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**WASTE LUBRICATING OIL RESEARCH: A Comprehensive
Characterization of Five Typical Re-refinery Feedstocks,
Part 5**

By

F. O. Cotton, M. L. Whisman,
J. W. Goetzinger, and J. W. Reynolds

Date Published—April 1977

Bartlesville Energy Research Center
Energy Research and Development Administration
Bartlesville, Oklahoma

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WASTE LUBRICATING OIL RESEARCH: PART 5

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WASTE LUBRICATING OIL RESEARCH:
A Comprehensive Characterization of Five
Typical Re-refinery Feedstocks

Part 5

by

F. O. Cotton,¹ M. L. Whisman,² J. W. Goetzinger,³ and J. W. Reynolds³

ABSTRACT

By use of procedures developed previously at this research center, five feedstock samples of used lubricating oil obtained from re-refineries were characterized in detail. A combination of silica-alumina gel and gel permeation chromatography was used to separate the oils into simpler fractions for analysis by low voltage mass spectrometry. The data show the various samples to be extremely similar, implying that an acceptable reclamation procedure should produce consistent re-refinery product with minimal effects from feedstock variations.

INTRODUCTION

A better understanding of the hydrocarbon compound types and the distribution of major hydrocarbon structural groups in used automotive lubricating oils is needed for the development and evaluation of efficient reclaiming technology. Therefore, the characterization of the petroleum base composition of typical re-refinery feedstocks represents a significant portion of the research efforts that have been directed toward the reclamation of used lubricating oils at the Bartlesville Energy Research Center (BERC). In this regard, an experimental procedure previously developed at BERC by Coleman and

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coworkers (1,2,3,4,5)⁴ for the characterization of the heavy ends of petroleum was employed. The principal features of the characterization procedure include separations using silica-alumina gel adsorption chromatography and gel permeation chromatography with mass spectral analysis of the fractions produced. These techniques appeared to be ideal for the study of lubricating oil basestocks and/or feedstocks. Although the procedure is not simple or easily performed, the equipment and experienced personnel were available for application to the problems of lubricating oil composition without need for further analytical development and evaluation.

Four previous publications (6-9) have described the compositional variations among 30 re-refinery feedstocks derived from sources in 20 states. Variations attributed to geographical or seasonal derivation of feedstocks were presented in these publications. However, a less detailed characterization of composition was presented for these 30 feedstocks and this report, part 5 of the series, is an expanded characterization of five of these oils.

SAMPLES

The sources of the five samples chosen for this investigation are listed in table 1. Five states - California, Utah, Oklahoma, Illinois, and Mississippi - were the central collection points for the oils. Tables 2 and 3 summarize some of the physical and chemical properties of the oils, indicating the extent of contamination and additive levels. Table 4 contains elemental analyses which also reflect the degree and nature of contamination.

TABLE 1. - Sources of the five representative used lubricating oils for detailed basestock characterization

Sample Number	Central collection point
1465.....	San Francisco, CA
1480.....	Salt Lake City, UT
1481.....	Lyons, IL
1484.....	Jackson, MS
1498.....	Bartlesville, OK

The simulated-distillation boiling ranges of the five samples were determined by ASTM method D-2887, Boiling Range Distribution of Petroleum Fractions by Gas Chromatography. Table 5 presents these boiling points from the initial to the end point. These boiling ranges were useful in eliminating possible compounds based upon boiling point as well as being help-

ful in making the proper selection of correlation tables to be used for identification purposes.

⁴ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 2. - Physical properties of five representative used lubricating oils
selected for detailed compositional study

Sample Number	Viscosity		Viscos- ity index	Specific gravity 60/60° F	BS & W, percent	Water, percent	Pentane insolubles, percent	Benzene insolubles, percent	Fuel dilution, percent	Anti- freeze ¹
	SUS 100° F	SUS 210° F								
1465	255	56.7	168	0.904	8	2.8	1.15	0.81	5.7	Positive
1480	300	60.8	162	.914	23	15.5	2.64	.49	6.8	Do.
1481	310	59.9	149	.906	14	4.2	2.82	1.14	3.6	Do.
1484	305	59.5	149	.903	16	7.8	.92	.71	6.8	Do.
1498	415	67.7	143	.908	.4	.4	2.09	1.86	1.6	Do.

¹ Positive: greater than 0.1 percent.

TABLE 3. - Physical and chemical properties of five representative used lubricating oils selected for detailed compositional study

Sample Number	Carbon residue, percent	Ash, percent	Flash point, °F	Pour point, °F	Saponification Number	Total acid Number	Total base Number	Nitrogen, percent	Sulfur, percent
1465	3.78	1.47	204	-35	11.38	5.28	1.46	0.104	0.39
1480	2.72	.99	380	-45	13.19	2.87	2.29	.060	.46
1481	3.26	1.38	380	-40	12.26	5.00	1.53	.087	.53
1484	2.86	1.10	375	-40	11.90	3.36	1.55	.070	.41
1498	2.18	2.20	365	-40	16.85	5.70	1.52	.100	.47

TABLE 4. - Metals and phosphorus content of five representative used
lubricating oils selected for detailed compositional study

Sample Number	Element, ppm																
	Ba	Ca	Mg	Na	P ^{1/}	Zn	Al	Cr	Cu	Fe	K	Mn	Ni	Pb	Si	Sn	V
1465	180	1775	311	64	1080	1201	12	9	33	137	31	3	1	4720	< 15	6	0
1480	260	1431	227	660	764	860	10	7	41	129	20	8	0	4890	38	NA	0
1481	203	1358	458	102	1015	1233	12	8	38	212	33	3	0	10410	36	NA	0
1484	520	1170	182	100	674	660	11	8	18	179	57	4	2	4560	37	NA	0
1498	59	2670	338	69	1341	1574	25	14	16	342	29	4	1	11165	14	14	0

NA - Not analyzed.

^{1/} Analytical method used was ASTM D1091-64. All other values by atomic absorption.

TABLE 5. - Simulated boiling range distributions by ASTM Method D-2887
for five used lubricating oils, °C (°F)

Percent	Sample Number				
	1465	1480	1481	1484	1498
IBP	259 (498)	218 (425)	221 (430)	180 (355)	199 (390)
5	343 (649)	291 (555)	332 (630)	257 (495)	343 (649)
10	364 (687)	343 (650)	363 (685)	332 (630)	366 (691)
20	384 (723)	382 (719)	387 (728)	383 (721)	387 (729)
30	401 (753)	403 (758)	404 (759)	406 (762)	404 (759)
40	414 (778)	417 (783)	417 (783)	426 (798)	416 (781)
50	427 (800)	432 (810)	431 (808)	443 (830)	429 (804)
60	439 (822)	448 (838)	446 (834)	462 (863)	441 (825)
70	455 (851)	463 (865)	457 (855)	476 (889)	456 (852)
80	475 (887)	486 (907)	482 (900)	504 (939)	477 (891)
90	504 (940)	520 (968)	510 (950)	534 (993)	509 (948)
95	527 (980)	543 (1010)	535 (995)	556 (1033)	535 (995)
97.6				571 (1060)	
98.4		571 (1060)			
98.7					571 (1060)
99			571 (1060)		
EP	568 (1055)	582 (1080)	577 (1070)	593 (1100)	577 (1070)

EXPERIMENTAL

The starting materials for this study were four fractions of each sample obtained by separating the whole sample through a dual packed silica-alumina gel adsorption column by gradient elution. The only pre-treatment given the five oils was a dehydration step to remove water and gasoline. All other contaminants and additives remained in the oil and were separated along with the hydrocarbon components into four well-defined concentrates: saturates, monoaromatics, diaromatics, and polyaromatic-polar compounds. Percentages throughout the report refer to eluted oil from the adsorption column, normalized to a whole oil basis.

The aromatic fraction concentrates derived from the silica-alumina gel adsorption separation were further subjected to a gel permeation chromatography technique (1) selected to separate each aromatic concentrate into approximately 35 to 40 less complex subfractions. This latter separation is essentially a separation according to molecular size. Certain representative subfractions as determined by Hirsch and coworkers (2) were analyzed by low ionizing voltage mass spectrometry, and assignments of compound types were made using the GPC-MS correlations which had been developed for this specific gel permeation chromatographic column.

The percentage of material at any given mass/charge (m/e) ratio was determined from the ion intensity and tabulated to give a total percentage in the subfraction for each nominal mass Z series. These m/e ratios versus percent total ion intensity were plotted and gave a profile of the distribution. Figure 1 is included as an example of plotting m/e ratios against percent of total ion intensity for the monoaromatic fraction of one of the five oils of this study.

Compound type identification was made by comparing the peak of these distributions with the previously determined GPC-MS correlations of Hirsch.

RESULTS AND DISCUSSION

High resolution mass spectral analyses were made for a few representative subfractions for the purpose of verifying identifications, identifying unknown components, and discovering components that might be present but obscured by the more abundant compounds. The massive amount of interpretation necessary for the data generated by the high resolution mass analyses, weighed against the information obtained from it, made it impractical to process all of the fractions in this manner. However, it can be assumed that the components discovered by the high resolution mass analyses are not limited to the fractions processed.

FIGURE 1. - MS distribution profile of the monoaromatic concentrate from the GPC separation of used oil 1480.

Saturates

Table 6 shows the structure of the saturate fractions and is included in this report for convenient reference, although no further separation was made of the saturate portion of the oils. The average percentage of saturates in these samples was 76.3 percent, which compares with an overall average of 76.7 percent for the 30 used oils previously studied and reported. As shown in table 6, the percentages attributed to each of the ring structures are similar for all five oils.

Monoaromatics

The major compound types found in the monoaromatic fractions of the five representative re-refinery feedstocks were alkylbenzenes and their naphthenologs. The total of these compound types averaged 12.9 percent with the maximum difference between oils being 0.7 percent. The alkyl-, alkylnaphtho-, and alkyldinaphthenobenzenes made up more than half of the percentage attributed to monoaromatics in all five oils. The quantities of all the benzenes were consistently similar for all of the oils analyzed. Table 7 gives a list of all the compound types found in the monoaromatic concentrates of the five analyzed used lube oils and an assignment of quantity of each.

Because of the close similarities found for the major compound types, any differences in the five representative oils would be expected to be in the minor components. In the monoaromatic fraction, only sample 1498 was lacking in arenocyclic sulfides. Since the average percentage of arenocyclic sulfides is only 0.37 percent of the whole oil, the presence of a minute quantity of arenocyclic sulfides in sample 1498 cannot be ruled out. Diarenocyclic sulfides appear in sample 1480 only, but the total amount is less than 0.1 percent and is confined to just one of the analyzed fractions. However, the diarenocyclic sulfides do appear in several of the mass spectral Z series (-20S, -22S, -24S, and -26S) which makes their presence believable. Benzothiophenes were indicated in three of the five oils but the quantity in each oil was less than 0.01 percent. Some unknown compounds appeared in samples 1480 and 1481 but the quantities were extremely small.

Although a small quantity of diaromatic compound types (diarenocyclic sulfides and benzothiophenes) were found in the monoaromatic portion of the used oils, the fact that these compound types amounted to less than 0.1 percent is indicative of an effectual separation.

Diaromatics

Alkylnaphthalenes and their naphthenologs are the major compound types found in the diaromatic fractions of the five oils. The total alkylnaphthalenes varied between oils by 0.5 percent and averaged 3.2 percent. Quantitative assignments for all of the compound types found in the diaromatic portion of the whole oils are shown in table 8.

TABLE 6. - Semiquantitative distributions of compound types found in saturate fractions derived from five representative used lubricating oils selected for detailed compositional study

Sample Number	Percent of whole sample	O rings, percent ^{1/}	1 ring, percent	2 rings, percent	3 rings, percent	4 rings, percent
1465	75.51	25.0 (18.9)	27.0 (20.4)	18.5 (14.0)	11.9 (9.0)	17.7 (13.3)
1480	76.37	25.3 (19.4)	26.3 (20.1)	18.9 (14.4)	12.3 (9.4)	17.2 (13.2)
1481	76.78	25.4 (19.5)	26.8 (20.6)	18.5 (14.2)	12.1 (9.3)	17.2 (13.2)
1484	76.14	25.2 (19.2)	25.9 (19.7)	19.0 (14.4)	13.0 (9.9)	16.9 (12.9)
1498	76.28	26.1 (19.9)	30.9 (23.6)	19.2 (14.7)	10.9 (8.3)	12.9 (9.8)
Average of 30 samples	76.7	26.3 (20.2)	27.2 (20.9)	18.8 (14.4)	12.0 (9.2)	15.7 (12.0)
Standard Deviation	±1.6	±1.7	±1.2	±0.4	±0.8	±1.4

^{1/} - Percentages given as percent of saturates, with percent of whole oil in parentheses.

TABLE 7. - Semiquantitative analysis and compound type assignments for the monoaromatic portion of five representative used lubricating oils

Mass .Z Series	Probable major compound types	Percent of whole oil sample					Average
		Sample 1465	Sample 1480	Sample 1481	Sample 1484	Sample 1498	
-6	Alkylbenzenes	2.34	2.53	2.30	2.27	2.48	2.38
-8	Alkylindanaphthenobenzenes	2.74	2.86	2.66	2.82	2.96	2.81
-10	Alkylindanaphthenobenzenes	2.59	2.54	2.41	2.60	2.40	2.51
-12	Alkylindanaphthenobenzenes	2.23	2.11	2.13	2.13	1.97	2.11
-14	Alkylindanaphthenobenzenes	1.54	1.45	1.45	1.49	1.37	1.46
-16	Alkylpentanaphthenobenzenes	1.05	.94	.92	1.04	.83	.96
-18	Alkylhexanaphthenobenzenes	.59	.56	.50	.60	.52	.55
-20	Alkylheptanaphthenobenzenes	.083	.072	.088	.17	.18	.12
-22	Alkylactanaphthenobenzenes	.027	.023	.023	.024	.048	.029
-24	Alkylnonanaphthenobenzenes	-- ^{1/}	--	--	--	.006	.001
	Percent, major compounds	13.190	13.085	12.481	13.144	12.764	12.930
Probable minor compound types							
	<u>Arenocyclic sulfides</u>						
-16S, -6S ₂	Alkylbenzopentacyclic sulfides, alkylthienocyclic sulfides	.143	.092	.091	.142	--	.094
-18S, -8S ₂	Alkylbenzohexacyclic sulfides, alkylthienobicyclic sulfides	.184	.126	.124	.149	--	.117
-20S, -10S ₂	Alkylbenzohexacyclic sulfides, alkylthienotricyclic sulfides	--	trace	--	--	--	--
-8S, -12S ₂	Alkylbenzocyclic sulfides, alkylthienotetracyclic sulfides	--	--	--	--	--	--
-10S, -14S ₂	Alkylbenzobicyclic sulfides, alkylthienopentacyclic sulfides	--	.025	.053	.098	--	.035
-12S, -16S ₂	Alkylbenzotricyclic sulfides, alkylthienohexacyclic sulfides	--	.029	.062	trace	--	.018
-14S, -18S ₂	Alkylbenzotetracyclic sulfides, alkylthienoheptacyclic sulfides	.027	.060	.079	trace	--	.033
	<u>Diarenocyclic sulfides</u>						
-20S, -24S ₂	Alkylidibenzotetracyclic sulfides, alkylbenzothienoheptacyclic sulfides, alkylidithienotricyclic sulfides	--	.024	--	--	--	.005
-22S, -12S ₂	Alkylidibenzopentacyclic sulfides, alkylbenzothienocyclic sulfides, alkylidithienotetracyclic sulfides	--	.024	--	--	--	.005
-24S, -14S ₂	Alkylidibenzohexacyclic sulfides, alkylbenzothienobicyclic sulfides, alkylidithienopentacyclic sulfides	--	.022	--	--	--	.004
-26S, -16S ₂	Alkylidibenzohexacyclic sulfides, alkylbenzothienotricyclic sulfides, alkylidithienohexacyclic sulfides	--	.016	--	--	--	.003
-20S ₃							
	<u>Benzothiophenes</u>						
-10S	Alkylbenzothiophenes	.003	--	--	.003	.002	.002
-12S	Alkylindanaphthenbenzothiophenes	.004	--	--	.006	.003	.003
-12	Unknown	--	.016	--	--	--	.003
-16	Unknown	--	--	.046	--	--	.009
-18	Unknown	--	--	.046	--	--	.009
-18, -4	Unknown	.071	.090	.062	.104	--	.065
	Percent, minor compounds	0.432	0.524	0.563	0.502	0.005	0.405
	Total percent	13.62	13.61	13.04	13.65	12.77	13.34

^{1/} Dash indicates no evidence of compound type was found.

TABLE 8. - Semiquantitative analysis and compound type assignments for the diaromatic portion of five representative used lubricating oils

Mass Z Series	Probable major compound types	Percent of whole oil sample					Average
		Sample 1465	Sample 1480	Sample 1481	Sample 1484	Sample 1498	
-12	Alkyl naphthalenes	0.418	0.539	0.380	0.563	0.491	0.478
-14	Alkyl diphenylalkanes ^{1/}	.104	--2/	.037	--	.055	.039
-14	Alkyl naphthenonaphthalenes and/or alkyl diphenylalkanes or alkyl biphenyls ^{1/}	.682	.836	.696	.800	.675	.738
-16	Alkyl dinaphthenonaphthalenes and/or alkyl naphthenodiphenylalkanes or alkyl naphthenobiphenyls ^{1/}	.715	.713	.730	.702	.635	.699
-18	Alkyl trinaphthenonaphthalenes and/or alkyl dinaphthenodiphenylalkanes or alkyl dinaphthenobiphenyls ^{1/}	.529	.516	.590	.516	.475	.525
-20	Alkyl tetranaphthenonaphthalenes and/or alkyl trinaphthenodiphenylalkanes or alkyl trinaphthenobiphenyls	.313	.406	.351	.341	.276	.337
-22	Alkyl pentanaphthenonaphthalenes and/or alkyl tetranaphthenodiphenyl- alkanes or alkyl tetranaphthenobiphenyls	.197	.243	.222	.227	.170	.212
-24	Alkyl hexanaphthenonaphthalenes and/or alkyl pentanaphthenodiphenyl- alkanes or alkyl pentanaphthenobiphenyls	.110	.149	.141	.147	.101	.130
-26	Alkyl heptanaphthenonaphthalenes and/or alkyl hexanaphthenodiphenyl- alkanes or alkyl hexanaphthenobiphenyls	.011	--	--	--	.016	.005
-28	Alkyl octanaphthenonaphthalenes and/or alkyl heptanaphthenodiphenyl- alkanes or alkyl heptanaphthenobiphenyls	.005	--	--	--	--	.001
	Percent, major compounds	3.084	3.402	3.147	3.296	2.894	3.165
Probable minor compound types							
	<u>Benzothiophenes</u>						
-105	Alkyl benzothiophenes ^{1/}	.207	.253	.274	.203	.180	.223
-125	Alkyl naphthenobenzothiophenes	.084	.123	.152	.120	.101	.116
-145	Alkyl dinaphthenobenzothiophenes	.071	.083	.107	.084	.079	.085
-165	Alkyl trinaphthenobenzothiophenes	.004	.043	.018	.011	.009	.017
-185	Alkyl tetranaphthenobenzothiophenes	--	possibly	.013	.004	.007	.005
-165	Alkyl trinaphthenobenzothiophenes and/or arenocyclic sulfides	--	--	.127	--	--	.025
-185	Alkyl tetranaphthenobenzothiophenes and/or arenocyclic sulfides	--	--	.024	--	--	.005
	<u>Dibenzothiophenes</u>						
-165	Alkyl dibenzothiophenes	3/	.007	--	.003	--	.002
-185	Alkyl naphthenodibenzothiophenes	3/	.002	--	.006	--	.002
-205	Alkyl dinaphthenodibenzothiophenes	3/	--	--	.012	--	.002
-225	Alkyl trinaphthenodibenzothiophenes	3/	--	--	trace	--	--
	<u>Aryl sulfides</u>						
-105, -145 ₂	Dinaphthenoalkylphenyl sulfides, pentanaphthenoalkylthienyl sulfides	--	--	--	.009	--	.002
-125, -165 ₂	Trinaphthenoalkylphenyl sulfides, hexanaphthenoalkylthienyl sulfides	--	--	--	.003	--	.001
-145, -45 ₂	Tetranaphthenoalkylphenyl sulfides, alkylthienyl sulfides	--	--	--	.005	--	.001
	<u>Arenocyclic sulfides</u>						
-165, -65 ₂	Alkyl benzopentacyclic sulfides, alkylthienocyclic sulfides	--	.021	.019	.026	--	.013
-185, -85 ₂	Alkyl benzohexacyclic sulfides, alkylthienobicyclic sulfides	--	.026	.023	.034	--	.017
-205, -105 ₂	Alkyl benzohexacyclic sulfides, alkylthienotricyclic sulfides	--	.031	.027	.041	--	.020
-85, -125 ₂	Alkyl benzocyclic sulfides, alkylthienotetracyclic sulfides	--	.033	--	.044	--	.015
-105, -145 ₂	Alkyl benzobicyclic sulfides, alkylthienopentacyclic sulfides	--	--	--	.034	--	.007
	<u>Benzofurans</u>						
-10(O)	Alkyl benzofuran	--	.002	--	--	--	--
-12(O)	Alkyl naphthenobenzofuran	--	.003	--	--	--	.001
-4	Unknown	--	.003	--	.011	--	.003
-6	Unknown	--	--	--	.002	--	--
-8	Unknown	--	--	--	--	--	--
-10	Unknown	--	--	--	.002	.010	.002
-12	Unknown	.009	--	--	.002	--	.002
-14	Unknown	--	--	--	--	--	--
-16	Unknown	--	--	--	--	--	--
-18	Unknown	--	--	--	.002	--	--
-20	Unknown	--	--	--	.002	--	--
-22	Unknown	--	--	--	.001	--	--
	Percent, minor compounds	0.375	0.630	0.784	0.661	0.386	0.567
	Total percent	3.46	4.03	3.93	3.96	3.28	3.73

^{1/} High resolution mass spectral data indicate the presence of alkyl benzofurans.

^{2/} Dash indicates no evidence of compound type found.

^{3/} Alkyl benzothiophenes were present but were not separated from hydrocarbon components.

The minor compound types identified in the diaromatic portion include benzothiophenes in all five oils, trace quantities of dibenzothiophenes in three oils, and arenocyclic sulfides, an overlap of monoaromatics, in three of the five oils. Aryl sulfides, a monoaromatic type, appeared at low molecular weights in sample 1484 as did most of the unidentified components listed as unknown in table 8.

High resolution mass spectral analyses revealed the presence of small quantities of benzo-furans and dibenzofurans which could not be separated from hydrocarbon components in the low voltage MS-GPC correlations.

Carbazoles and their naphthenologs were noted from the 70-eV data of the GPC fractions and confirmed by the high resolution mass data in the diaromatic portion of all five oils. These, however, were not included in the semiquantitative assessment since they were present in only very small quantities.

Polyaromatic and Polar

Table 9 gives the semiquantitative assignment of probable compound types found in the polyaromatic-polar portion of the five used lubricating oils. The assignment is indicative of the complexity of the concentrate. The aromatic hydrocarbon, the probable compound type, is listed first followed by those compound types having similar molecular weights which might be present or which might be confused with the primary component.

There is more variance in quantities of compound types in the polyaromatic-polar fractions than in the other two aromatic fractions, but the types of compounds present are consistent in all five sample feedstocks with few exceptions.

The major compound type found in the polyaromatic-polar concentrate was benzoindenes (acenaphthalenes, fluorenes, etc.) and their naphthenologs. These compounds averaged 4.3 percent of the whole oil with a maximum difference of 1.3 percent between the five feedstocks.

Dibenzothiophenes/naphthothiophenes, as well as cyclic sulfides and aryl sulfides, appeared in all five oils. The identification of an arenocyclic sulfide in sample 1484 and thien-indenes in sample 1465 is subject to question and is suggested only as a possibility. In spite of the fact that aryl sulfides and arenocyclic sulfides are monoaromatic by definition, they were eluted with the polyaromatic-polar concentrate which would indicate a polar behavior. There were more unknown compounds in the polyaromatic-polar fraction than in the other concentrates, especially in sample 1484. This is reasonable considering that these feedstocks contained all the contaminants and by-products of usage, as well as some of the original additives.

Carbazoles were found in the polyaromatic-polar fraction of all five oils but were not included in the semiquantitative analysis. The quantity of carbazoles is conservatively

TABLE 9. - Semiquantitative analysis and compound type assignments for the polyaromatic-polar portion of five representative used lubricating oils

Mass Z Series	Probable major compound types	Percent of whole oil sample					
		Sample 1465	Sample 1480	Sample 1481	Sample 1484	Sample 1498	Average
-16	Alkylbenzoindenes	0.944	0.731	0.716	0.405	0.688	0.697
-18	Alkyl-naphthenobenzoindenes and/or alkylphenanthrenes/anthracenes plus (-20[O]) alkylindaphthenobenzofuran plus (-22S) alkyltrindaphthenodibenzothiophenes	1.206	.930	.997	.604	1.038	.955
-20	Alkylindaphthenobenzoindenes and/or alkyl-naphthenophenanthrenes/anthracenes and/or alkylphenylnaphthalenes and/or alkyl-diacenaphthalenes	1.059	.932	.968	.691	1.109	.952
-22	Alkyltrindaphthenobenzoindenes and/or alkylindaphthenophenanthrenes/anthracenes and/or alkyl-naphthenodiacenaphthalenes and/or alkyl-dibenzoindenes and/or alkylpyrenes	.991	.791	.749	.774	1.067	.874
-24	Alkyltetranaphthenobenzoindenes and/or alkyltrindaphthenophenanthrenes/ anthracenes and/or alkylindaphthenodiacenaphthalenes and/or alkyl- naphthenodibenzoindenes and/or alkyl-naphthenopyrenes and/or alkyl- benzophenanthrenes/anthracenes plus (βS) cyclic sulfides	.449	.531	.505	.488	.410	.477
-26	Alkylpentanaphthenobenzoindenes and/or alkyltetranaphthenophenanthrenes/ anthracenes and/or alkyltrindaphthenodiacenaphthalenes and/or alkyl- naphthenodibenzoindenes and/or alkyltetranaphthenodibenzoindenes and/or alkyl-naphthenophenanthrenes/anthracenes	.211	.161	.213	.412	.174	.234
-28	Alkylhexanaphthenobenzoindenes and/or alkylpentanaphthenophenanthrenes/ anthracenes and/or alkyltrindaphthenodibenzoindenes	.153	.108	.152	.303	.105	.164
-30	Alkylheptanaphthenobenzoindenes and/or alkylhexanaphthenophenanthrenes/ anthracenes and/or alkyltetranaphthenodibenzoindenes	.091	--1/	--	--	.027	.024
-32	Alkyl-octanaphthenobenzoindenes and/or alkylheptanaphthenophenanthrenes/ anthracenes and/or alkylpentanaphthenodibenzoindenes	.008	--	--	--	--	.002
	Percent, major compounds	5.112	4.184	4.300	3.677	4.618	4.378
Probable minor compound types							
-14	Naphthenonaphthalenes plus (-16[O]) alkyl-dibenzofuran	.071	.040	.022	.027	.046	.041
	<u>Dibenzothiophenes/naphthothiophenes</u>						
-16S	Alkyl-dibenzothiophenes/naphthothiophenes	.172	.162	.175	.112	.151	.154
-18S	Alkyl-naphthenodibenzothiophenes/naphthothiophenes	.136	.125	.155	.102	.114	.126
-20S	Alkylindaphthenodibenzothiophenes/naphthothiophenes	.039	.148	.217	.195	.035	.127
-22S	Alkyltrindaphthenodibenzothiophenes/naphthothiophenes	.018	.059	.047	.143	.054	.064
-24S	Alkyltetranaphthenodibenzothiophenes/naphthothiophenes	--	--	--	.145	.034	.036
	<u>Thienoindenes</u>						
-14S	Alkylthienoindenes	.015	--	--	--	--	.003
-16S	Alkyl-naphthenothienoindenes	.028	--	--	--	--	.006
-18S	Alkylindaphthenothienoindenes	.013	--	--	--	--	.003
	<u>Cyclic sulfides</u>						
βS	Alkylcyclic sulfides	.185	.045	.087	.072	.240	.126
-2S	Alkylbicyclic sulfides	.176	.270	.392	.204	.412	.291
-4S	Alkyltricyclic sulfides	.251	.335	.446	.291	.335	.336
-6S	Alkyltetra-cyclic sulfides	--	--	--	.208	.247	.091
-8S	Alkylpentacyclic sulfides	--	--	--	.211	.077	.058
-10S	Alkylhexacyclic sulfides	--	--	--	.144	.065	.042
-12S	Alkylheptacyclic sulfides	--	--	.051	.094	--	.029
	<u>Aryl sulfides</u>						
-4S ₂ , -14S	Alkylthienyl sulfides, alkyltetranaphthenophenyl sulfides	.078	.057	.038	.061	.146	.076
-6S ₂ , -16S	Alkyl-naphthenothienyl sulfides, alkylpentanaphthenophenyl sulfides	.179	.294	.130	.066	.238	.181
-8S ₂ , -18S	Alkylindaphthenothienyl sulfides, alkylhexanaphthenophenyl sulfides	.080	.205	.063	--	.245	.119
	<u>Arenocyclic sulfides</u>						
-6S ₂ , -16S	Alkylthienocyclic sulfides, alkylbenzopentacyclic sulfides	--	--	--	--	--	--
-8S ₂ , -18S	Alkylthienobicyclic sulfides, alkylbenzohexacyclic sulfides	--	--	--	--	--	--
-10S ₂ , -20S	Alkylthienotricyclic sulfides, alkylbenzohexacyclic sulfides	--	--	--	.084	--	.017
-16	Unknown	.060	--	--	--	.091	.030
-18	Unknown	.058	--	--	.034	.114	.041
-20	Unknown	.174	.016	.023	.024	.045	.056
-20	Unknown	.068	--	--	--	--	.014
-22	Unknown	.012	--	--	--	--	.002
-24	Unknown	.056	.041	.084	.025	.039	.049
-24	Unknown	.011	.011	--	.041	.049	.022
-24	Unknown	--	--	--	.079	--	.016
-26	Unknown	.197	--	--	.057	.095	.070
-26	Unknown	--	--	--	.056	--	.011
-28	Unknown	.199	--	--	.013	.054	.053
-28	Unknown	--	--	--	.055	.105	.032
-28	Unknown	--	--	--	.039	--	.008
	Percent, minor compounds	2.276	1.808	1.930	2.582	3.051	2.329
	Total percent	7.39	5.99	6.23	6.26	7.67	6.71

1/ Dash indicates no evidence of compound type found.

estimated to be less than 0.6 percent of the whole oil based on an analysis of sample 1465 which contained the most nitrogen of all samples studied. The carbazoles in sample 1465 accounted for more than one-half of the nitrogen. On the basis of one nitrogen atom per molecule, the calculated value was 0.3 percent of the whole oil compared with 0.52 percent determined by Kjeldahl analysis.

High resolution mass spectral analyses confirmed the presence of carbazoles and oxygenates in all samples. There was also some evidence for additional sulfur compounds. However, the oxygenates and additional sulfur compounds in most cases were indistinguishable in the low resolution mass data from the identified compounds and therefore, the quantity was not assessed.

Nitrogen and Sulfur

Nitrogen and sulfur content was determined on each whole aromatic concentrate for all five of the feedstocks. Table 10 shows the experimentally determined quantities for nitrogen and sulfur. Also included in table 10 is the calculated value for sulfur, based on one sulfur atom per molecule, from the assigned quantities of sulfur compounds. The sum total of sulfur calculated from the assignments agrees very well with the experimentally determined sulfur values on the whole concentrate, which indicates that the sulfur compound analyses made by GPC-mass spectral correlations were reasonably correct. Although no quantitative assignments were made for the nitrogen compounds, the presence of carbazoles was noted and confirmed by high resolution mass analysis.

SUMMARY AND CONCLUSIONS

Major compound types listed in tables 6, 7, 8, and 9 account for an average of 96.7 percent of the whole oil sample. This percentage was consistent for all five samples with the greatest difference between samples being 0.9 percent. This leaves only 3.3 percent of the whole sample to be attributed to minor quantities of sulfur compounds, nitrogen compounds, oxygenates, and other hydrocarbons. This 3.3 percent also includes several unidentified compound types. Despite the fact that some of these minor compound types are associated with the major types because they were not resolved, any real difference between the five used oils could be expected to be within this 3.3 percent. Note the comparatively small percentage of the whole oil attributed to each of the minor compound types. Even in this area, many of the identified compound types were found in all five oils.

Figure 2 is a graphic presentation of the compositional structure of the five used lubricating oil feedstocks studied. The quantity of each compound type can easily be compared relative to the whole oil and relative to each of the other four oils.

TABLE 10. - Nitrogen and sulfur content of five
representative used lubricating oils

Sample Number	Nitrogen, percent	Sulfur, percent	
		Experimental	Calculated ^{1/}
MONOAROMATIC			
1465	0.0	0.14	0.17
1480	.004	.18	.19
1481	.006	.20	.18
1484	.005	.11	.18
1498	.006	.09	.004
DIAROMATIC			
1465	NA	0.93	0.87
1480	NA	1.62	1.22
1481	NA	1.36	1.46
1484	NA	1.02	1.15
1498	NA	.80	.84
POLYAROMATIC AND POLAR			
1465	0.516	1.72	1.48
1480	.374	3.87	2.23
1481	.409	3.18	2.21
1484	.364	2.40	2.61
1498	.500	2.08	2.17

NA - Not analyzed.

^{1/} Calculated on the basis of one sulfur atom per molecule.

FIGURE 2. - A graphic presentation of the compositional structure of five used lubricating oils.

This detailed characterization of five representative used oil composites is believed to document further the similarity of composition of re-refinery feedstocks. Appropriate processing technology and adequate quality control should produce consistent products within a given plant as well as between plants that composite feedstocks through the normal accumulation of collections in a tank. This is not to say that product between re-refineries will be consistent to the extent that a common additive formulation would serve the entire industry, nor is it to say that products would be consistent between re-refineries using different technologies. These data do imply, however, that an acceptable reclamation procedure with adequate quality controls should produce a consistent product from that plant with only minimal effects from feedstock variations.

ACKNOWLEDGMENT

The authors are indebted to Dr. Gene P. Sturm, Jr., of the Bartlesville Energy Research Center of the U.S. Energy Research and Development Administration for the high resolution mass spectral analyses and his assistance in the interpretation of the data. The work of J. E. Dooley, project leader, and others of the mass spectral group for the low voltage analyses is also greatly appreciated.

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