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DETERMINATION OF SYNTHETIC HYDROCARBONS IN HYBRID MINERAL OIL LUBRICANTS

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by

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An analytical gas chromatographic procedure has been developed to qualitatively and quantitatively detect polyalpha olefins such as oligomers of decene-1 in hybrid mineral oil lubricants. The polyalpha olefin synthetic hydrocarbons used in hybrid lubricants are narrow boiling compounds producing specific peaks as compared to the broad range gaussian type distribution of mineral oils. Difficult base line definition and undetectable components such as C_{60}^{+} oligomers produce errors which are acceptable even if larger than desired.

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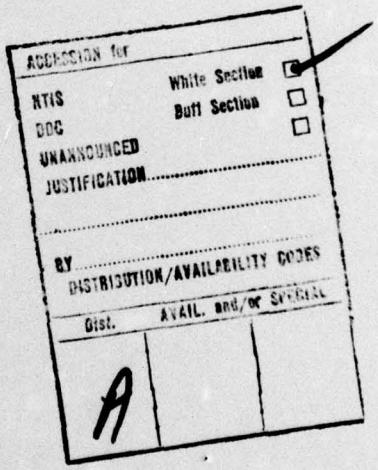

INTRODUCTION

The Army develops and maintains specifications for the procurement of all lubricants used in Department of Defense ground-powered equipment and has the custodial responsibility for the specifications which the Federal Government uses to purchase principal automotive lubricants used in both combat and administrative fleets.

Advanced equipment needs have imposed stringent lubrication requirements and have caused the Army to consider modern lubricant formulation technology which includes pure and hybrid blends of synthetic and mineral oil base stocks. In Army lubrication research programs, the properties and physical performance characteristics of many synthetic and mineral oil-based lubricants have been evaluated[1] and efforts to provide chemical analysis approaches to better characterize these lubricants have been intensified.[2] 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. Additionally, these analytical methods are potentially beneficial in providing quality assurance, detecting contaminants, and data for determining composition to performance correlations.

Synthetic hydrocarbons of the polyalpha olefin type are one class of synthetic lubricant base stock which has been identified in certain ester hybrid lubricants. In the work cited in reference 2 concerning development of analytical approaches to the characterization of synthetic lubricant base stocks, no procedures were established for base stock blends of polyalpha olefins and mineral oil.

The properties of both polyalpha olefins (specifically, oligomers of decene-1) and mineral oil lubricant base stocks are similar since they are both hydrocarbons. However, the boiling point distribution chromatograms of polyalpha olefins (PAO) are relatively simple compared to those of mineral oils. The PAO oligomers are narrow boiling compounds producing specific peaks as compared to the broad range gaussian-type distribution of mineral oil lubricants.[2] Based on these properties, a program was initiated to demonstrate the qualitative and quantitative ability of gas chromatography to detect and measure PAO in PAO-mineral oil-based lubricants.

TABLE 1. BOILING POINT DISTRIBUTION FOR TEST FLUIDS

Boiling Point Distribution, wt % Off	Boiling Point, °C		
	Mineral Oil AL-6519-L	PAO Sample A (4 cs)	PAO Sample B (6 cs)
IBP	331	326	302
5	360	404	414
10	373	410	417
20	395	415	423
30	414	417	428
40	432	420	474
50	451	423	484
60	473	426	490
70	502	428	506
80	534	434	526
90	568	481	538
95	600	488	557
last % off/BP	96.2/606	99.5/532	99.5/586
Residue	3.8%	0	0

EXPERIMENTAL

Two PAO samples A and B were used to prepare mixtures of PAO in a fully formulated mineral oil based lubricant (AL-6519-L). The boiling point distributions for the neat mineral oil lubricant and the PAO samples are given in Table 1. The gas chromatographic (GC) operating parameters are detailed in the

[1] S.J. Lestz, J.A. Russell (USAFLRL), and T.C. Bowen and M.E. LePera (USAMERADCOM), "Evaluation of Synthetic Automotive Crankcase Lubricants for Military Applications," AFLRL Interim Report No. 71, AD A023613, December 1975.

[2] L.L. Stavinoha, G.E. Fodor, F.M. Newman and S.J. Lestz, "Analytical Approach to the Characterization of Military Lubricants," AFLRL Interim Report No. 77, AD A027397, March 1976.

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TABLE 2. CARBON NUMBER DISTRIBUTION OF PAO SAMPLES

	Carbon Number Distribution, wt %				
	C_{20}	C_{30}	C_{40}	C_{50}	Other
PAO Sample A	3	78	17	2	0
PAO Sample B	1	32	36	24	8

appendix and were used for all GC analyses contained in this report. An nC_{13} -nC_{15} internal standard was used for quantitation.

RESULTS AND DISCUSSIONS

Both of the PAO samples A and B contain C_{20}, C_{30}, C_{40}, and C_{50} hydrocarbons boiling at 330, 421, 485, and 527°C, respectively. Table 2 contains the carbon number distribution for the PAO samples using peak areas related to the internal standard to determine concentrations.

The boiling point calibration standard was a mixture of C_5-C_{40} *n*-saturates. The standard's chromatogram is shown in Figure 1. The chromatograms for PAO samples A and B and the mineral oil (AL-6519-L) are also reproduced in Figure 1. The AL-6519-L mineral oil sample is a fully-formulated multipurpose (API SE/CD) high-base engine lubricant. The gas chromatographic characteristics of AL-6519-L in Figure 1 are representative of both military and commercial mineral oil based lubricants in that the GC chromatograms are of a gaussian-type having very small, if any, distinguishing *peak* features. Additives in fully formulated mineral oil lubricants have not been distinguishable as peaks.

Based on the *n*-saturate boiling point calibration, the boiling point range for the PAO components by carbon number are indicated in Table 3. The middle boiling point given in Table 3 corresponds to the middle of the peak, and the range approximately covers the majority of the peak base in Figure 1 using peak side extrapolation. It should be noted that the PAO carbon numbers in Table 3 do not correspond to the *n*-saturate carbon numbers with respect to boiling points. This is further emphasized in Figure 1 where the C_{20}, C_{30}, C_{40}, and C_{50} PAO hydrocarbons correspond to nC_{19}, nC_{27}, nC_{34}, and nC_{41}, respectively.

TABLE 3. BOILING POINT RANGE FOR PAO COMPONENTS BY CARBON NUMBER

	Carbon Number			
	C_{20}	C_{30}	C_{40}	C_{50}
Middle Boiling Point, °C	330	421	485	527
Range, °C	319-338	405-433	457-518	518-549

TABLE 4. CHROMATOGRAPHIC ANALYSIS RESULTS FOR MIXTURES OF PAO AND MINERAL OIL

PAO Sample Code	PAO Concentration In Lubricant AL-6519-L wt %		Analytical Variation	
	Known	Analysis Average* (No. of Runs)	Maximum Deviation from Known	Average Error, %
A	10.0	7.9(4)	– 3.1	–21
A	21.8	19.1(3)	– 3.3	–12
A	51.5	55.3(3)	+10.7	+ 7.4
A	100	100.6(1)	+ 0.6	+ 0.6
B	10.3	6.8(2)	– 4.2	–34
B	29.8	24.5(5)	– 9.2	–18
B	50.5	42.7(3)	– 8.9	–15.4
B	100	92.0(1)	– 8.0	– 8.0
B	10.3	10.3(2)*	– 1.5*	0 *
B	29.8	23.8(3)*	– 8.2*	–20 *
B	50.5	44.7(3)*	– 8.9*	–10.5*

*Laboratory data system results except for asterisk (*) values which were obtained using a planimeter.

Known mixtures of PAO samples A and B and the mineral oil lubricant, AL-6519-L, were prepared and analyzed. The analytical data for these mixtures have been summarized in Table 4. Generally, low values were obtained but repeatability was considered reasonable. The errors encountered in analyzing the mixtures is due, in part, to the baseline characteristics of the samples with respect to computing capabilities. The

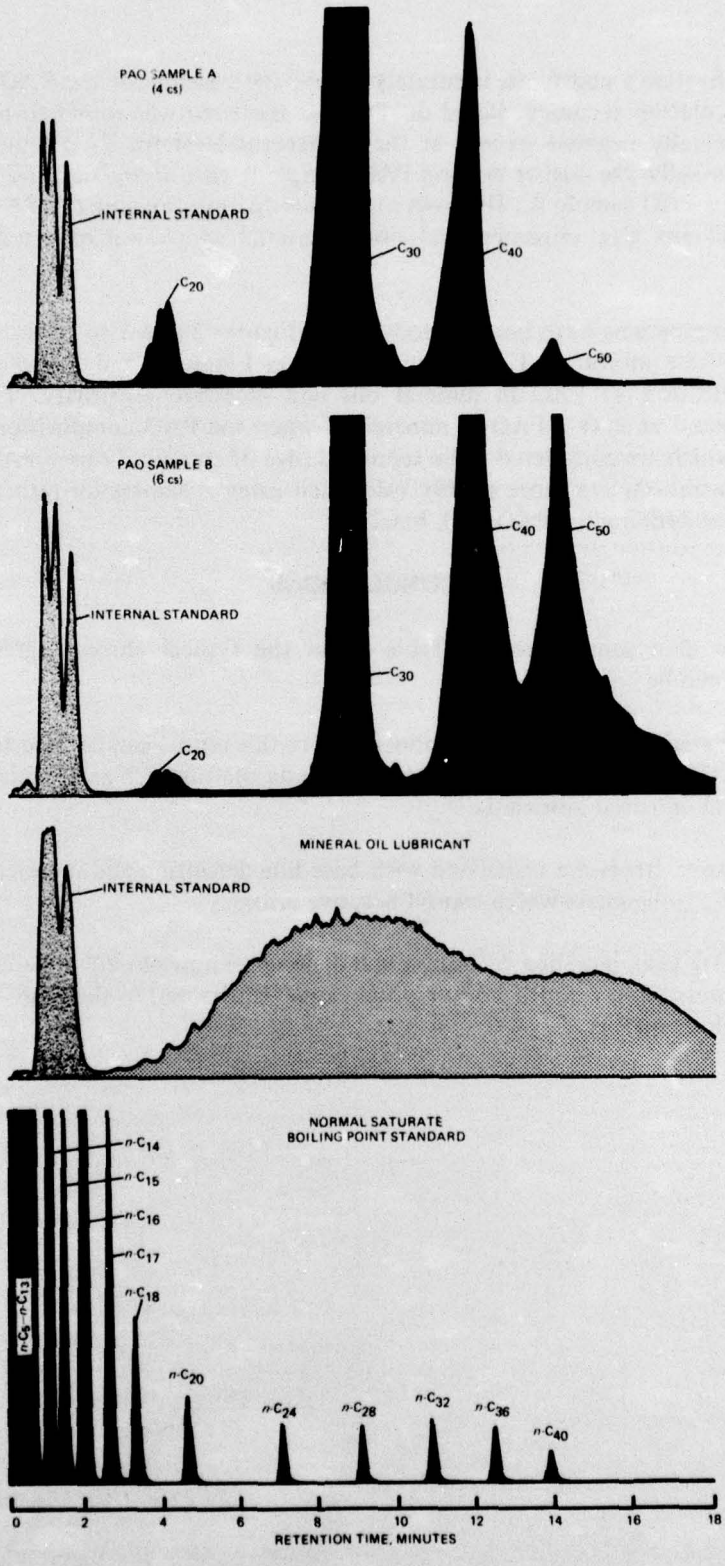

FIGURE 1. GAS CHROMATOGRAMS FOR PAO SAMPLES, A MINERAL OIL LUBRICANT, AND A BOILING POINT STANDARD

Laboratory Data System's ability to accurately define the baseline of the PAO component peaks will affect the calculation accuracy. Based on Table 4, the error was found to have a considerable range and was generally negative except at the 50-percent level for PAO sample A which gave a positive error. Generally the higher boiling PAO sample B gave more negative errors in absolute magnitude than did PAO sample A. The lower accuracy for mixtures of the PAO sample B was in part due to loss of any C_{60} oligomers and other material which was reported as "8% other" in Table 2.

Typical chromatograms have been reproduced in Figures 2 and 3 to demonstrate the baseline characteristics of these mixtures. The chromatograms in Figures 2 and 3 also provide a basis for qualitative identification of PAO in mineral oils and illustrate sensitivity. The lower limit of sensitivity is estimated at 2 wt % PAO in mineral oil when the PAO composition is similar to PAO samples A and B which are considered to be representative of commonly used PAO base stocks. The lower PAO concentrations are more readily calculated using a planimeter rather than a computer due to difficulties in defining the PAO peak baselines.

CONCLUSIONS

Based on the data summarized in Table 4 and the typical chromatograms reproduced in Figures 2 and 3, it can be concluded:

1. That the analytical procedure demonstrated in this report can be used to qualitatively and quantitatively detect the presence of polyalpha olefins such as the oligomers of decene-1 in mineral oil based lubricants.

2. Quantitative errors are associated with base line definition and undetectable components such as C_{60} oligomers which caused negative errors.

3. Some PAO peak base-line definition will depend on how closely different mineral oil base stocks approach a smooth boiling point curve as opposed to the more well-defined peaks of polyalpha olefins.

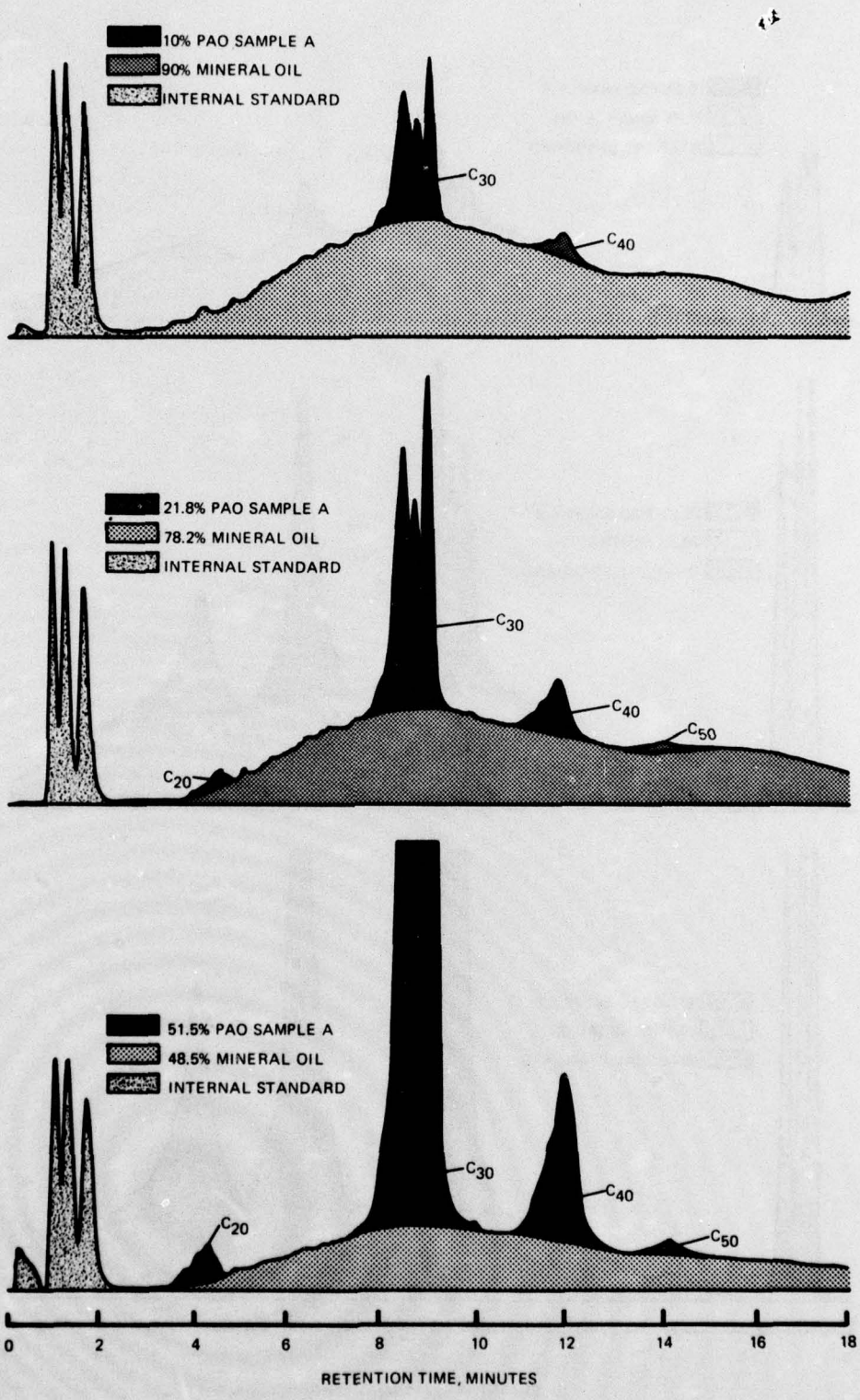

FIGURE 2. GAS CHROMATOGRAM FOR MIXTURES OF PAO SAMPLE A AND A MINERAL OIL

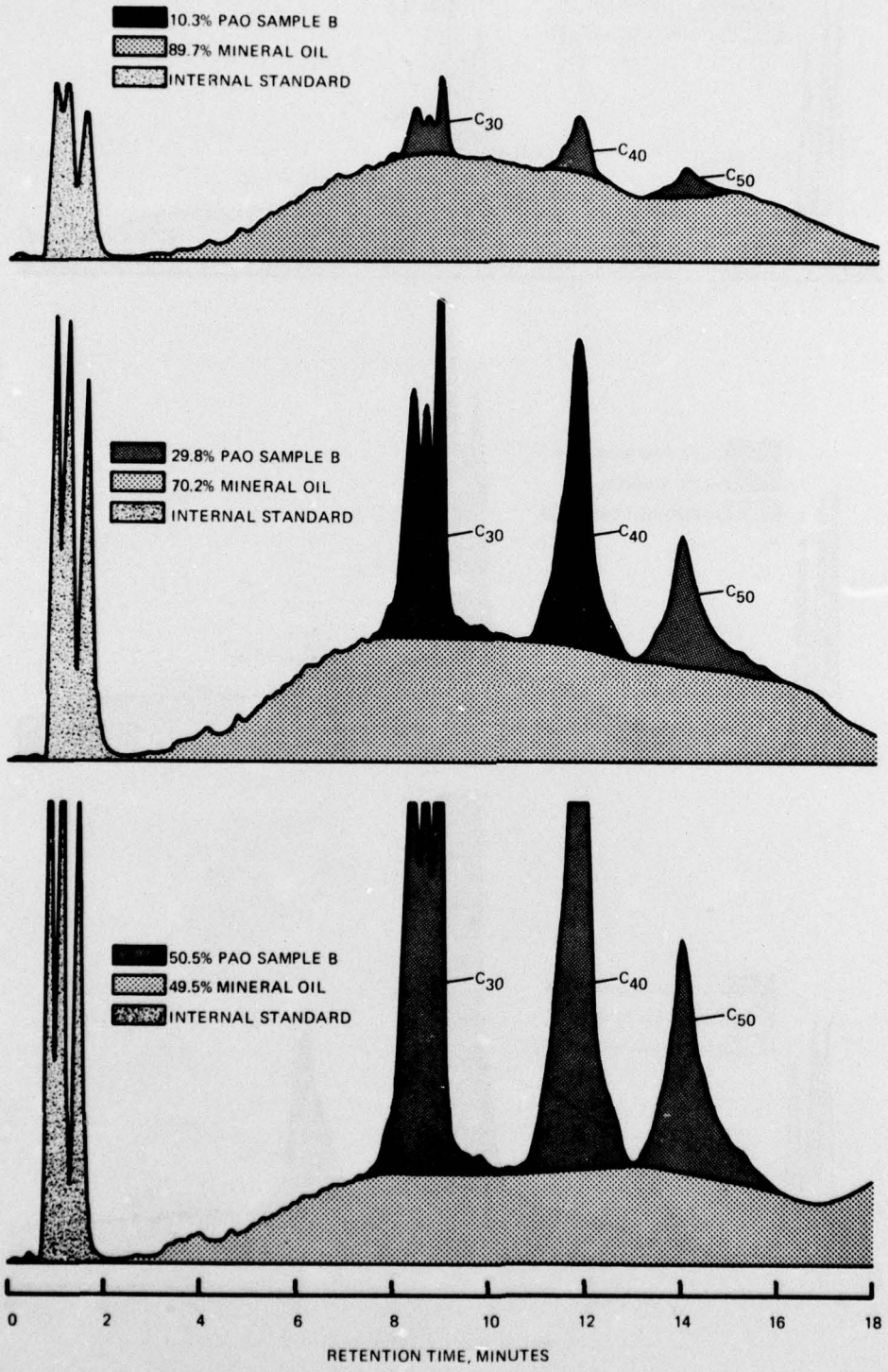

FIGURE 3. GAS CHROMATOGRAMS FOR MIXTURES OF PAO SAMPLE B AND A MINERAL OIL

APPENDIX

GAS CHROMATOGRAPHIC OPERATING PARAMETERS

Columns:	1.2 meter by 0.32 centimeter O.D. 10% Dexsil 300 on 45/60 mesh Chromosorb P, A.W.
Column Oven:	200°C for 2 min; 200°C to 450°C @ 15°C/min, hold for 5 minutes
Detector:	450°C Dual HFID
Inlet:	Water-cooled septum, air-cooled movable port with inlet injector heater block at 325°C.
Syringe:	Inject 2.0 µl with 3-inch (7.6 centimeter) needle fully inserted.
Laboratory Data System:	HP 3352 normalization method with timed events for defining baseline.
Sample Preparation:	Weigh out 5-gram oil sample into 10-ml volumetric flask. Add 0.56 g of internal standard composite into flask and dilute to 10-ml volume with carbon disulfide to lower the viscosity. Shake flask to mix components and let stand prior to analysis. Internal standard composite is prepared by weighing out equal amounts of n-C_{13}, n-C_{14}, and n-C_{15} into a stoppered vial.

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