wider range of more volatile nonpolar column coatings. Both of these chromatographic systems employ cool septum inlet arrangements to eliminate sample fractionation during injection and inlet sample pyrolysis that can occur with constant high-temperature inlets.

Some direct analyses of neutral fractions from hybrid lubricants, such as AL-5594 (Table 5) which contained 73 wt percent polyalpha olefin, also provided an analysis of the synthetic hydrocarbon composition. In the case of AL-5594, the synthetic hydrocarbon composition was determined by this approach, using peak normalization to be 3 wt percent C_{20}, 86 wt percent C_{30}, 9 wt percent C_{40}, and 2 wt percent C_{50} oligomers of decene-1. Oligomers of decene-1 are distinguishable from conventional mineral oil in that their GC chromatographic "fingerprints" show specific peaks which correspond to average boiling points of 174°, 330°, 431°, 489° and 534 °C for C_{10}, C_{20}, C_{30}, C_{40}, and C_{50} oligomers of decene-1, respectively.(36) This same general analytical approach was used to describe mineral oil and polyalkylated benzenes in hybrid base stocks.

C. Parent Acid/Alcohol Identification

Identification of the alcohols from the hydrolysis of dibasic esters was accomplished by GC analysis of manufacturer-supplied base stock alcohols used in the preparation of

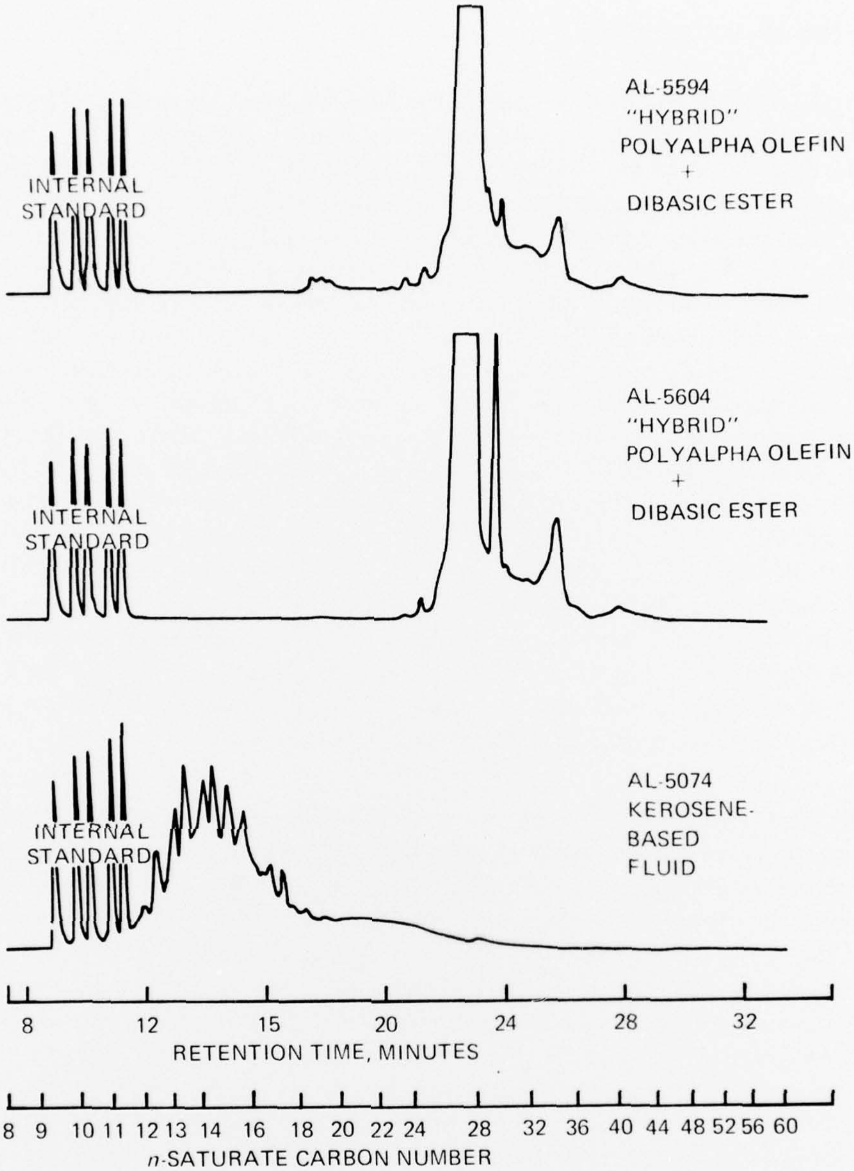


FIGURE 7. BOILING POINT DISTRIBUTION OF THREE HYDRAULIC LUBRICANTS

esters. An alcohol silylation approach was chosen (rather than direct alcohol fraction analysis) which would give sharper, better defined peaks. Both silylated acidic and alcoholic hydrolysis products were analyzed by GC under the same conditions given for the unreacted lubricant; however, peak normalization techniques and an appropriately higher detector sensitivity were used. The peaks attributed to the alcohols or acids were normalized to 100 wt percent and reported for each lubricant in Table 5 as mono-alcohols and dicarboxylic acids. The poly-alcohols and mono-carboxylic acids in Table 5 are combined to describe polyol ester base stock.

D. Implications of Analytical Approach

Referring back to Figure 4, classification of a lubricant according to major base stock type was the first step in the quantitative determination of lubricant base stock composition. This has not always been readily done on the basis of spectroscopy and chromatography when hybrid mixtures or pure esters were involved. In particular, differentiation between polyol and dibasic esters has not become evident until after hydrolysis was accomplished. As hydrolysis products, dibasic esters provide liquid alcohols and solid acids while polyol esters yield liquid acids and solid alcohols. Additionally, the silylated polyol acids were not completely resolvable by GC due to overlapping of derivatization reagent with silylated C_4 and C_5 mono-acids. Polyol ester base stocks such as AL-6307 have thus best been analyzed by other established methods(37) using direct GC analysis of acid hydrolysis products and parent polyol analysis by valeric acid ester formation. Three lubricants (AL-6367, AL-6307, and AL-5738) in Table 5 provided alcoholic hydrolysis products which were essentially free of any alcoholic materials and were composed primarily of neutral materials. Additionally, the acid hydrolysis products were liquid as opposed to solids which indicated that polyol esters were present in the original lubricants prior to hydrolysis. Based on this information, appropriate standards were chosen and the ester compositions determined. Mixtures of polyol ester and dibasic ester base stocks would be difficult to accurately analyze. The small 1-percent quantity of dibasic ester indicated in AL-6367 and AL-5738 was estimated based on direct acid analysis and supported by the type and quantity of alcohol in the neutral hydrolysis fraction.

Hence, from this discussion, it can be seen that some ''back stepping'' and reanalysis in reference to Figure 4 is necessary in the process of characterizing lubricants. This is further emphasized in the case of direct hydrolysis of mixed dibasic esters and synthetic hydrocarbons such as polyalkyl benzenes and oligomers of decene-1 (referred to as polyalpha olefins in Table 5). As an example, the infrared spectra indicated that AL-5594 was an ester-based lubricant. However, not until analysis of the alcoholic hydrolysis fraction of AL-5594 (containing ether soluble neutrals) was attempted did it become apparent that synthetic hydrocarbons were present as a portion of the base stock. These unhydrolyzable components appear as unreacted lubricant in the alcoholic fraction during direct or derivative GC analysis. Assay of the initial lubricant base stock composition was then determined based upon the identification of the particular ester which then provided for proper standard selection for analytical infrared spectrometry. If a proper ester standard was not available, then preparative HPLC was used to provide a gravimetric recovery determination of the polar (ester) and nonpolar (synthetic hydrocarbon base stock composition. In either case, additional information was derived regarding the neutral (unhydrolyzable) base stock by GC analysis at the appropriate time. Oligomers of decene-1 are definable by boiling point peaks in the neutral hydrolysis fraction and are, on this basis, easily distinguished from mineral oil base stocks which give a gaussian-type boiling point distribution having very small, if any, distinguishing chromatographic peak features. This distinguishing characteristic allowed definition of the hydrocarbon base stock in AL-5738 to be mineral oil.

If initial IR spectroscopy indicated that polyalkylated benzenes were present as in the case of AL-5140, GC boiling point distribution was not adequate for final assay. Final assay tabulated in Table 5 again relied on gravimetric HPLC preparative scale separation into the less polar polyalkylated benzenes and the more polar diester base stocks of the lubricant.

E. Extension of Methodology to Used Oil Analyses

Used oil base stocks can be characterized after the pentane insolubles are removed. In the case of used hydraulic fluids, prior "cleanup" has not usually been necessary since engine combustion contaminants are not present. In the process of converting from petroleum to synthetic-base hydraulic fluids in fielded M60A1 tank turrets, a laboratory assay procedure was developed and established at USAMERADCOM (Fort Belvoir, Virginia) for used oil samples from the field to monitor the concentration of the discontinued oil still present in the mechanical systems.(38) This was a particularly simple analysis (using decane internal standard in a gas chromatographic method) due to the much higher volatility of the discontinued oil (AL-5074 in Figure 7). Alternatively, referring to Table 5, an assay procedure based on the ester composition of AL-5594 could have been established.

In the flammability *testing* of either new or used (new-generation) synthetic-based hydraulic fluids, no problems or inconsistencies in *testing* these fluids as opposed to mineral oil-based fluids have been encountered.(39)

Fuel contamination in used oils has also been determined by the same gas chromatographic boiling point distribution procedures such as that used to develop Figure 7, except for choice of internal standard (*n*-tetradecane for gasoline and *n*-nonane or *iso*-octane for diesel fuel) and more sensitive data reduction techniques. Standard methods for fuel dilution in used mineral oils by gas chromatography have been published by the American Society for Testing and Materials.(40) Due to the high boiling point distribution of synthetic lubricants, these same fuel dilution methods will apply to used synthetic lubricants. While diesel fuel dilution methods exclude SAE 5, 10, 20, and multigrade conventional mineral-oil based lubricants due to fuel-lubricant volatility overlap, no such limitation would appear to exist for synthetic-based lubricants of the type represented in Tables 4 and 5.

IV. SUMMARY

In summary, it has been the general experience that the introduction of synthetic base stock into the engine oil scene has not had significant impacts on most of the analytical procedures for oils except for the use of infrared analysis and for fuel dilution by gas chromatography. In the case of infrared, it has been practically rendered useless for used oils except where the oil is known not to contain esters. In the case of gas chromatographic analysis for diesel fuel dilution, this method has been enhanced where diesel fuel dilution of ester-based used oils are involved. When used oils of unknown origin are analyzed, great caution must be exercised due to the introduction of synthetic and hybrid lubricants into the supply system. While comprehensive analytical methodology has been made available, no simple, rapid method has yet been devised for the petroleum chemist to thoroughly characterize lubricant base stocks.

Nonstandardized tests such as microfiltration, blotter spot tests, and spectrometric metals analysis may not give diagnostic results equivalent to mineral-oil-based lubricants if the synthetic oil base stocks interfere with the methods through matrix or physical/chemical interactions with test materials.

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