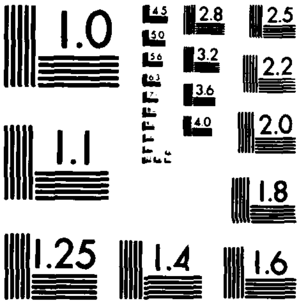
AD-A112 098   MONSANTO RESEARCH CORP DAYTON OHIO DAYTON LAB   F/G 11/8
TURBINE ENGINE LUBRICANT RECLAMATION.(U)
DEC 81   G L BEEMSTERBOER, R J BRUNS   F33615-79-C-2052
UNCLASSIFIED   MRC-DA-1057   AFWAL-TR-81-2053   NL

1 OF 2
AD
A112098



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

(12)

AFWAL-TR-81-2053

TURBINE ENGINE LUBRICANT RECLAMATION

George L. Beemsterboer and Richard J. Bruns
MONSANTO RESEARCH CORPORATION
Dayton Laboratory
Dayton, Ohio 45407

December 1981

Interim Report for Period 1 September 1979 - 1 February 1981

Approved for public release; distribution unlimited.

AERO PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

GABeane IV
G. A. BEANE IV
Project Engineer

Howard F Jones
HOWARD F. JONES
Chief, Lubrication Branch

FOR THE COMMANDER

Benito P. Botteri
BENITO P. BOTTERI, Asst Chief
Fuels and Lubrication Division
Aero Propulsion Laboratory

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFWAL/POSL, WPAFB, OH 45433 to help us maintain a current mailing list."

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER AFWAL-TR-81-2053

2. GOVT ACCESSION NO. AD-A112098

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle) TURBINE ENGINE LUBRICANT RECLAMATION

5. TYPE OF REPORT & PERIOD COVERED Interim Report 1 September 1979 - 1 February 1981

6. PERFORMING ORG. REPORT NUMBER MRC-DA-1057

7. AUTHOR(s) George L. Beemsterboer and Richard J. Bruns

8. CONTRACT OR GRANT NUMBER(s) F33615-79-C-2052

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Monsanto Research Corporation
Dayton Laboratory, 1515 Nicholas Road
Dayton, OH 45407

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 3048 06 11

11. CONTROLLING OFFICE NAME AND ADDRESS
Aero Propulsion Laboratory
AFWAL/POSL/G. A. Beane IV
Wright-Patterson AFB, OH 45433

12. REPORT DATE December 1981

13. NUMBER OF PAGES 121

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

15. SECURITY CLASS. (of this report) Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Reclamation
Synthetic turbine oils
MIL-L-7808
Additives
Esters
Distillation
Adsorbents
Reclaimed base stock
Gas chromatography
High performance liquid chromatography
Pilot-plant scale-up

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A distillation and adsorption treatment for reclaiming used MIL-L-7808 turbine oils was investigated. A viable additive package was tested on different MIL-L-7808 type virgin base stocks. Fifteen used oils were analyzed by acid number, high performance liquid chromatography, and gas chromatography. A distillation process utilizing caustic (sodium hydroxide) pretreatment was developed on 500-ml and 13-litre scales. Adsorption treatment of distilled oils with calcium hydroxide followed by attapulgus clay was examined. Preparations for

20. ABSTRACT (continued)

large-scale (25 and 250 gal) reclamations are currently under way to elucidate the validity of caustic distillation and adsorbent treatment parameters.

FOREWORD

This technical report was prepared by Monsanto Research Corporation (MRC), 1515 Nicholas Road, Dayton, Ohio 45407. The effort was sponsored by the Aero Propulsion Laboratory (APL), Air Force Wright Aeronautical Laboratories (AFWAL), Air Force Systems Command, Wright-Patterson AFB, Ohio, under Contract No. F33615-79-C-2052 for the period 1 September 1979 to 1 February 1981. The work herein was accomplished under Project 3048, Task 304806, Work Unit No. 30480611, "Turbine Engine Lubricant Reclamation," with Mr. G. A. Beane IV, AFWAL/POSL, as Project Engineer.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF TABLES

SUMMARY

The objective of this program is to improve upon the purification process and additive replenishment package, developed in an earlier program (Technical Report AFAPL-TR-78-50), for reclaiming used synthetic turbine engine oil meeting MIL-L-7808G specifications. The program is also to demonstrate the effectiveness of the total process by successfully reclaiming 12 batches of used synthetic oil representing a variety of MIL-L-7808 compositions.

Base stocks formulated by five different manufacturers were selected for MIL-L-7808H testing using MRC's proposed additive package.

Conditions were established for optimizing a sodium hydroxide distillation followed by calcium hydroxide and attapulgus clay treatment. The use of activated charcoal was found to provide no distinct performance advantages over nonuse.

Two reclaimed and reformulated used oil samples were evaluated using selected MIL-L-7808H tests, with encouraging results.

Presently we are preparing for pilot-plant scaleup for reclamation of various used oil lots which were supplied by the Aero Propulsion Laboratory.

1. INTRODUCTION

The re-refining and reuse of petroleum base oils has been a successful standard practice in railroad, automotive, and aircraft industries for many years. More recently, the reclamation of synthetic aviation oils has proven successful in those applications involving a specific and known formulation. However, this is not representative of normal U.S. military aircraft operational experience where numerous brands of specification products consisting of widely differing base stocks and additive packages are normally mixed in service. An estimated total of up to one million quarts of used ester based oils are generated each year and could be collected for reclamation. Reclamation of these oils for reuse in military aircraft turbine engines represents a significant potential source of supply in the event of serious availability problems. Furthermore, reclamation could offer a significant cost savings if the technique developed is also economical and technically effective. Currently available information suggests that the ester base stocks are not significantly degraded during use. Therefore, there is potential for recovery of large portions of the used oils.

An earlier program, described in AFAPL-TR-78-50, demonstrated the potential feasibility of recycling used MIL-L-7808G oils to a satisfactory performance level.

The objective of this program is to improve upon the purification process and additive replenishment package described in AFAPL-TR-78-50, and to demonstrate the effectiveness of the total process by successfully reclaiming 12 batches of used synthetic oil representing a wide variety of MIL-L-7808 compositions.

2. SUMMARY OF THE FIRST OIL RECLAMATION PROGRAM

A process for reclaiming of a used synthetic turbine engine oil meeting MIL-L-7808G specifications was developed. Techniques for characterizing new and used 7808G oils were developed and applied. The components of a reclamation process were defined and the technical feasibility of the process was established.

Two additive packages developed for use in diester/triester base stock mixtures showed considerable promise.

A cost analysis of the process indicated that a continuous batch reclamation process at the 5000-gallon batch size would be cost effective.

Details of the first oil reclamation program can be found in Technical Report AFAPL-TR-78-50, "Reclamation of Synthetic Turbine Engine Oil Mixtures."

3. RESULTS AND DISCUSSION

The object of this program is to further improve the reclamation process developed earlier (summarized in Figure 1), define the variables within the process, verify the additive replenishment package, and demonstrate the effectiveness of the total process by reclaiming 12 batches of used synthetic oil to MIL-L-7808H specifications.

3.1 USED OIL CHARACTERIZATION

To determine how widely properties vary between used oil lots and to decide under what conditions some lots should be rejected for reclamation, Aero Propulsion Laboratory (APL) furnished us with 15 different used oil lots. Each lot was examined and characterized (See Appendix C for analysis procedures) by gas chromatography (GC), high performance liquid chromatography (HPLC), infrared (IR) analysis, and acid number. Table 1 lists the quantities and acid numbers of the 15 used oil lots received.

3.1.1 Infrared Spectrophotometry

Infrared (IR) analysis was performed on filtered and dried samples of the used oils to see if any gross differences were observable which would interfere with reclamation.

Examination of the IR spectra of used oils 0-79-01 through 0-79-15 and a diester base stock (Figures 2 through 7) show that all are quite similar and made from mixtures of both diester and triester type base stocks. All 15 oil samples show characteristic absorption at 1350 cm^{-1} for the diester and at 720 cm^{-1} for the typical

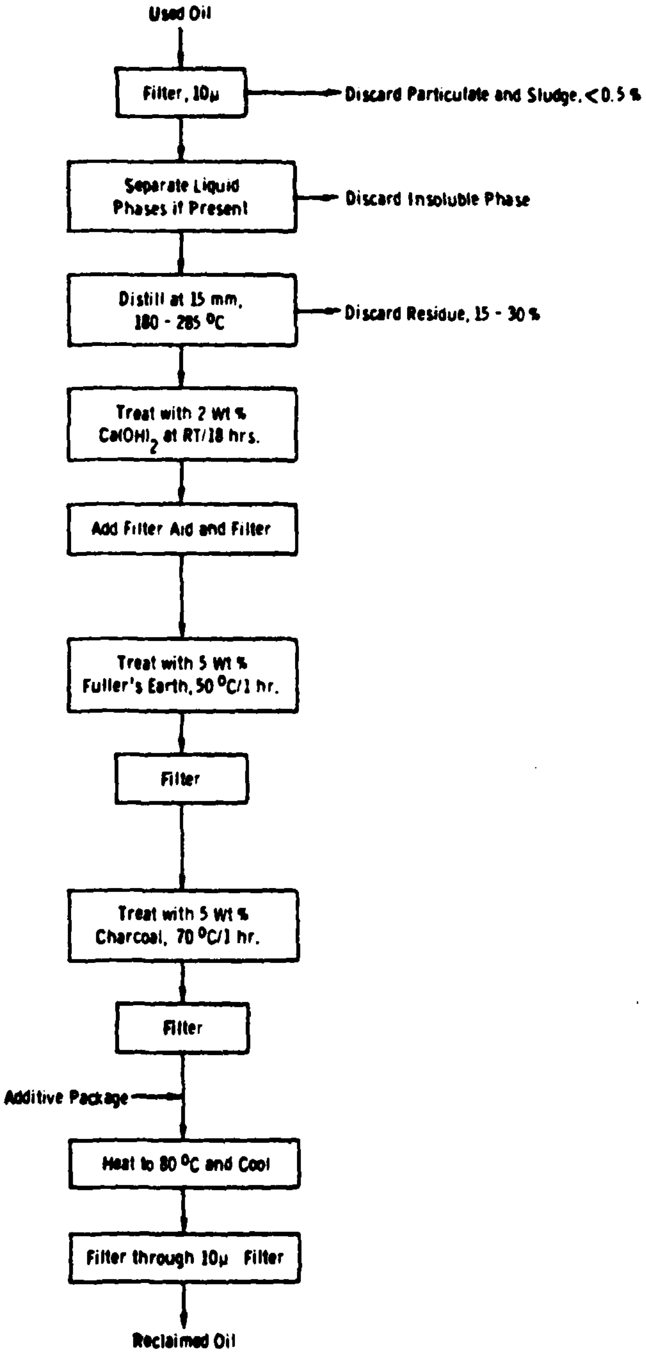
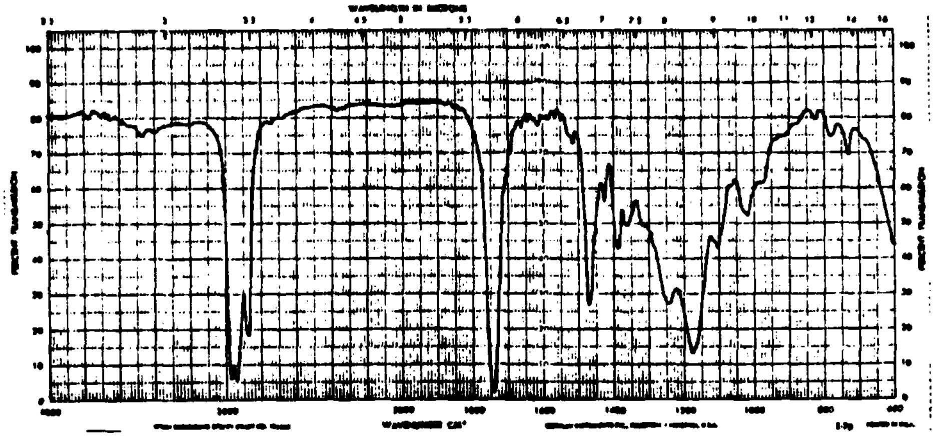


Figure 1. Reclamation process, first program.

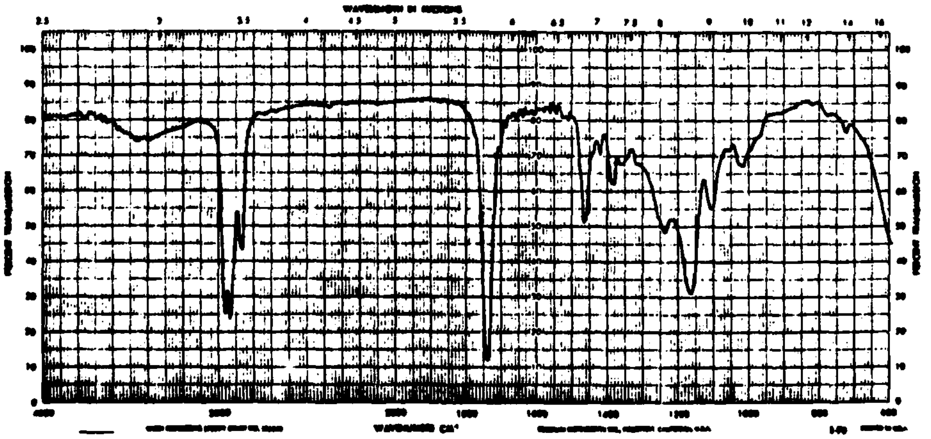
TABLE 1. ACID NUMBERS AND QUANTITIES OF OILS RECEIVED FROM APL

Oil number	Quantity, gal	Acid number
0-79-01	35	0.42
0-79-02	55	0.47
0-79-03	∼35	0.43
0-79-04	∼35	14.45
0-79-05	∼35	23.78
0-79-06	55	1.02
0-79-07	∼35	1.09
0-79-08	55	1.15
0-79-09	55	0.65
0-79-10	55	0.64
0-79-11	55	0.88
0-79-12	55	0.52
0-79-13	55	0.63
0-79-14	55	1.50
0-79-15	55	1.72



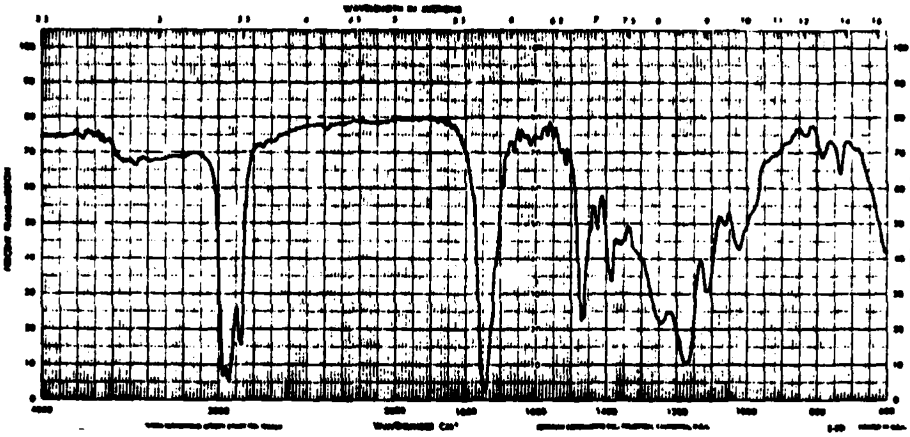
0-79-01

0-79-02

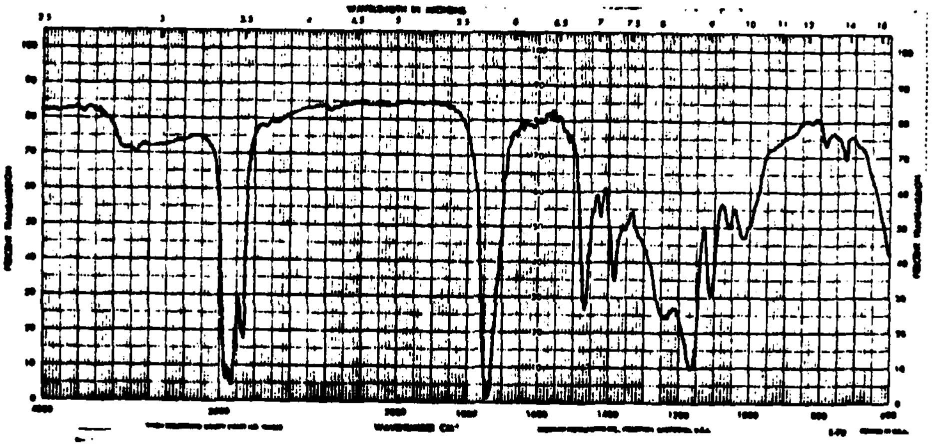


0-79-03

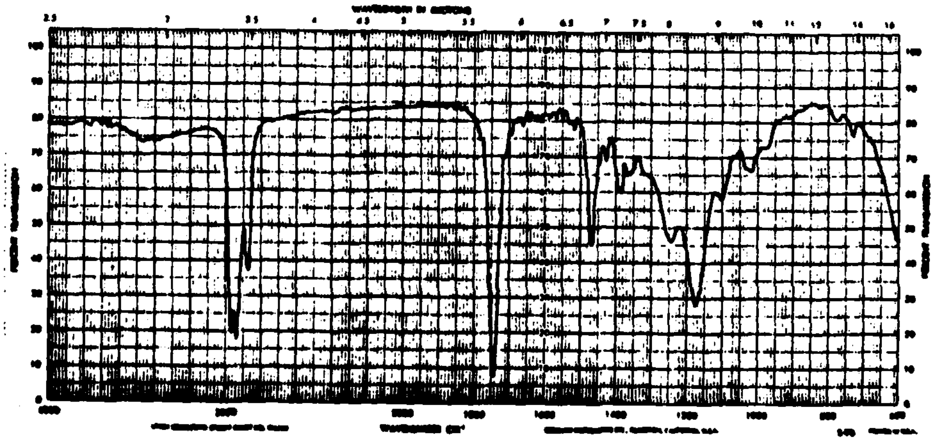
Figure 2. Infrared spectra of used oils.



0-79-04

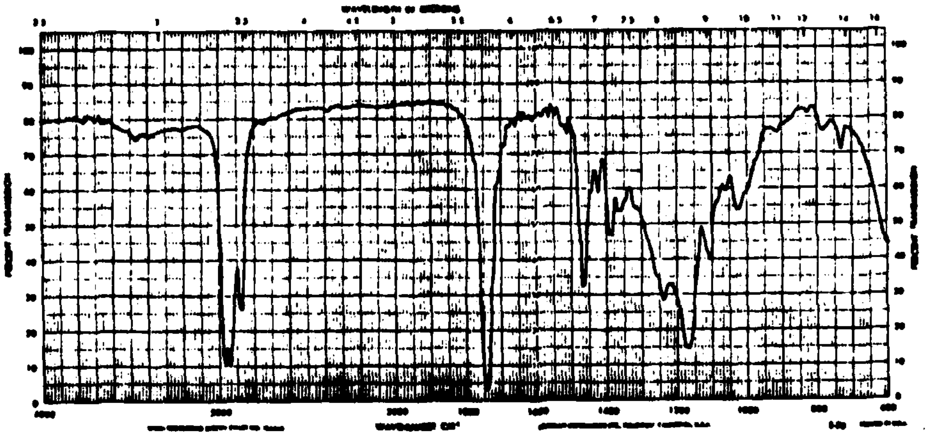


0-79-05

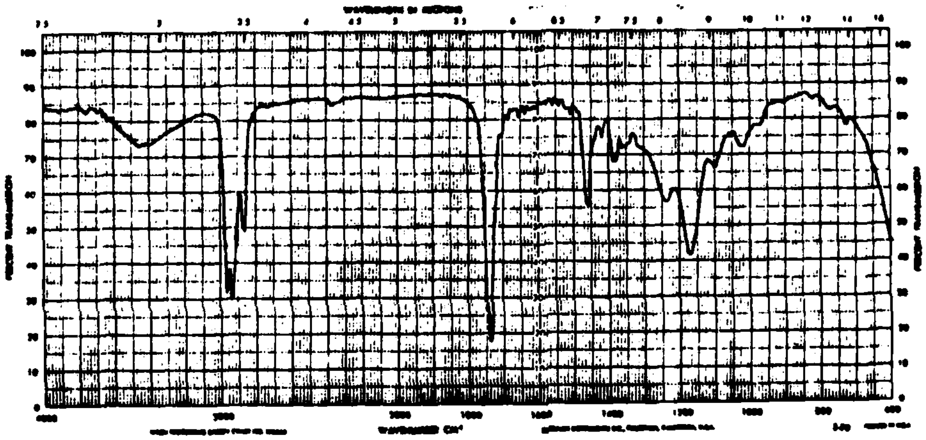


0-79-06

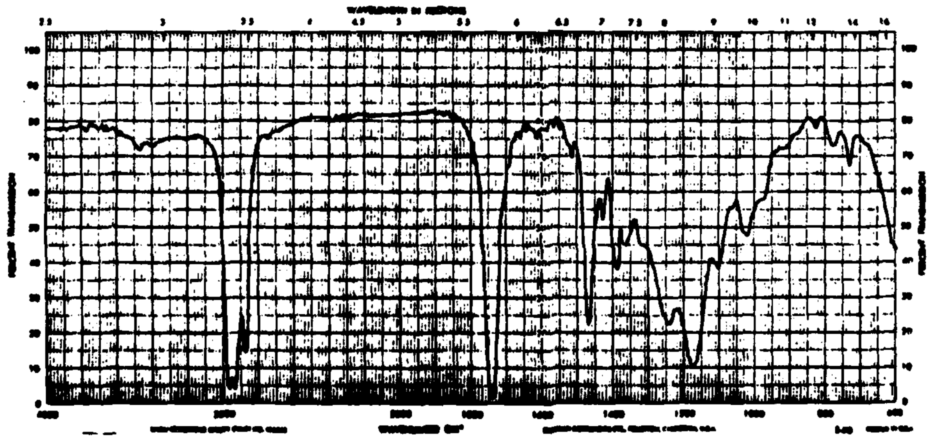
Figure 3. Infrared spectra of used oils.



0-79-07

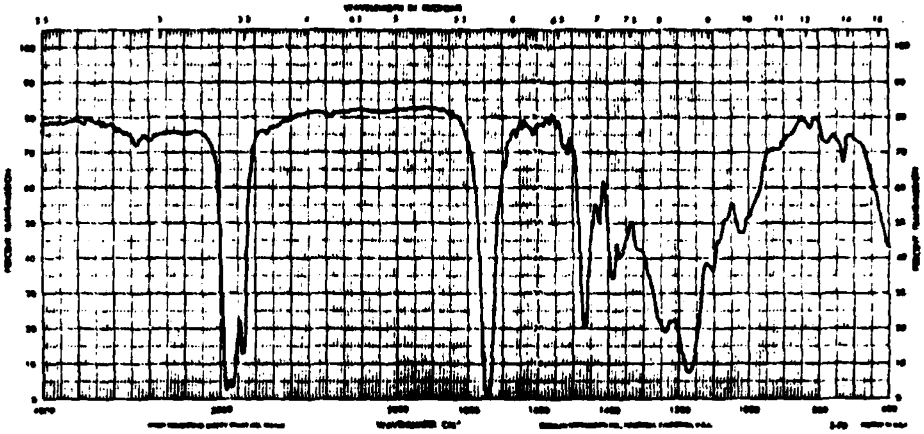


0-79-08

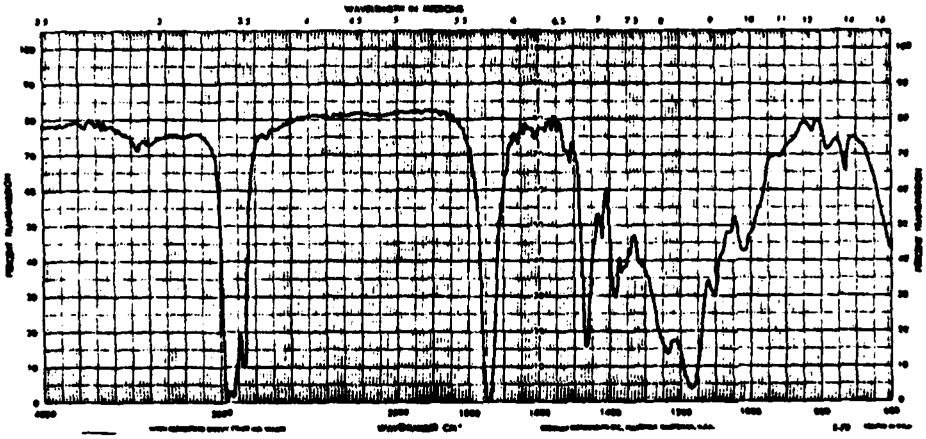


0-79-09

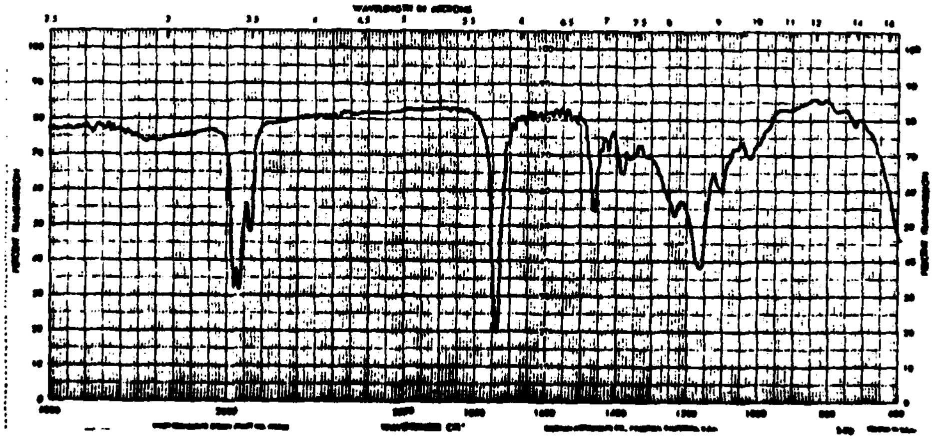
Figure 4. Infrared spectra of used oils.



0-79-10

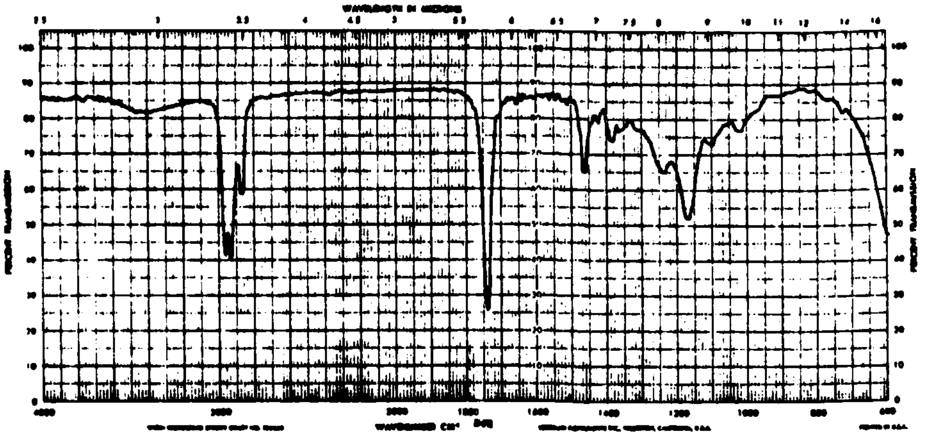


0-79-11

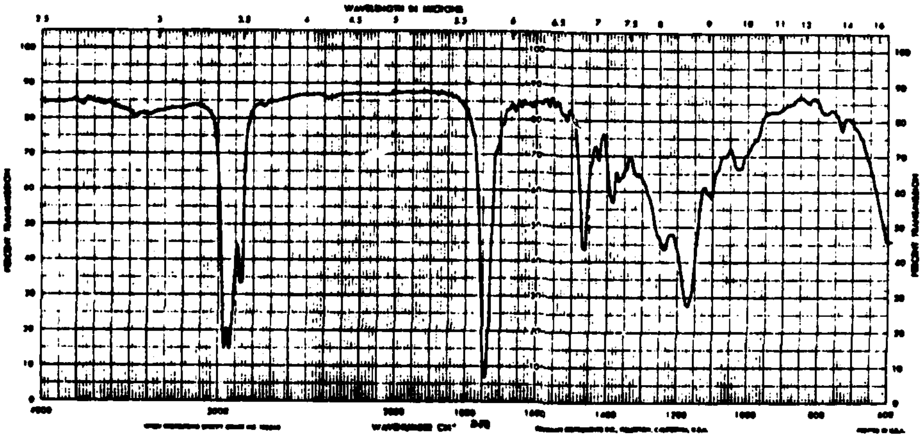


0-79-12

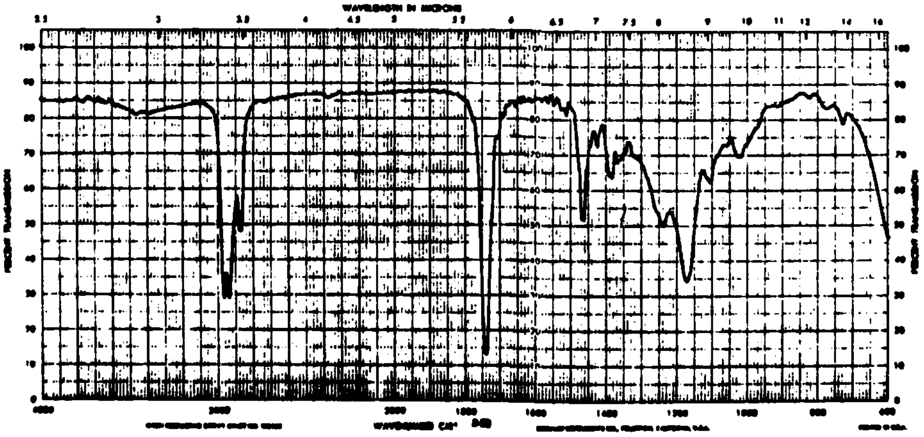
Figure 5. Infrared spectra of used oils.



0-79-13



0-79-14



0-79-15

Figure 6. Infrared spectra of used oils.

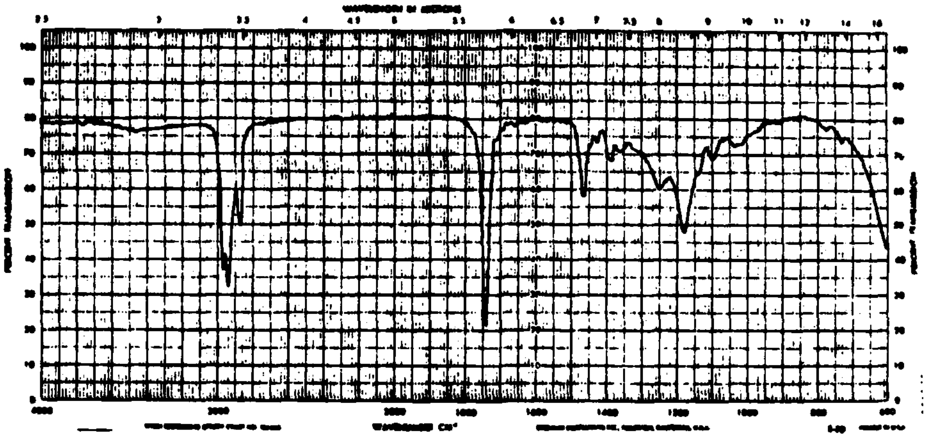


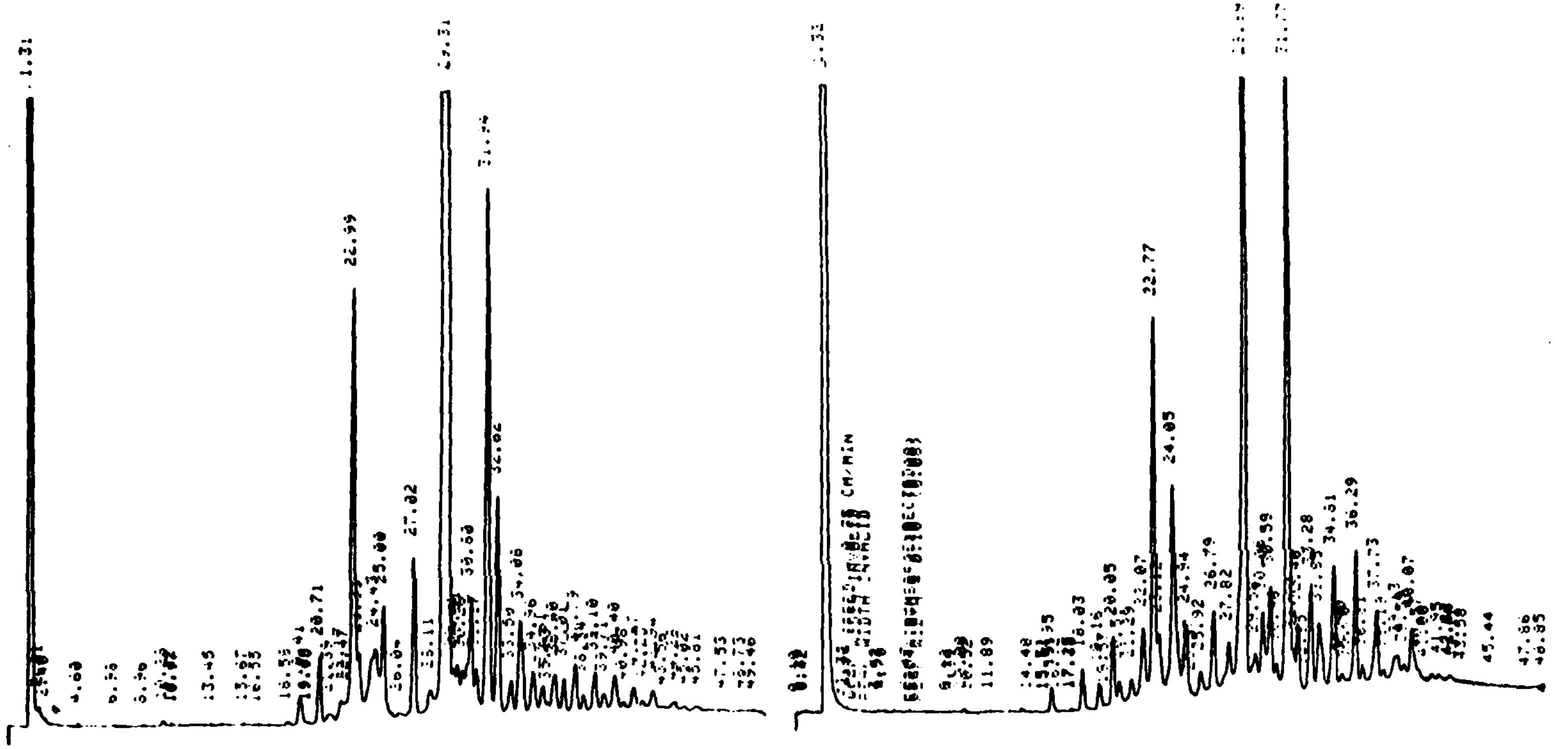
Figure 7. Infrared spectrum of commercially available di-2-ethylhexyl azelate base stock.

triester. Oils 0-79-03, -04, -05, and -09 show absorption at about 1100 cm^{-1}. This absorption is quite strong in 0-79-05 and is present to a lesser degree in samples 0-79-03, -04, and -09. The remaining oils show absorption in this area to a still lesser degree. This absorption is no doubt associated with the C-O-C bond in the ester, and its shape is influenced by the type of acid structure in the ester.

The IR spectra for all these oils suggest they are composed of di and tri esters, the diester portion being quite similar to the di-2-ethylhexyl azelate virgin base stock shown in Figure 7.

3.1.2 Gas Chromatography

Gas chromatography (GC) was also used to characterize the used oils. The chromatograms of the 15 used oils are shown in Figures 8 through 15. Also shown (Figure 16) is the chromatogram for a commercially available diazelate base stock. The major component of this base stock, which eludes at ∿28.22 min, and the minor peaks at ∿20.54, 22.76, 24.83, 26.85, 30.62, 32.4, and 34.07 min are seen in every sample of used oil that has been

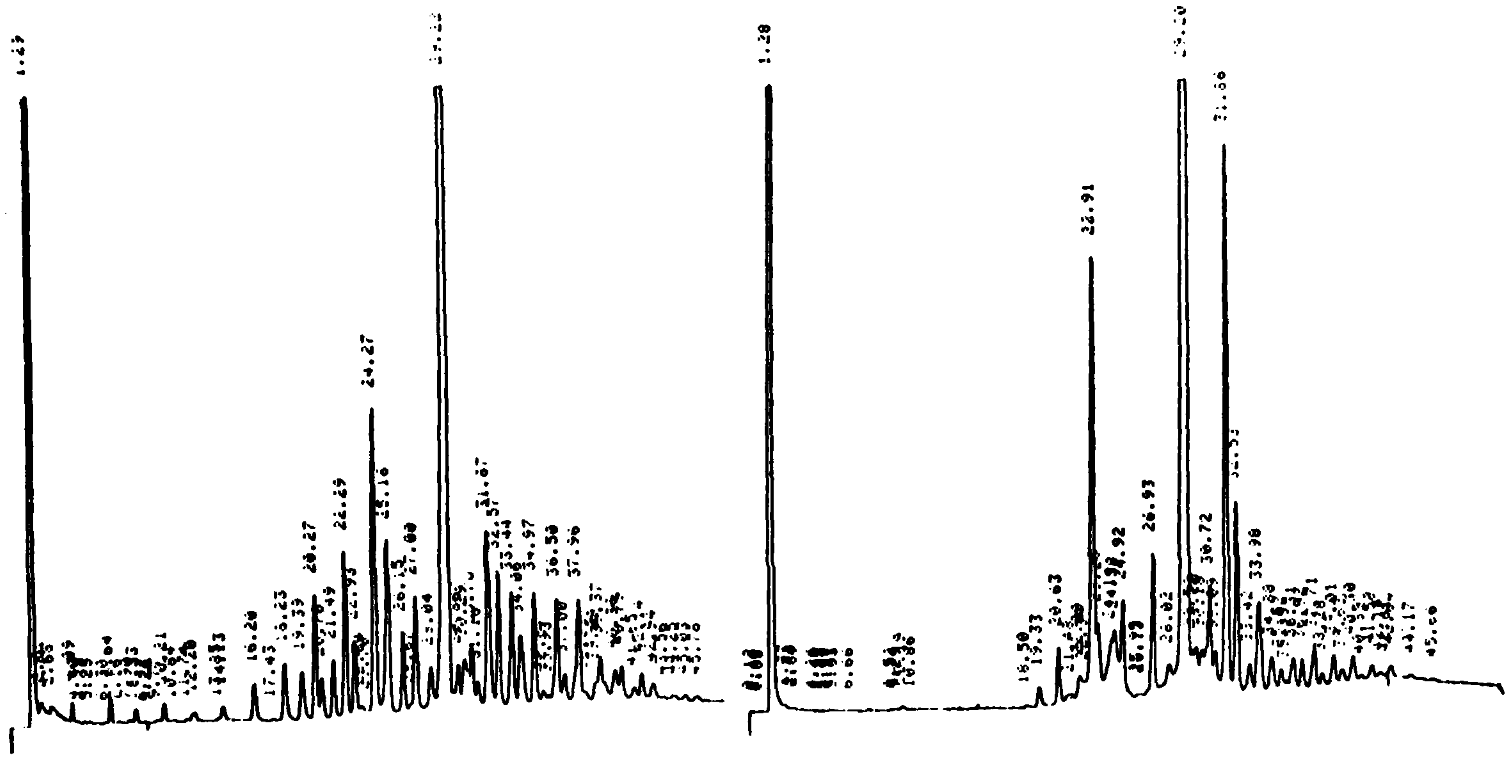


0-79-01

0-79-03

Figure 8. Gas chromatograms of used oils.

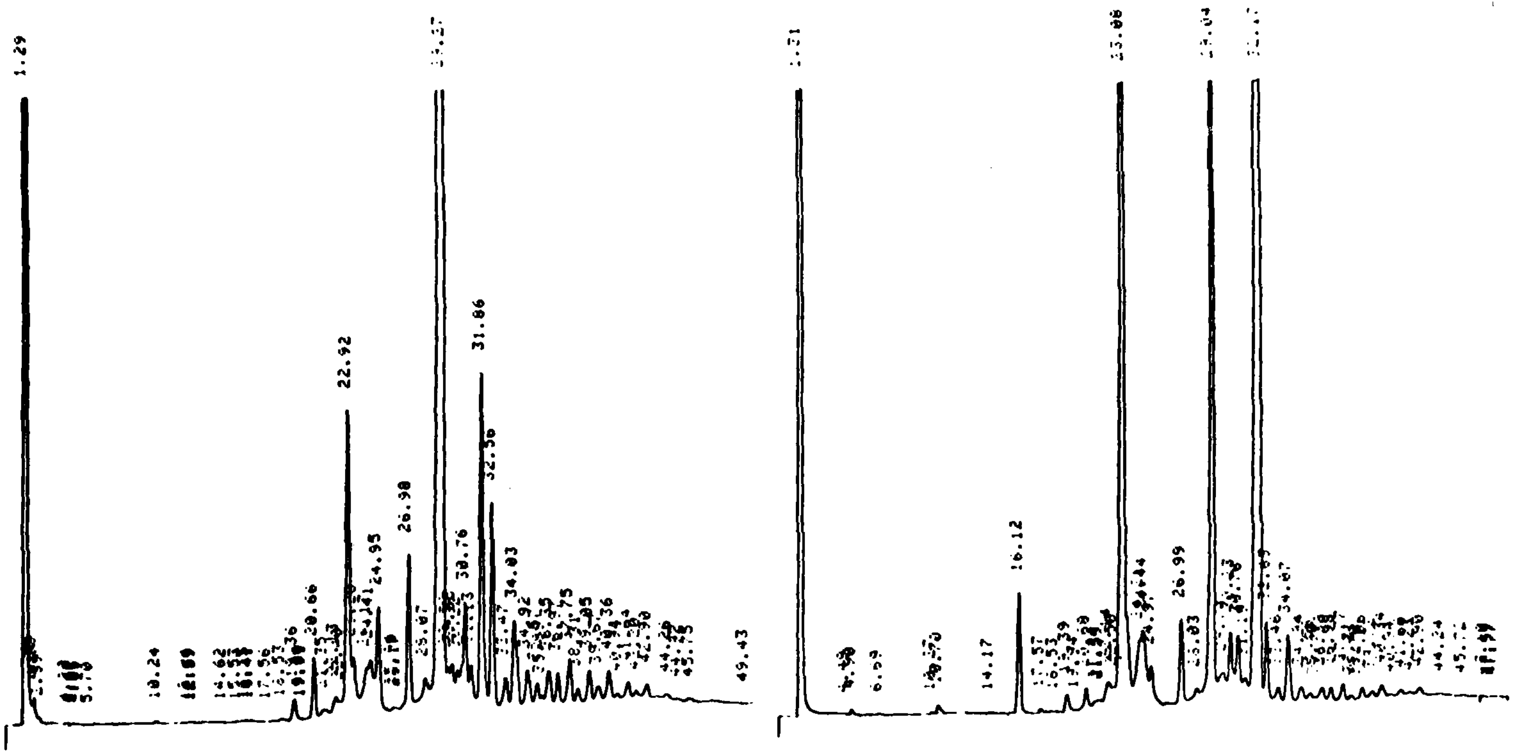
Copy available to DTIC does not permit fully legible reproduction



0-79-04

0-79-07

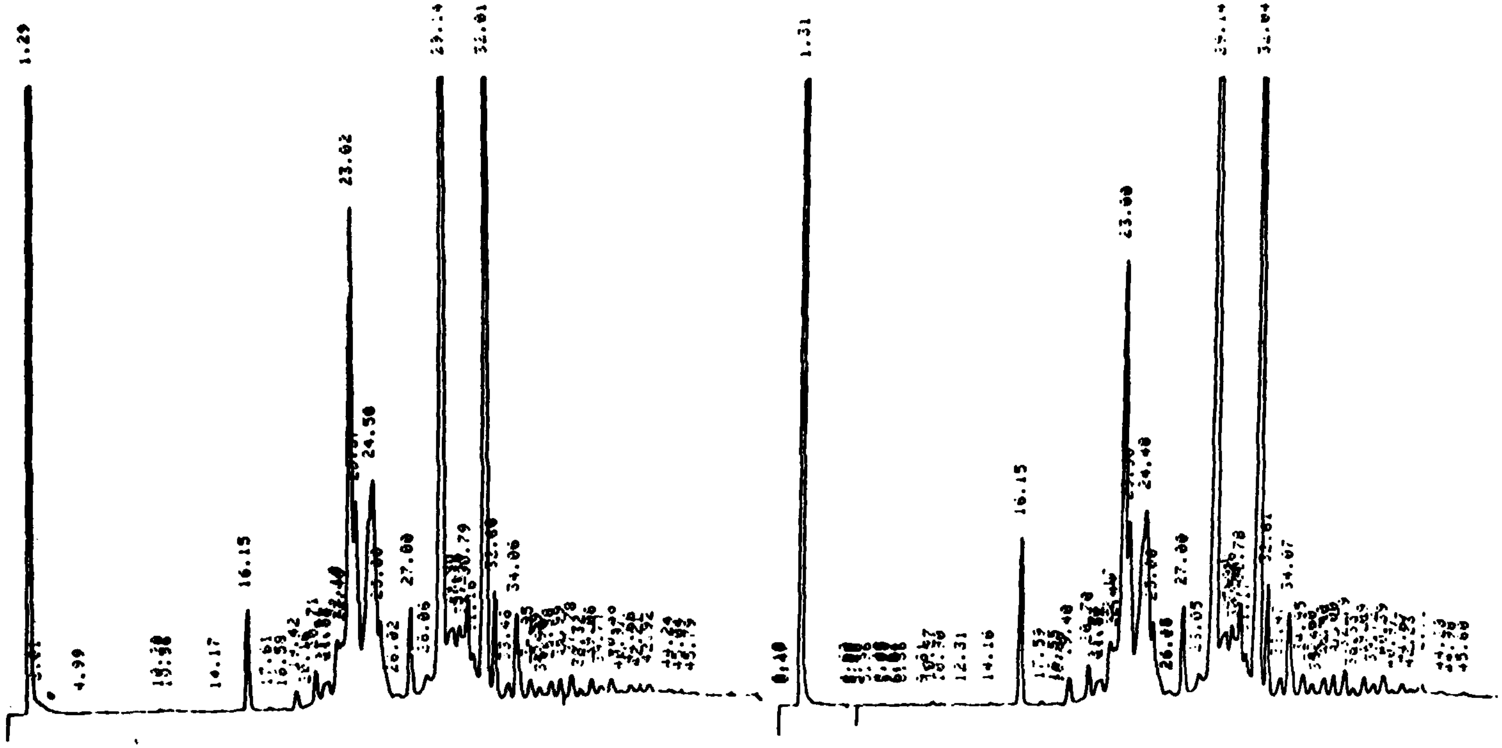
Figure 9. Gas chromatograms of used oils.



0-79-08

0-79-09

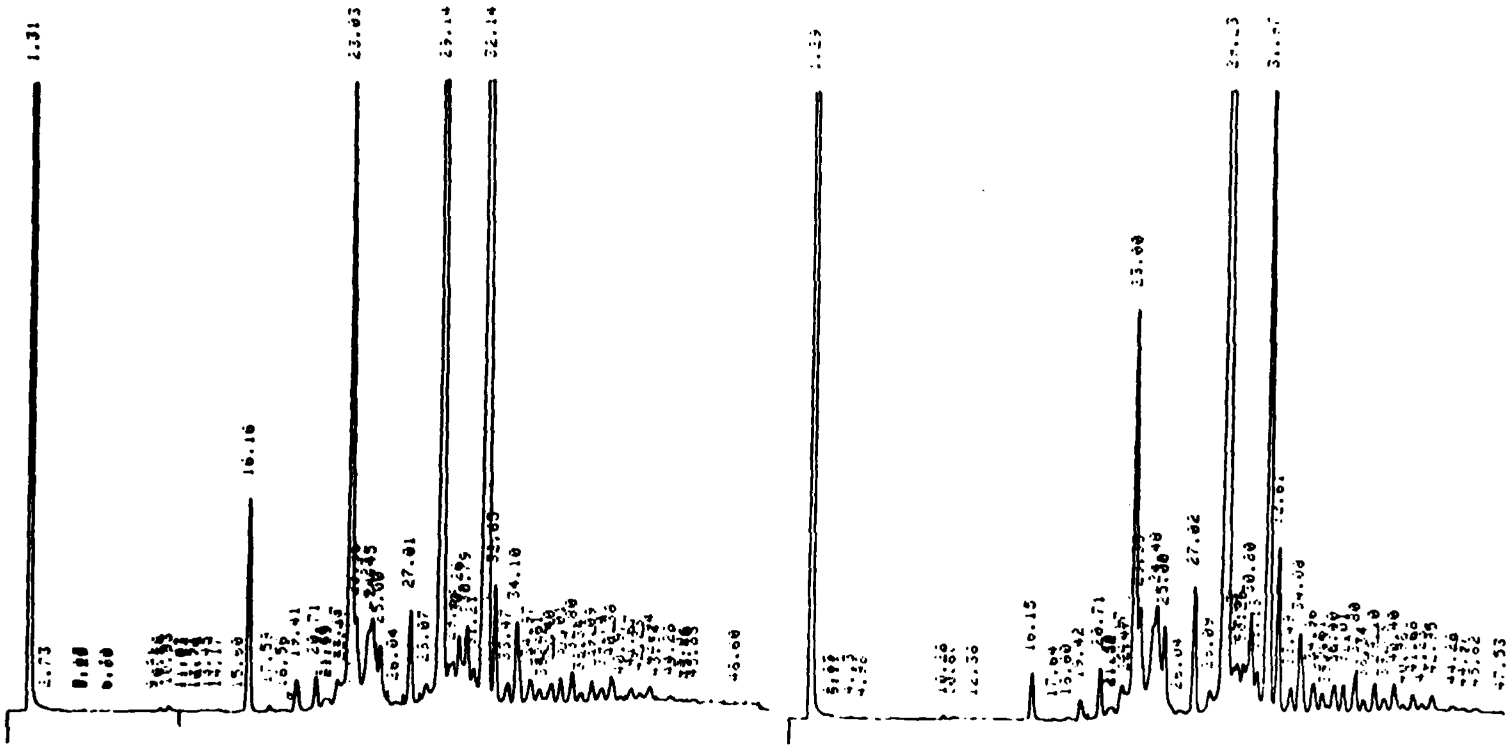
Figure 10. Gas chromatograms of used oils.



0-79-10

0-79-11

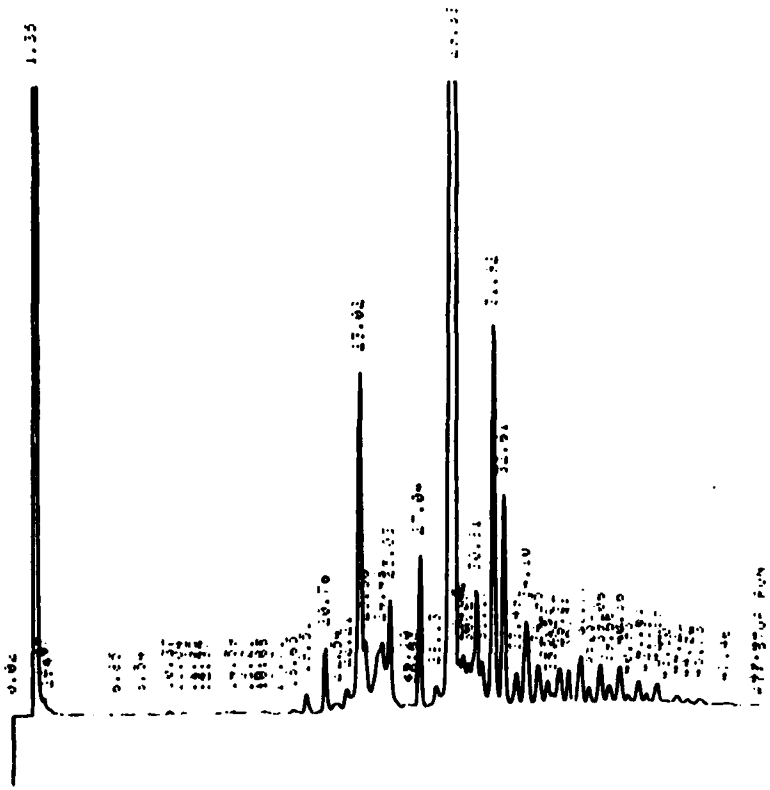
Figure 11. Gas chromatograms of used oils.



0-79-12

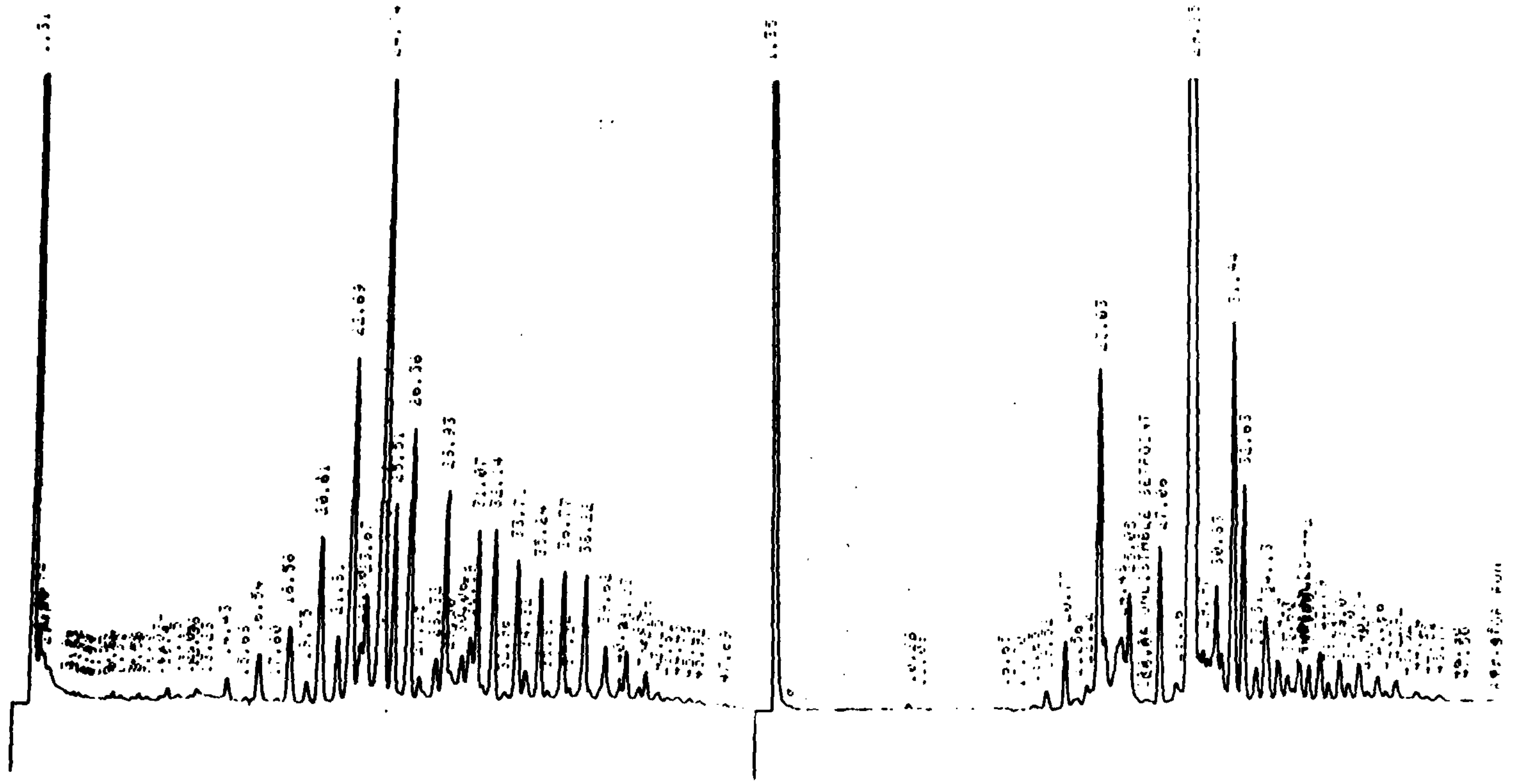
0-79-13

Figure 12. Gas chromatograms of used oils.



0-79-02

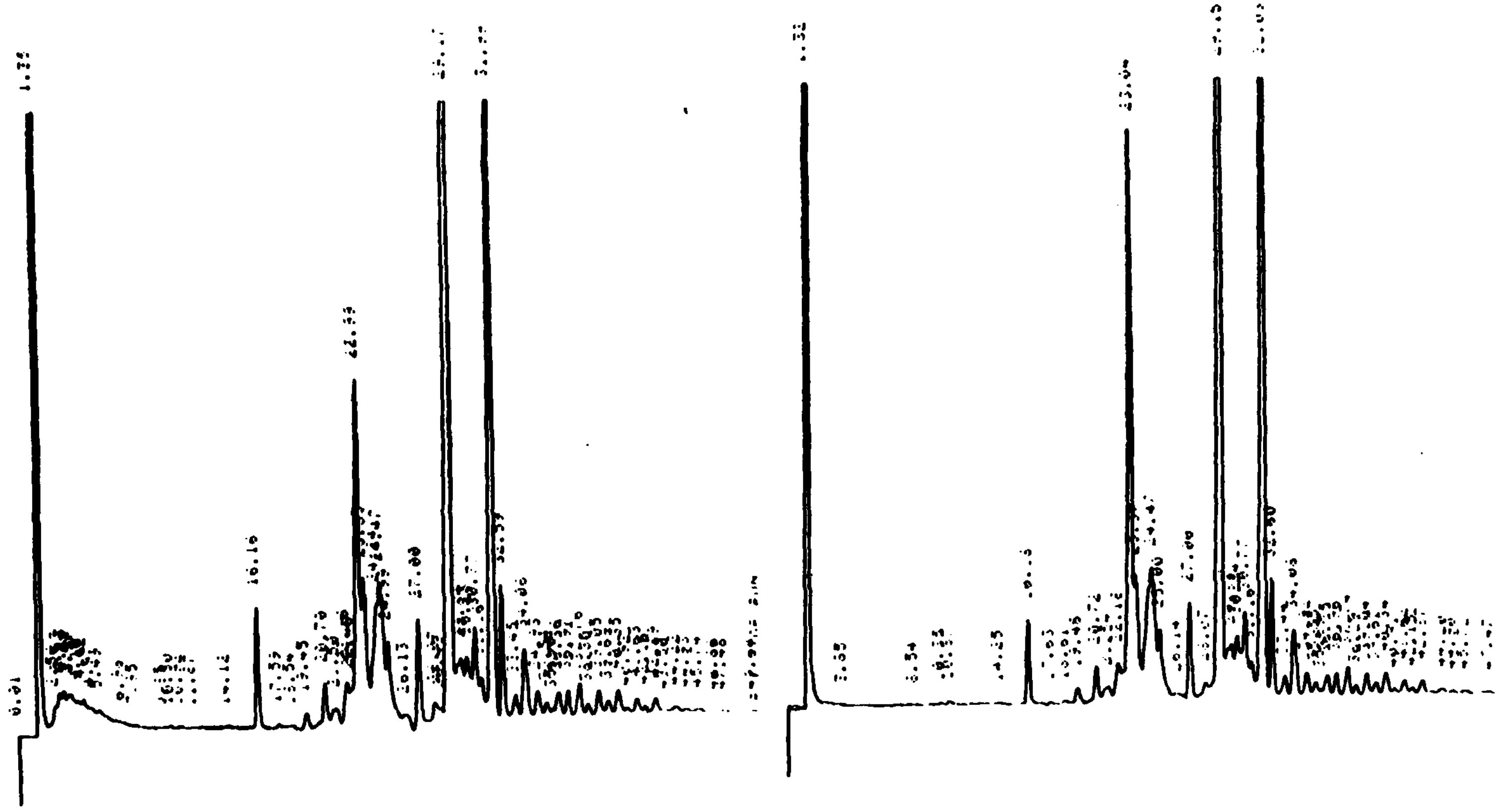
Figure 13. Gas chromatogram of used oils.



0-79-05

0-79-06

Figure 14. Gas chromatograms of used oils.



0-79-14

0-79-15

Figure 15. Gas chromatograms of used oils.

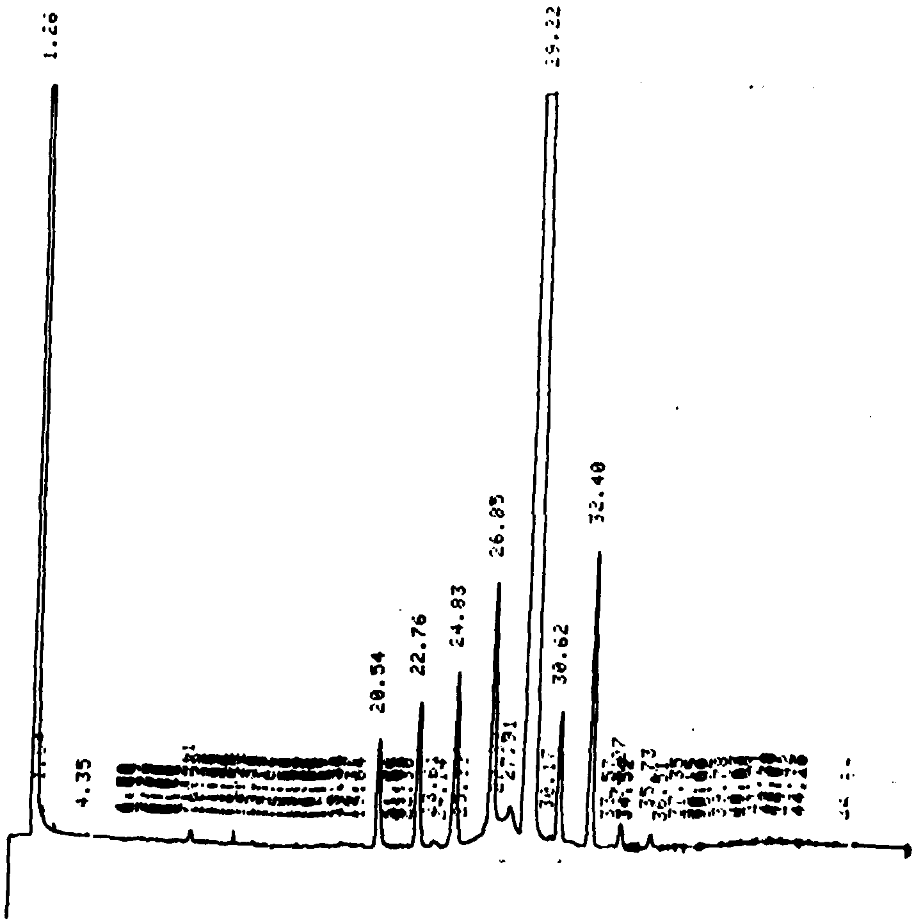


Figure 16. Gas chromatogram of commercially available di-2-ethylhexyl azelate base stock.

analyzed. All analyzed oil samples show peaks corresponding to those of the commercial diester but in varying concentrations. These oils are apparently based on mixtures of several components, some of which are quite high boiling in all the samples, but particularly in 0-79-03 ,-05, and -04.

Such close similarities exist between oil samples 0-79-01, 0-79-07, and 0-79-08 that they may be from the same base stock. Oil samples 0-79-09, 0-79-10, 0-79-11, 0-79-12, and 0-79-13, showing only minor differences, are very similar in composition to each other. Peak analysis of possible diester components suggests that in oils 0-79-03 and 0-79-04 approximately 48% of the composition is due to diester; in 0-79-01, 0-79-07, and 0-79-08 diester comprises approximately 70% of the composition. Of the remaining ten oils approximately 45% of the composition is due to diester.

3.1.3 High Performance Liquid Chromatography

Samples which were used for gas chromatographic analysis were examined by high performance liquid chromatography (HPLC) to detect aromatic additives and breakdown products and to establish patterns, if any, for the used oils.

Basic patterns emerged, showing many similarities between all oils. Samples 0-79-01, -02, -06, -07, -08, -10, -11, -12, -13, -14, and -15 are very similar. Sample 0-79-03 is unique in that its gross appearance is that of an almost unused oil. Samples 0-79-04 and 0-79-05 are similar, showing high concentrations of cresols. Note that these two oils had very high acid numbers, possibly attributable to the high cresol concentration at approximately 24+ min. Sample 0-79-09 is also unique and not readily comparable with the other 14 oils. Representative chromatograms of each group are shown in Figures 17 and 18. Chromatograms of all the used oils are provided in Appendix D.

3.2 OIL CHARACTERIZATION

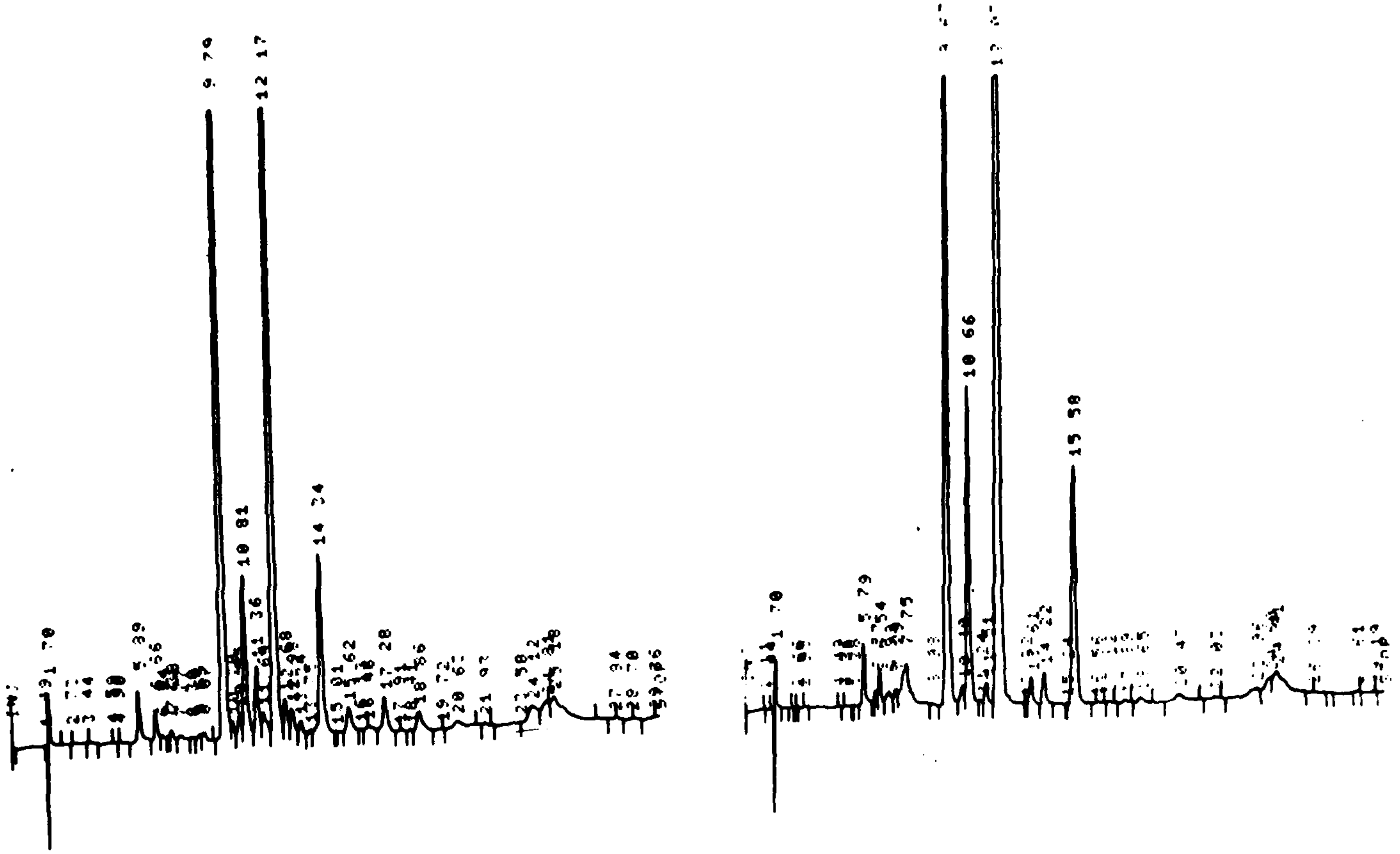
Six new oils, ATL 9118 through 9123, supplied by AFAPL represent new MIL-L-7808H that could ultimately be found in current used oil mixtures. These new oils were analyzed by HPLC and GC. Among the six oils, only four patterns were seen.

Three oils showed the same HPLC pattern: ATL 9118, 9119, and 9121 (the pattern is represented in Figure 19). They have peaks with the same retention times (rt's) as 4,4'-di-octyldiphenylamine (DODPA) or triphenyl phosphite (TPP), approximately 9.5-10 min; a peak corresponding to the rt's of 3,7-dioctylphenothiazine or N-phenyl-α-naphthylamine approximately 12.0-12.5 min; and a group of peaks corresponding the rt's of tricresyl phosphate and other cresols, 24.0 to 26 min. Sample ATL 9123 (Figure 20) has an additional major peak that corresponds to the rt of phenothiazine, approximately 15.7 min.

Samples ATL 9120 and 9122 (Figure 21) have certain identifiable peaks and, as of yet, major unidentified peaks. Many of these additive peaks are seen in the used oils also, but absolute identification was not completed.

GC's of the new oils are presented in Figures 22, 23, and 24. Molecular weight distribution in ATL 9118 and 9121, also between 9120 and 9123, would suggest possibly the same base stock components.

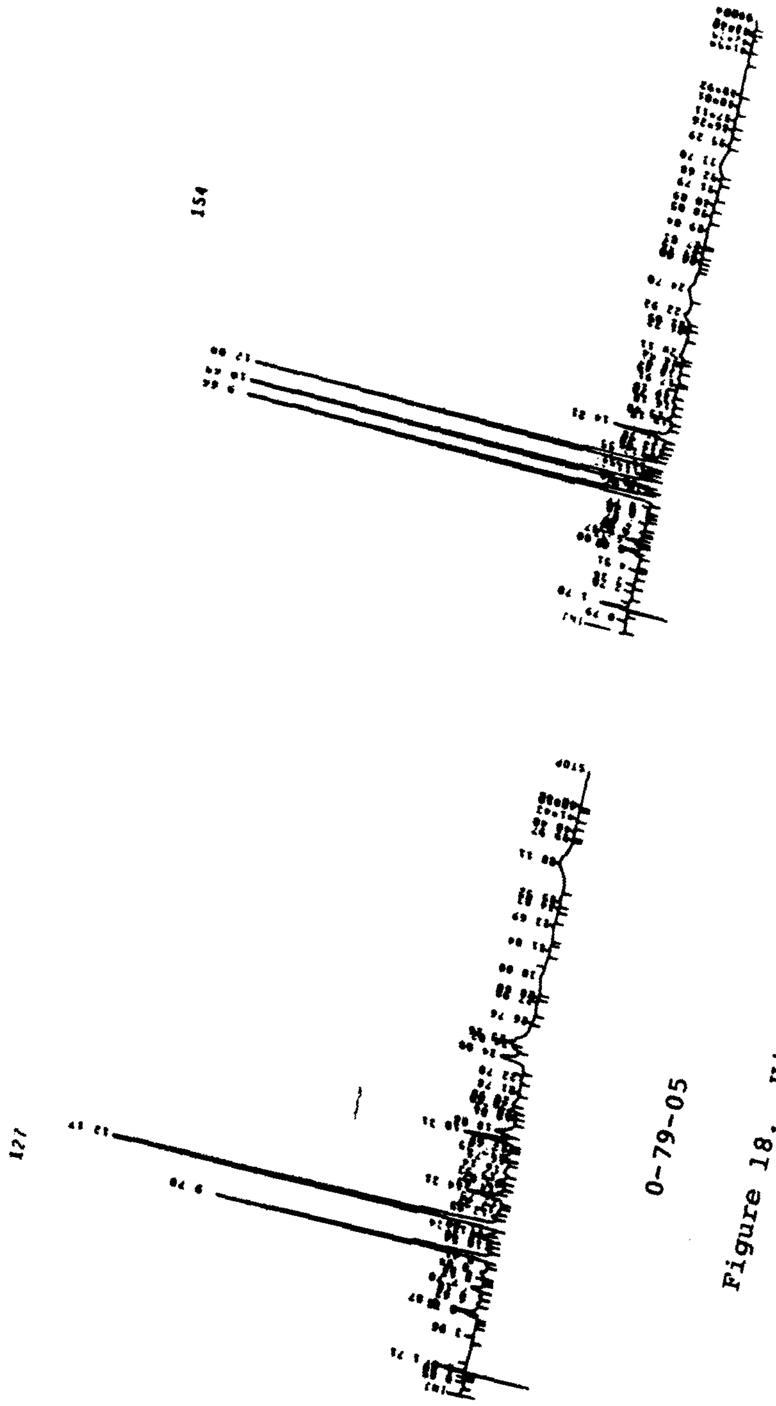
Throughout this report, the following designations will be used for oils at various stages of reclamation to more readily indicate the state in the reclamation process for any particular sample and eliminate the necessity for lengthy identification of each sample.



0-79-01

0-79-03

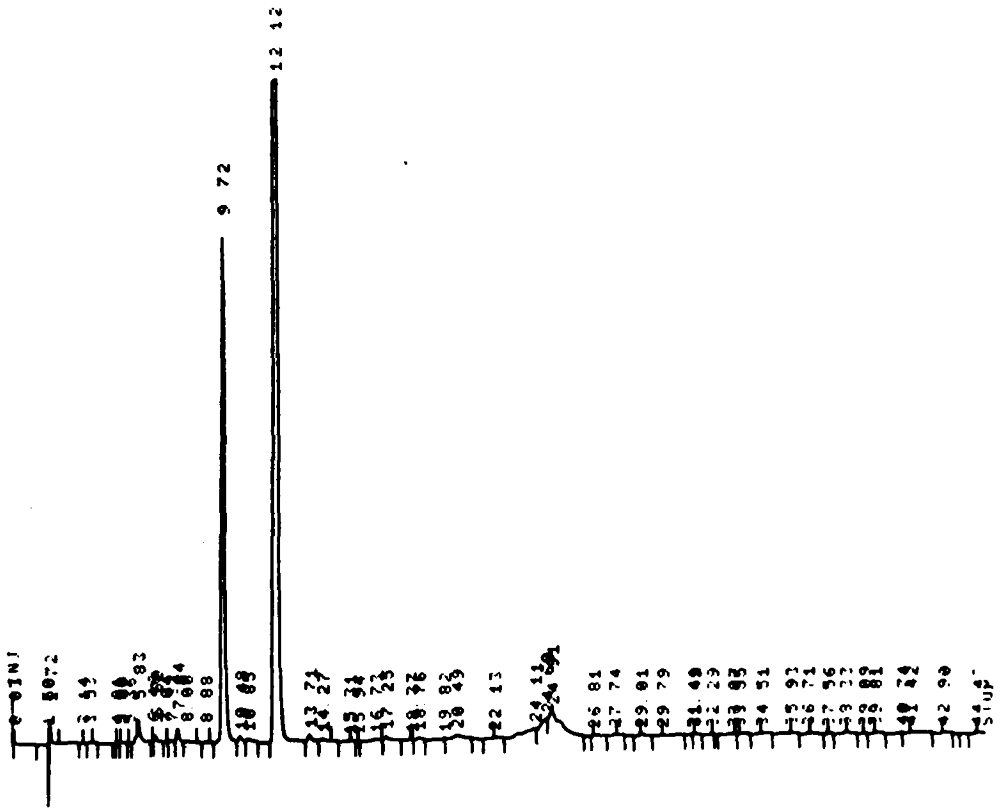
Figure 17. High performance liquid chromatography of used oils.



0-79-05

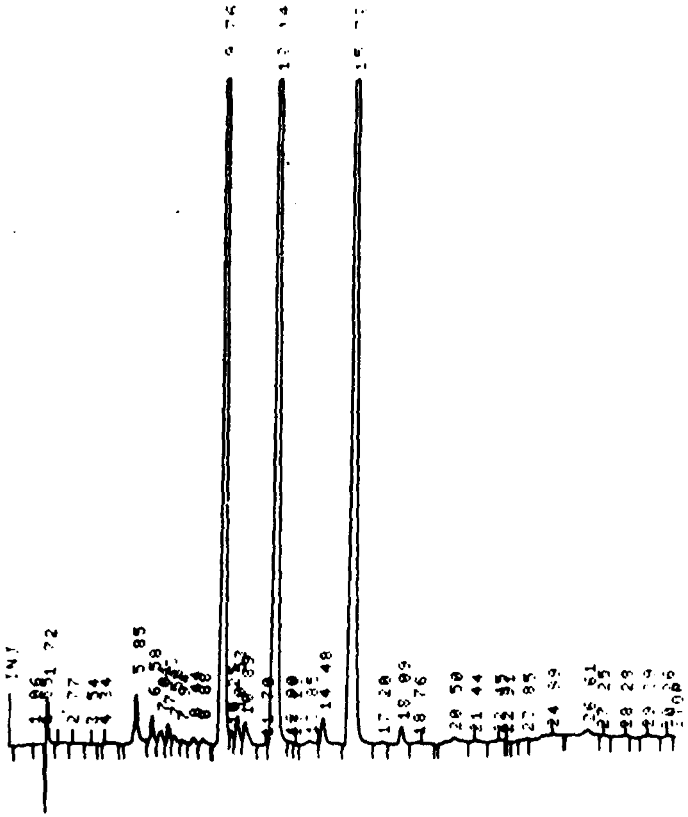
0-79-09

Figure 18. High performance liquid chromatography of used oils.



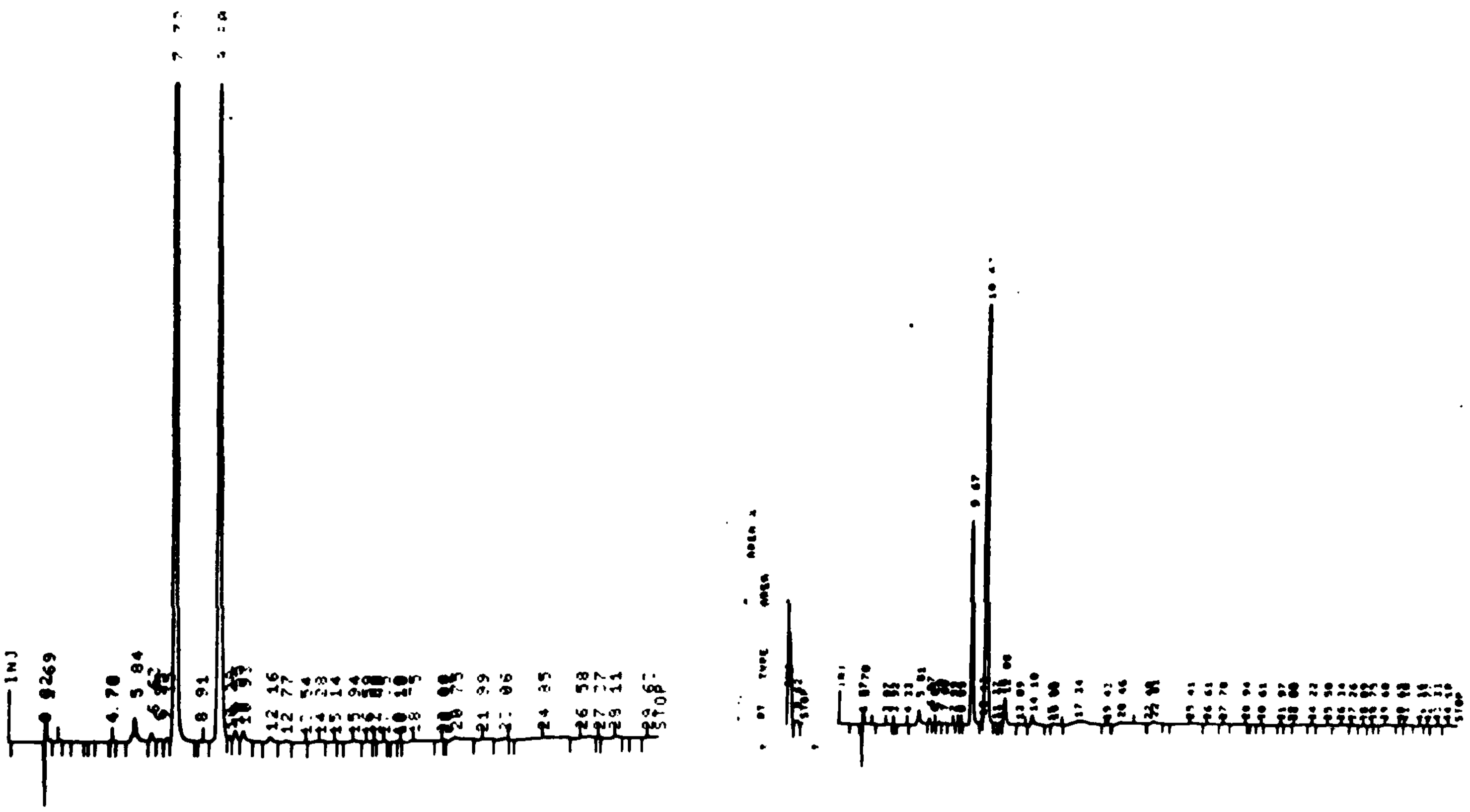
ATL 9121

Figure 19. HPLC representative of new oil ATL 9121.



ATL 9123

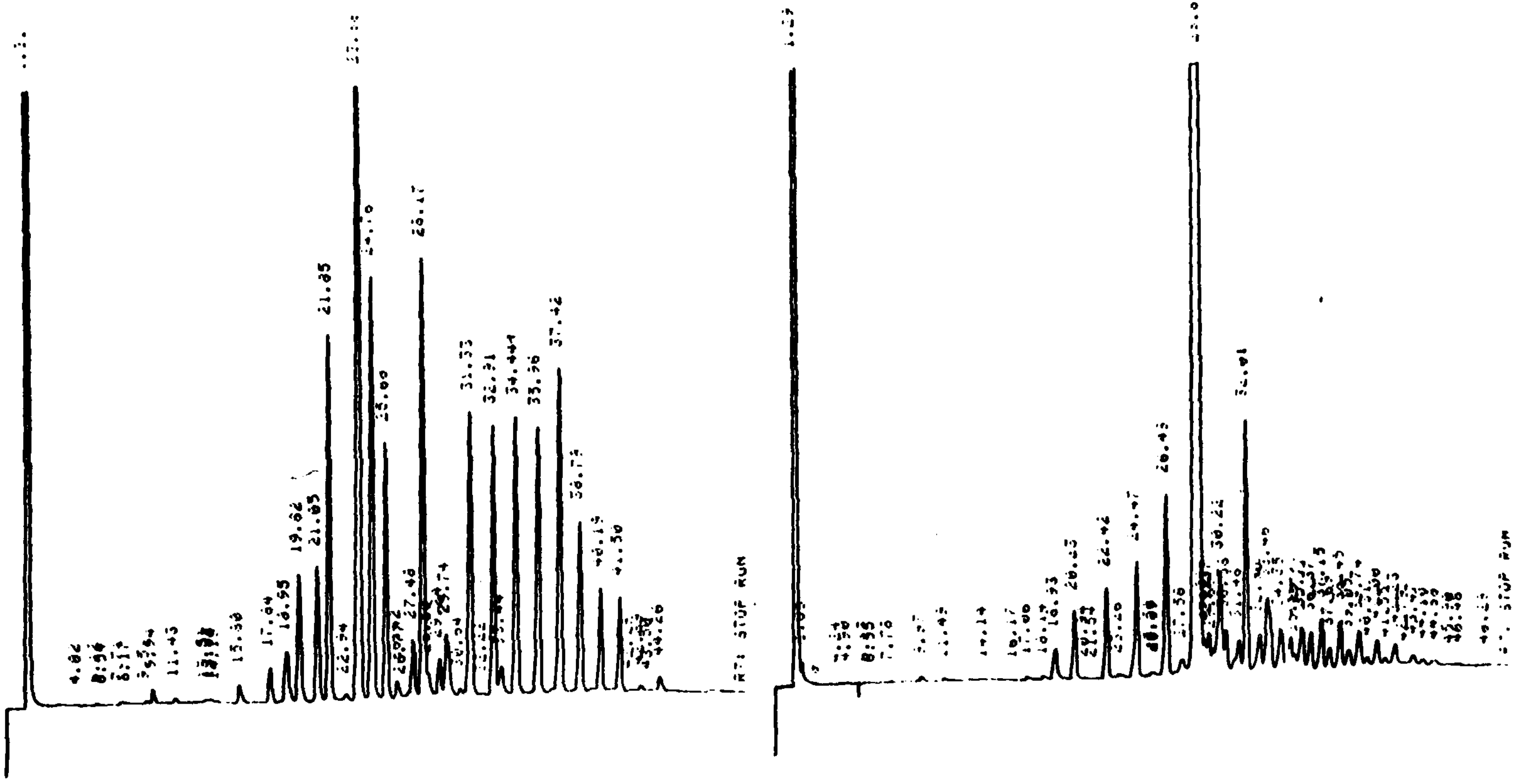
Figure 20. HPLC representative of new oil ATL 9123.



ATL 9120

ATL 9122

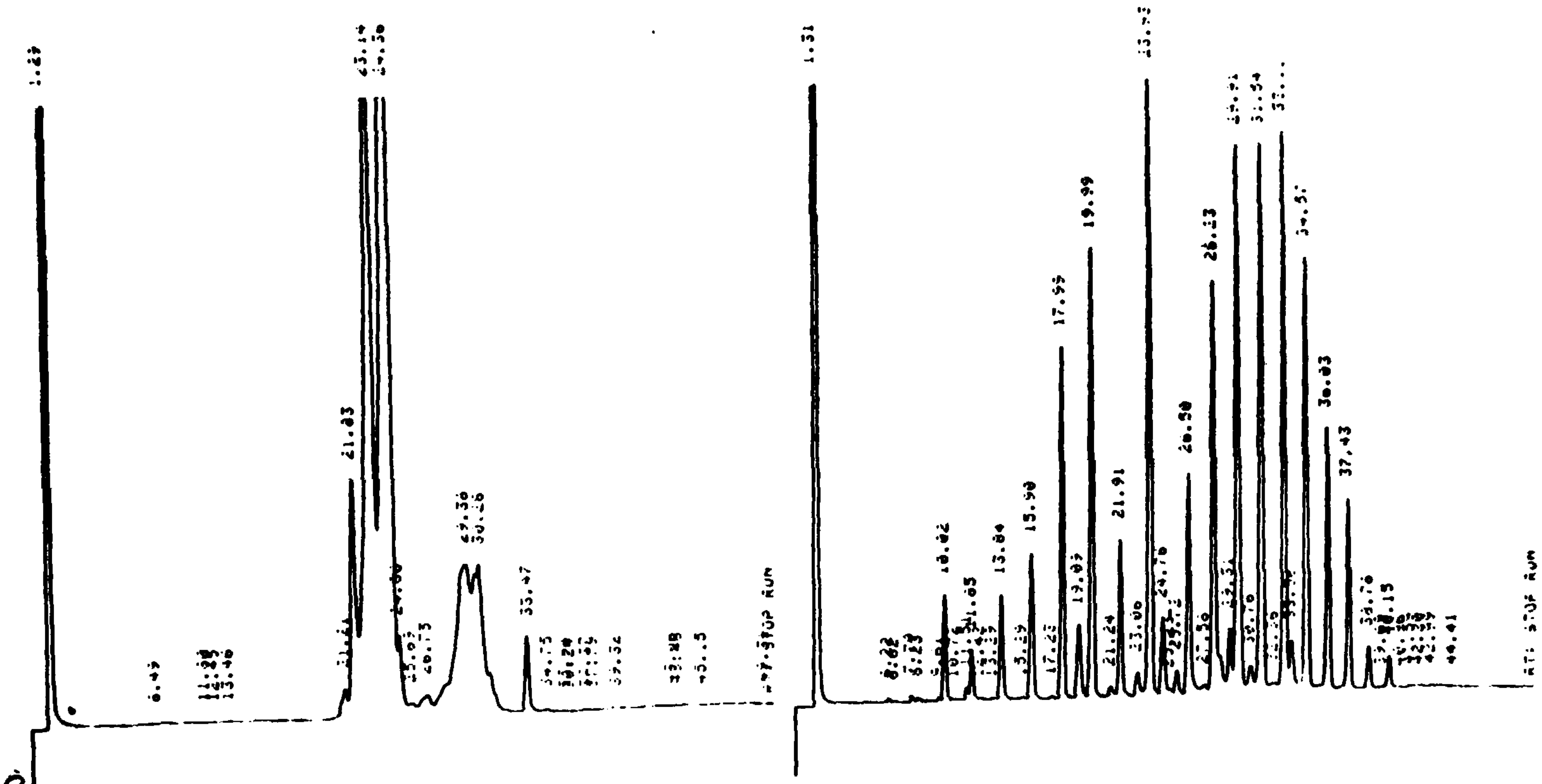
Figure 21. HPLC representative of new oils ATL 9120 and 9122.



ATL 9118

ATL 9119

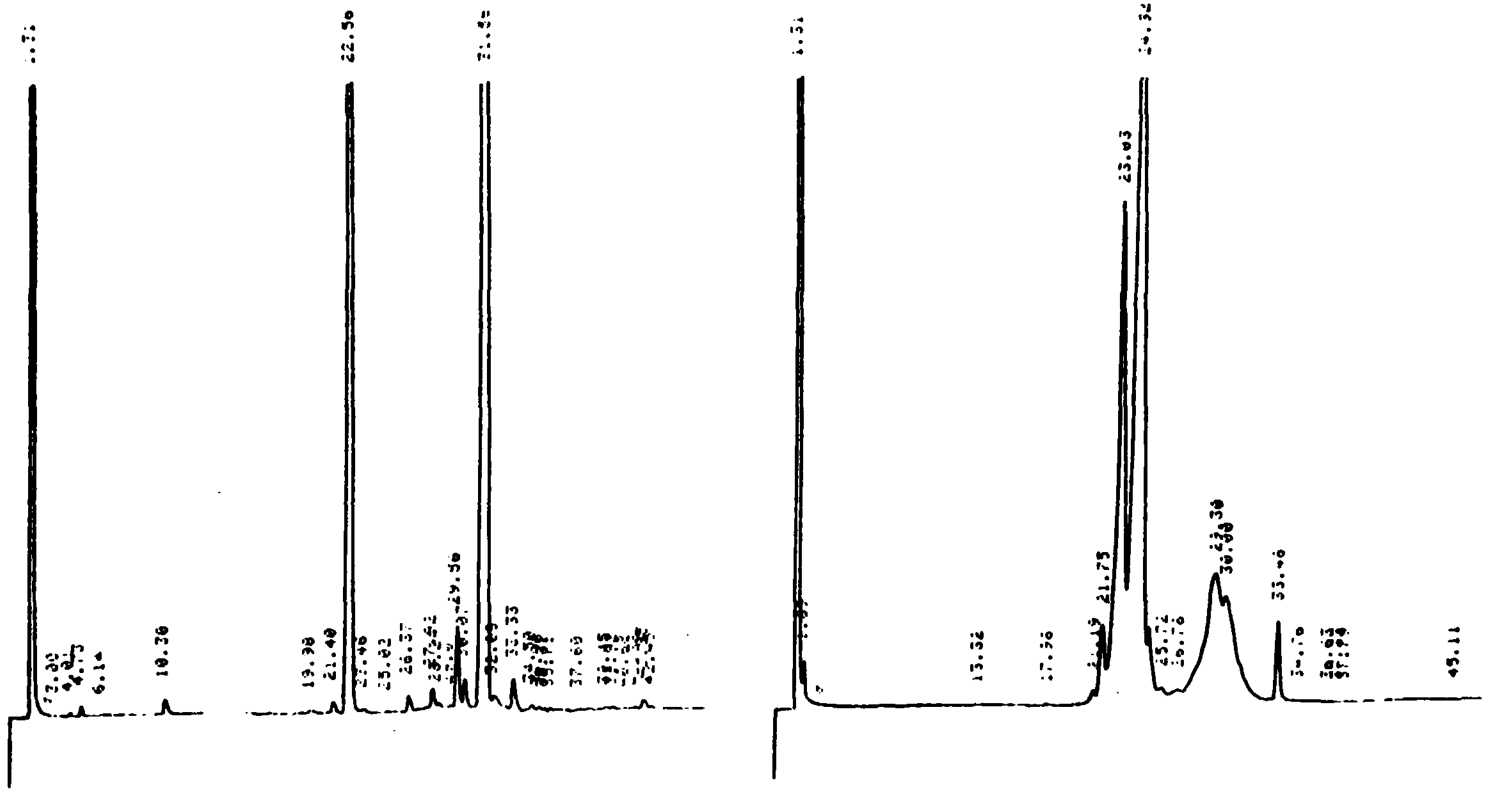
Figure 22. Gas chromatograms of new oils.



ATL 9120

ATL 9121

Figure 23. Gas chromatograms of new oils.



ATL 9122 **ATL 9123**

Figure 24. Gas chromatograms of new oils.

Designation	Sample description
Used oil	Oil as received from AFAPL.
Reclaimed base stock	Oil that has been processed, no replenishment of additives.
Reclaimed oil	Oil that has been processed and additives replenished.

3.3 ADDITIVE PACKAGE VALIDATION

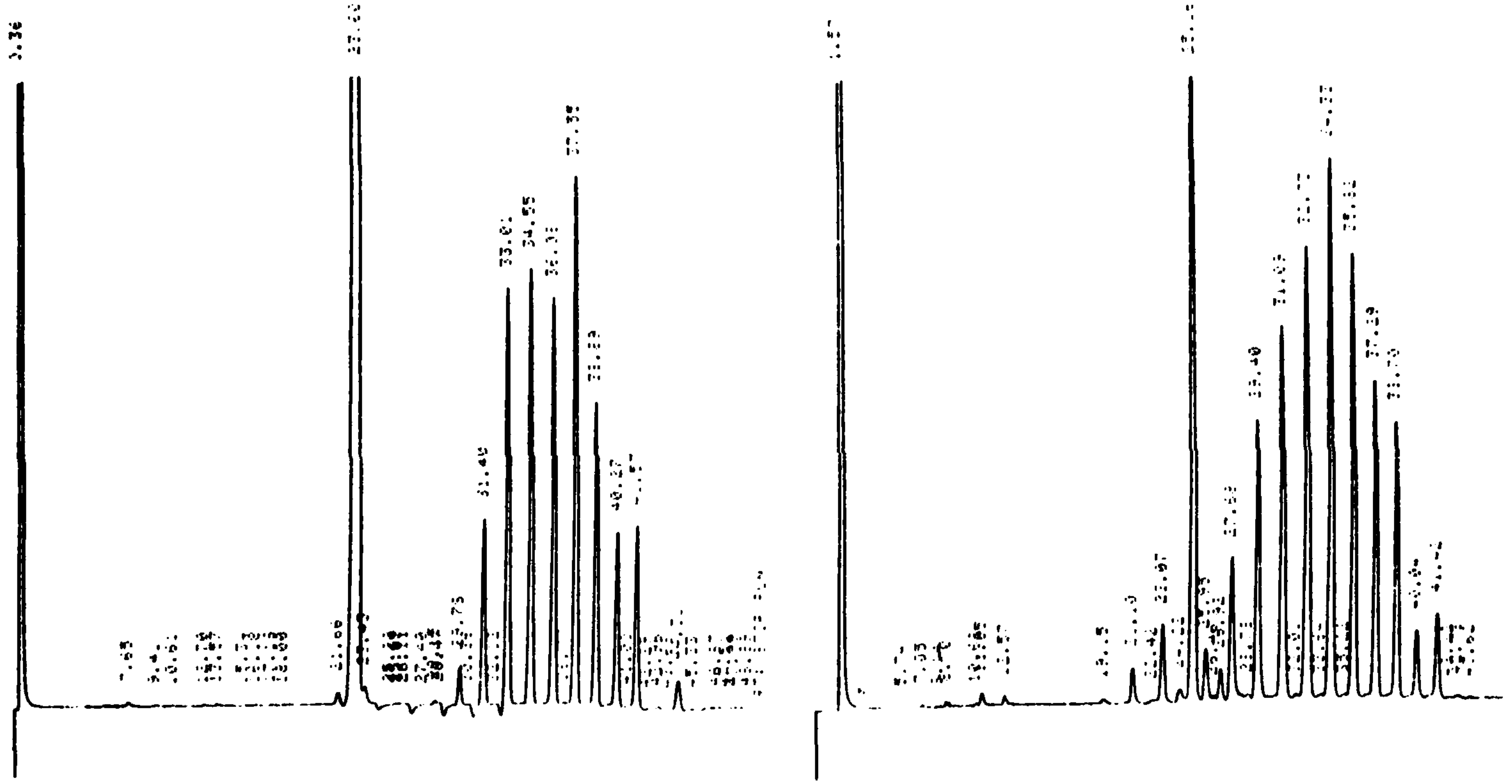
To validate our proposed additive package, GC's were run on six new oil samples supplied by APL, representing various manufacturers. Gas chromatograms labeled ATL 9118 through 9123 are seen in Figures 22, 23, and 24. From these chromatograms, we were able to select five base stock blends (without additives), supplied by various manufacturers and APL, that closely resembled the new oils with which to validate MRC's additive package.

3.3.1 Selection of Base Stocks for Use in Additive Package Validation

The following MIL-L-7808 type base stock blends were received from manufacturers:

Stauffer Chemical Company	~10 gal 7808H
Hatco	5 gal 7808H
Royal Lube	10 gal 7808H
ATL 9148 (from APL)	5 gal mix of polyols
ATL 9149 (from APL)	5 gal mix of diesters and polyols

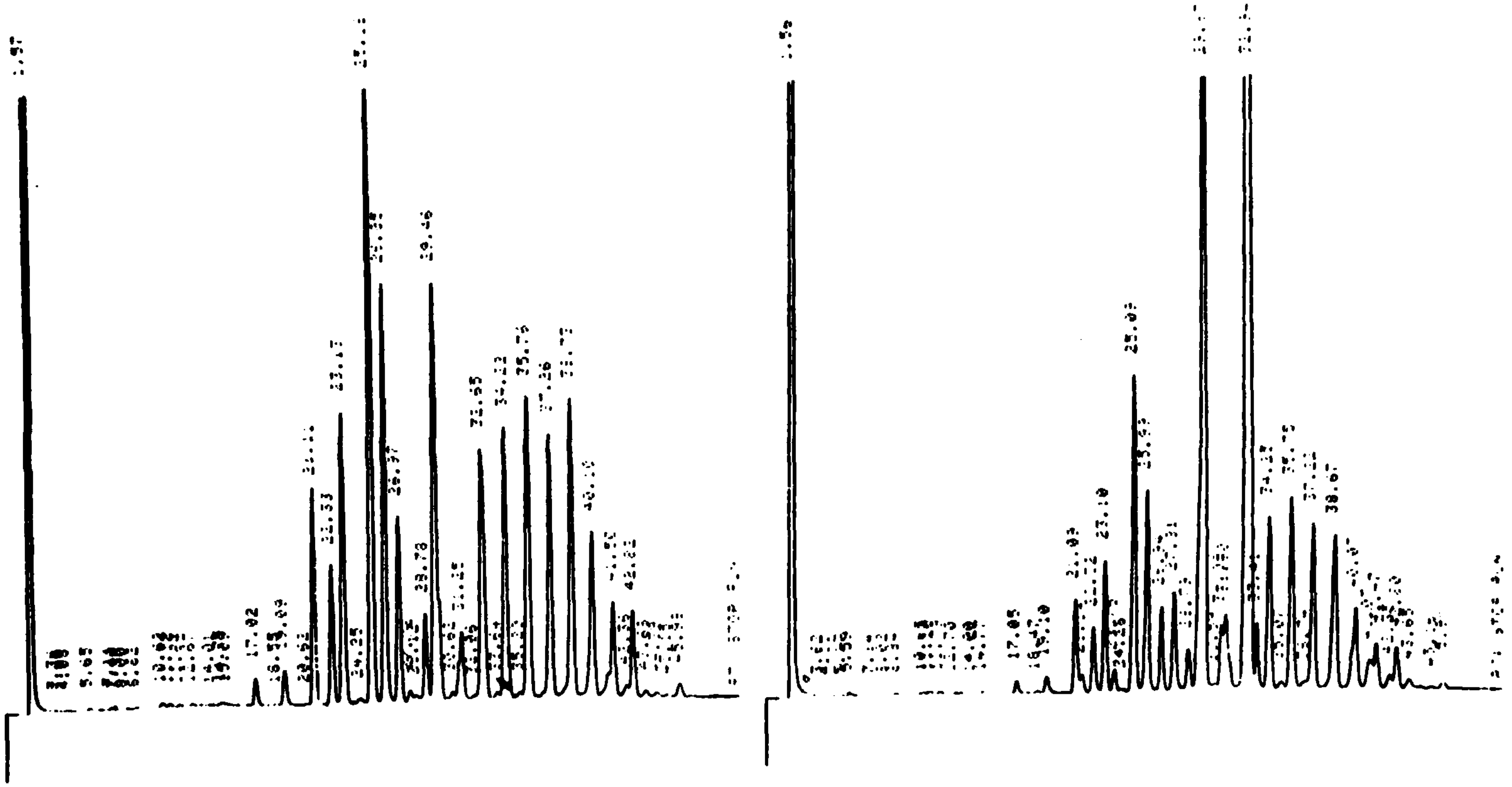
Figures 25, 26, and 27 show gas chromatograms of these base stocks. Figure 28 shows a base stock formulated (1:1:1:1 Royal Lube/Emery 2958/Emery 2932/Herculube 401) and tested with the additive package from the previous program (F33615-76-C-2037),



Hatco

Royal Lube

Figure 25. Gas chromatograms of formulated base stocks.



ATL 9148

ATL 9149

Figure 26. Gas chromatograms of formulated base stocks.

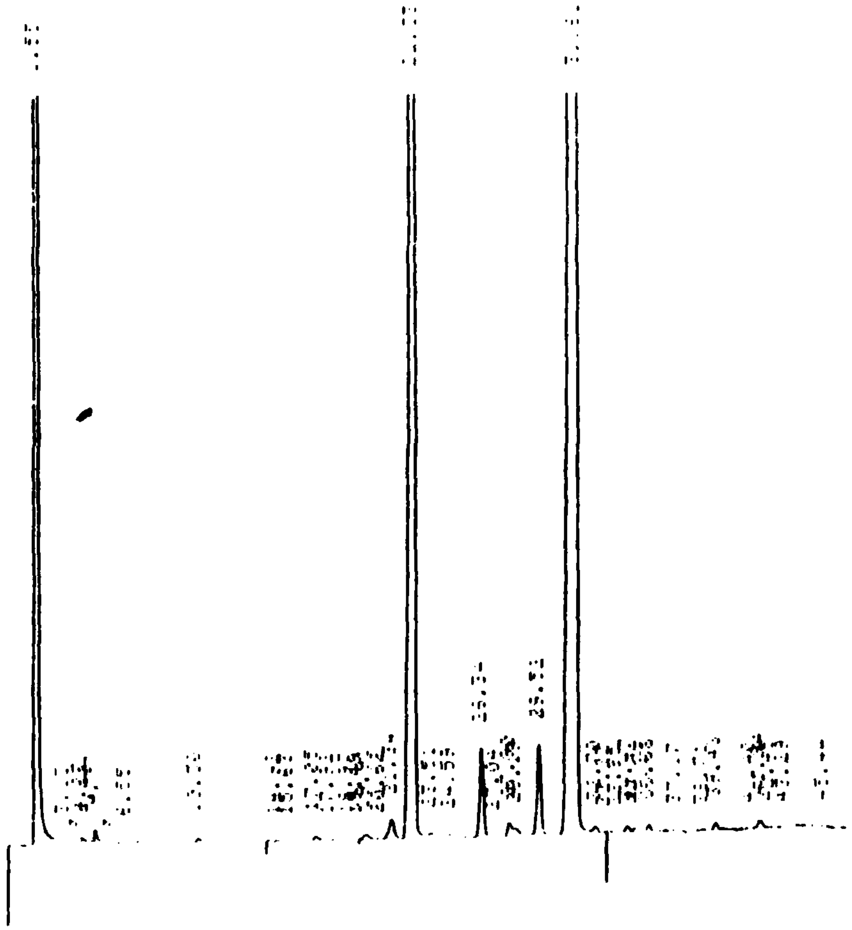
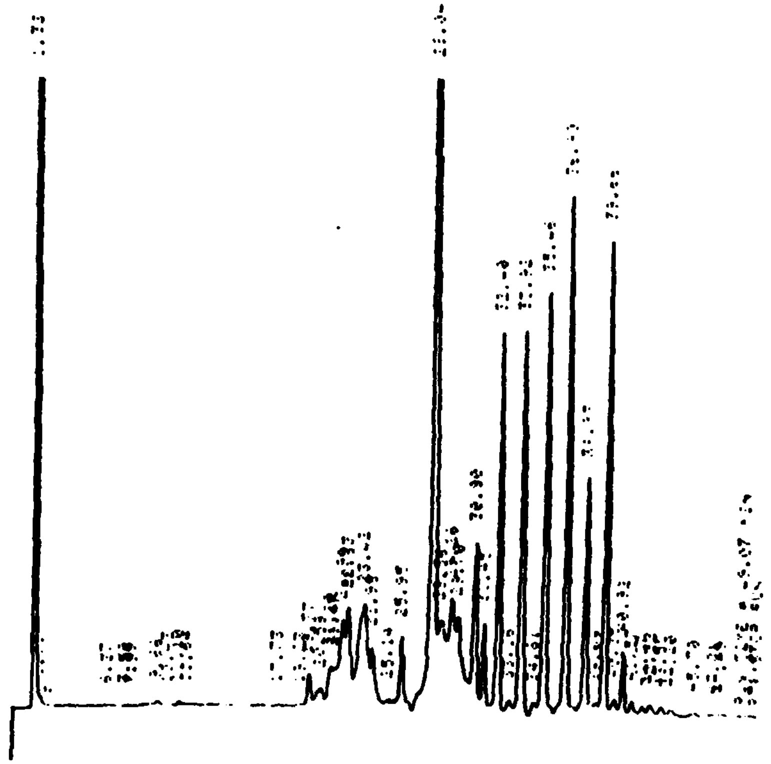


Figure 27. Gas chromatogram of Stauffer formulated base stock.



1:1:1:1

Royal Lube Diester, Emery 2958 and 2932, and Herculube 401

Figure 28. Gas chromatogram of base stock mixture tested earlier with a proposed additive package.

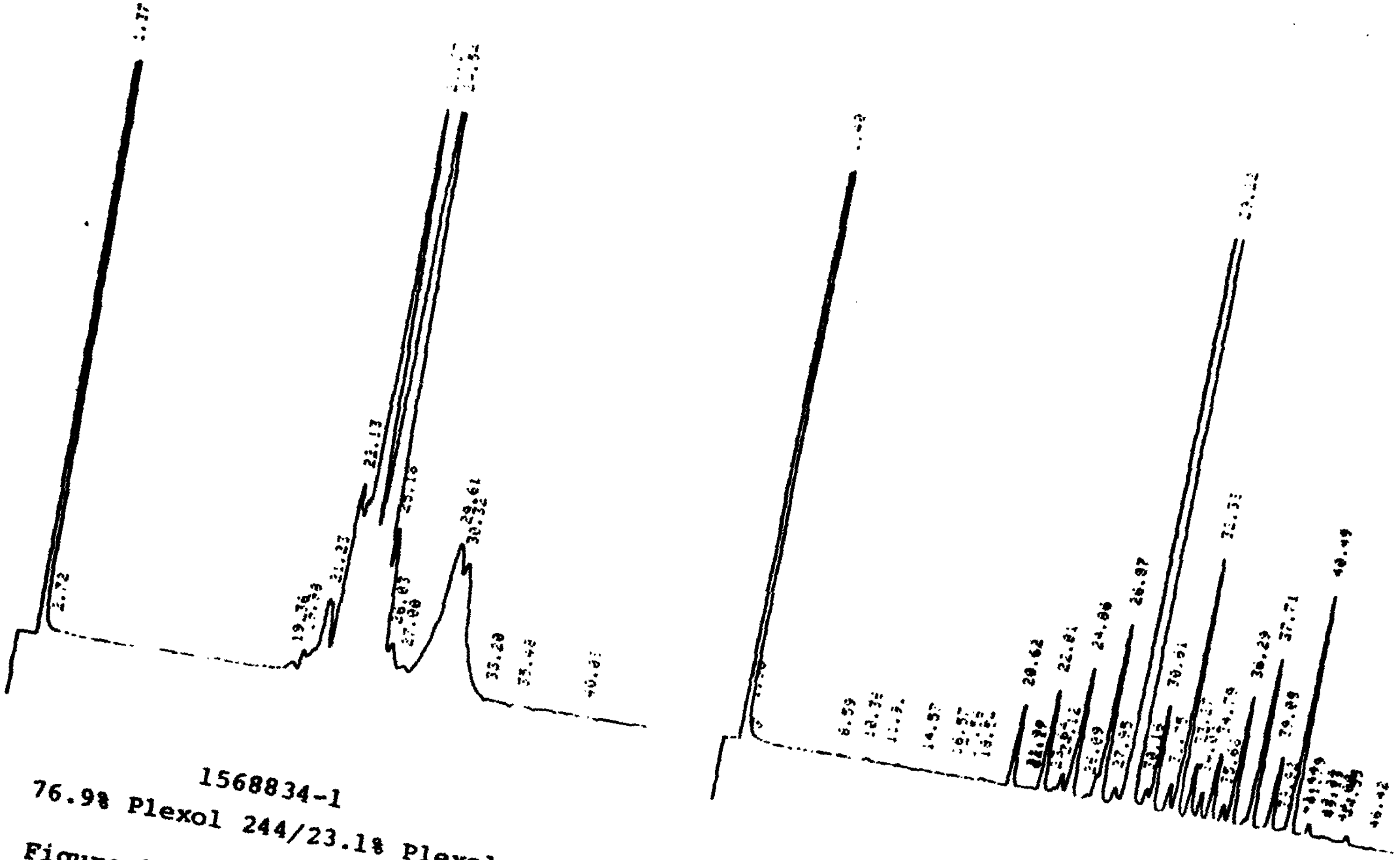
from which a gas chromatogram was not run at the time. Sample 1568834-2A (see Figure 29) represents another, similar sample which was also tested on the prior program.

Our initial tries at blending for viscosity requirements (Figures 29 and 30) show that GC patterns of blended base stocks somewhat match some of the new oils supplied by APL. By using 76.9% Plexol 244 (diisooctyl adipate, Rohm and Haas) and 23.1% Plexol 273 (diisodecyl adipate, Rohm and Haas) a pattern similar to those of oils 9120 and 9123 was produced. A combination of 85% Emery 2958 (di-2-ethylhexyl azelate, Emery Lubricants) and 15% Emery 2932 (trimethylol propane triester, Emery Lubricants) gave a pattern somewhat similar to those of oils 9121 and 9118. 92.6% Emery 2958 and 7.4% Emery 2939 (a 5-cSt polyol ester), produced a chromatogram similar to that of new oil 9119.

From these data we formulated and tested five additional base stocks with our additive package: ATL 9149, ATL 9148, Stauffer base stock, Hatco base stock, and a base stock of Plexol 244 and Plexol 273 (see Figure 29). They represent a wide variety of base stock formulations and seem to represent most of the used oils we have received and many of the new oil formulations we have examined.

3.3.2 MRC's Additive Package Added to Selected Base Stocks

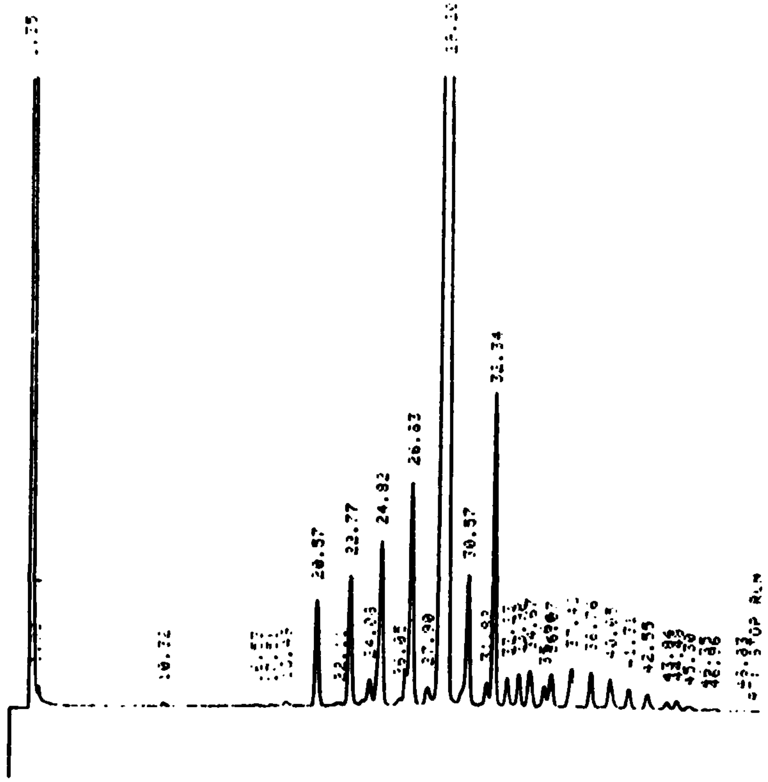
The 3,7-dioctylphenothiazine (DOPTA) used in the earlier program was replaced with phenyl-α-naphthylamine (PANA) since DOPTA is no longer produced in the United States. We also wanted to determine if the additive had a singular effect on the foam testing of a formulated base stock. Royal Lube base stock was formulated with all of the additives minus PANA and exhibited a foam volume of 5 mL. The formulated base stock with PANA had a foam volume of 45 mL. Additional testing of this base stock with PANA gave similar results (40-45 mL foam volume).



1568834-1
76.9% Plexol 244/23.1% Plexol 273

1568834-2A
85% Emery 2958/15% Emery 2932

Figure 29. Gas chromatograms of blends of commercially available base stocks.



1568834-3

92.6% Emery 2958/7.4% Emery 2939

Figure 30. Gas chromatogram of a blend of commercially available base stocks.

When informed of this foaming problem, the manufacturer provided a new supply of PANA, which produced a foam volume of 15 mL. This newer, cleaner appearing PANA was used to formulate the virgin base stocks.

The five selected virgin base stocks (Hatco, Stauffer, ATL 9148, ATL 9149, and Plexol) were formulated with:

1.0%	DODPA (dioctyldiphenylamine) - Van Lube 81
1.0%	PANA (phenyl-α-naphthylamine) - Uniroyal
2.0%	TCP (tricresyl phosphate) - Kronitrex AA FMC
0.1%	Ethyl antioxidant 703 - Ethyl Corp.
0.1%	TPP (triphenyl phosphite) - Eastman
0.1%	Benzotriazole - photo grade - Sherwin Williams
0.05%	Quinizarin (GAF - purified)

These oils were sent to Alcor for specific testing. They were evaluated in the following sequence to allow detection of the most common modes of failure.

1. Total acid number
2. Static foaming characteristics, test method 3213
3. Viscosity at -65°F, 100°F, and 210°F
4. Lead corrosion
5. Corrosion and oxidation stability, 96 hr at 392°F
6. Dynamic foaming characteristics
7. FA elastomer compatibility at 347°F
8. Gear load carrying rating (one gear, two determinations)
9. Silver and bronze corrosion
10. Deposition number

The results of these tests are included in Appendix A of this report. MRC's proposed additive package in the five selected base stocks had met all test specifications except the static foam test in one of the base stocks furnished by APL. A comparison of the MRC versus Alcor static and dynamic foam test results on the five formulated base stocks (see Table 2) suggests that the static foam volume of 115 mL for oil 1732509 (ATL 9149),

TABLE 2. SELECTED DATA FROM MIL-L-7808H TESTING

Oil	MRC static foam volume,[a] mL	Alcor static foam volume,[a] mL	Acid number[b]	Alcor dynamic foam volume,[a,c] mL	Viscosity at 210°F, cSt	Viscosity at -65°F, cSt 35 min
Hatco 1732506	15	15	0.20	10	3.0	12,136
Stauffer 1732510	25	30	0.25	10	3.1	13,925
Rohm and Haas 1732511	35	35	0.14	10	3.0	11,341
ATL 9148 1732508	60	100	0.22	10	3.4	14,462
ATL 9149 1732509	90	115	0.17	10	3.5	16,642
ATL 9148[d]	5					
ATL 9149[d]	0					

[a] Maximum 100 mL.

[b] Maximum allowable acid number is 0.30.

[c] Foam volumes same at both 176°F and 230°F, 1000 cc air.

[d] Base stock with no additives; only static foam volume tested.

although near the specification limit, was only marginally over. Another oil (1732511, Rohm and Haas), though not out of specifications as far as corrosion and oxidation stability (96 hr at 392°F), did exhibit high magnesium corrosion and oxidation values.

Effects on acid numbers, viscosity, and foam volume of the same additive package in various MIL-L-7808 fluids, produced by unique manufacturing processes, are seen in Table 2. The base stocks received from AFAPL seem to be much more affected by the formulation process than the commercially available virgin base stocks. The cause of this effect on the APL base stocks is unknown.

The interaction on PANA with the APL-supplied base stocks may contribute to the higher than normal foam volumes. After the virgin base stocks had already been formulated, PANA from another supplier arrived for testing. Table 3 compares test results for PANA from Union Carbide and from Uniroyal; both produced equal response. The data suggest base stock interaction with the additive package, specifically with PANA.

TABLE 3. COMPARING FOAM TEST RESULTS PANA FROM TWO SUPPLIERS

MRC's additive package with	Foam test volume, mL Royal lube base stock	ATL 9149 base stock
Uniroyal PANA	15	115
Union Carbide PANA	25	120

3.3.3 Effect of Additive Package on Viscosity

From the previous contract, an increase in viscosity was expected from the addition of our proposed additive package to base stock oils. Results were much more sporadic than expected. These random viscosity increases (see Table 4) fall into distinct patterns, making future viscosity increase predictions much more difficult.

TABLE 4. VISCOSITY INCREASES DUE TO ADDITIVE ADDITION

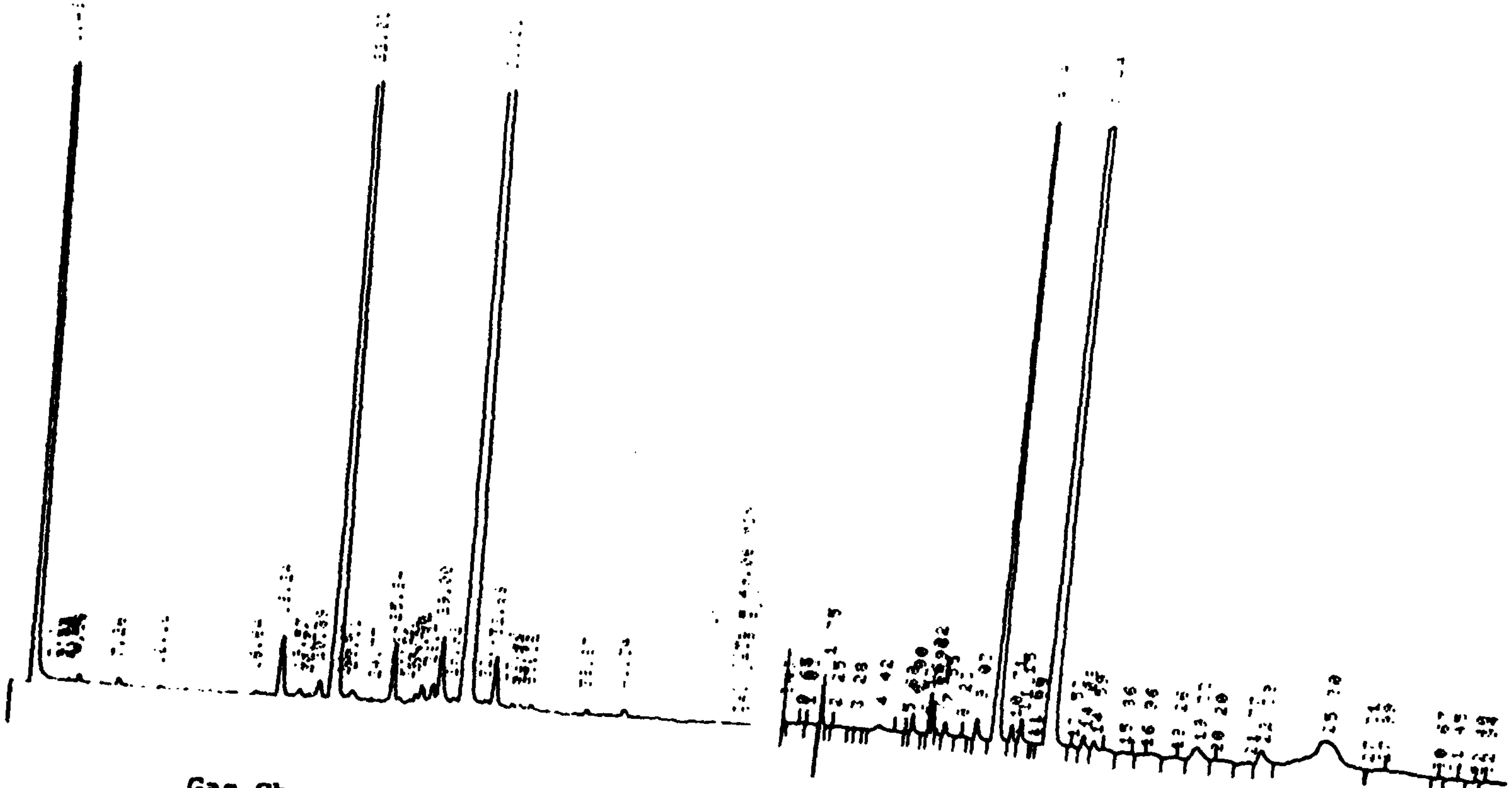
	Percent increase when viscosity measured in cSt at			
	-20°F		100°F	
ATL 9149	16.9	Pattern 1	3.0	Pattern 1
ATL 9148	17.0		3.6	
Rohm and Haas	27.6	Pattern 2	10.0	Pattern 2
Stauffer	22.9		8.0	
Hatco	7.6	Pattern 3	0.4	Pattern 3

3.3.4 Chromatograms of Additives in Base Stock

Chromatograms of MRC's additive package in Stauffers base stock are shown in Figure 31. All the high performance liquid chromatograms of the formulated fluids tested by Alcor are the same. The gas chromatograms of the formulated fluids are duplications of those for the base stocks without additives, although PANA does appear at 18.24 min in each chromatogram.

3.3.5 Estimated Additive Shelf Life

According to their manufacturers, the additives contained in MRC's additive package have different shelf lives. DODPA and PANA should be tested yearly; quinizarin and ethyl antioxidant 703 should not be used if stored over 2 years; and TCP, benzotriazole (BT), and TPP are unaffected by storage.



Gas Chromatogram

High Performance Liquid Chromatogram

Figure 31. Chromatograms of Stauffer base stock with MRC additive package.

3.4 DISTILLATION STUDY

Distillation ideally should be included in the early part of any reclamation process to remove any low boiling material (water, toluene, etc.) and major contamination such as degraded additives and polymeric esters. Removal of the major contaminants insures lower effective absorbent treatment levels in subsequent process steps.

3.4.1 Distillation of Neutralized Used Oils

In the earlier program, a straight takeover distillation was performed. In the current program, a literature search revealed a paper on commercial oil reclamation which suggests that treatment of oils with metallic sodium prior to distillation reduces the formation of nondistillable impurities [1]. The metallic sodium also reacts to form nondistillable compounds with some degradation products. Since any water of low boilers would normally be removed during the topping step on distillation, it was felt we could add aqueous or alcoholic caustic solutions to the oil prior to distillation and possibly achieve the same effects. During this study, sodium hydroxide (NaOH) at 5% volume dissolved in water/isopropyl alcohol (1/1) was added to the oil just prior to distillation. The amount of NaOH added to the oil was based on the stoichiometric amount (or proportions thereof) necessary to neutralize the acid number. Figure 32 shows a graph comparing the effects of varying the percentage of NaOH on the acid numbers of the 2nd (main) and 3rd (secondary) fractions. The samples were distilled under the same conditions and cut-off points. Oil 0-79-14 was used for this experiment. Acid numbers of the same oil distilled without NaOH treatment are presented with the graph.

---

[1] Reynolds, J. W.; Whisman, M. L.; Brinkman, D. W.; Goetzinger, J. W.; Cotton, F. O. "From Oil:Oil," Chemtech, October 1979.

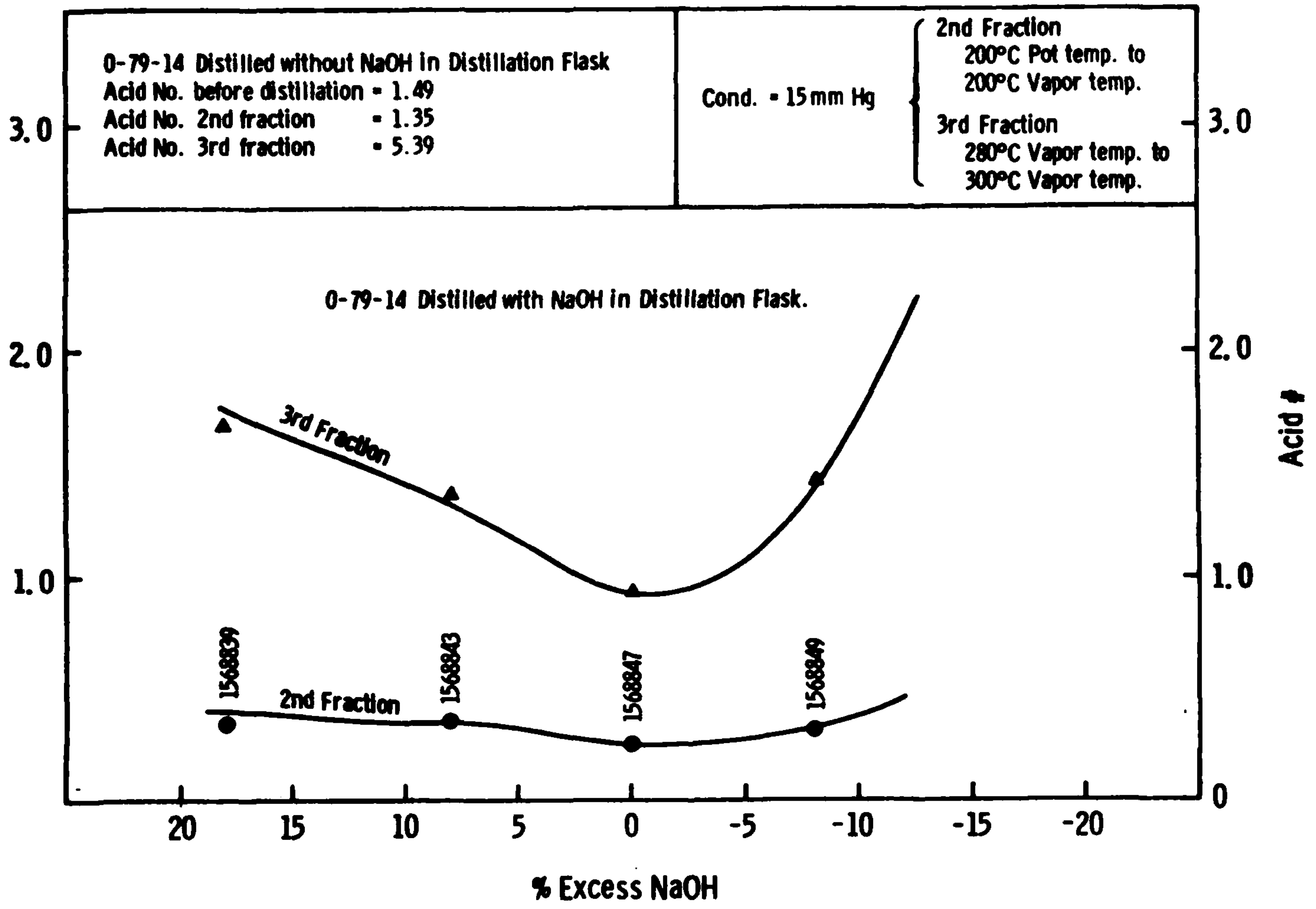


Figure 32. Acid numbers of distillate fractions, after varying NaOH level in used oil 0-79-14.

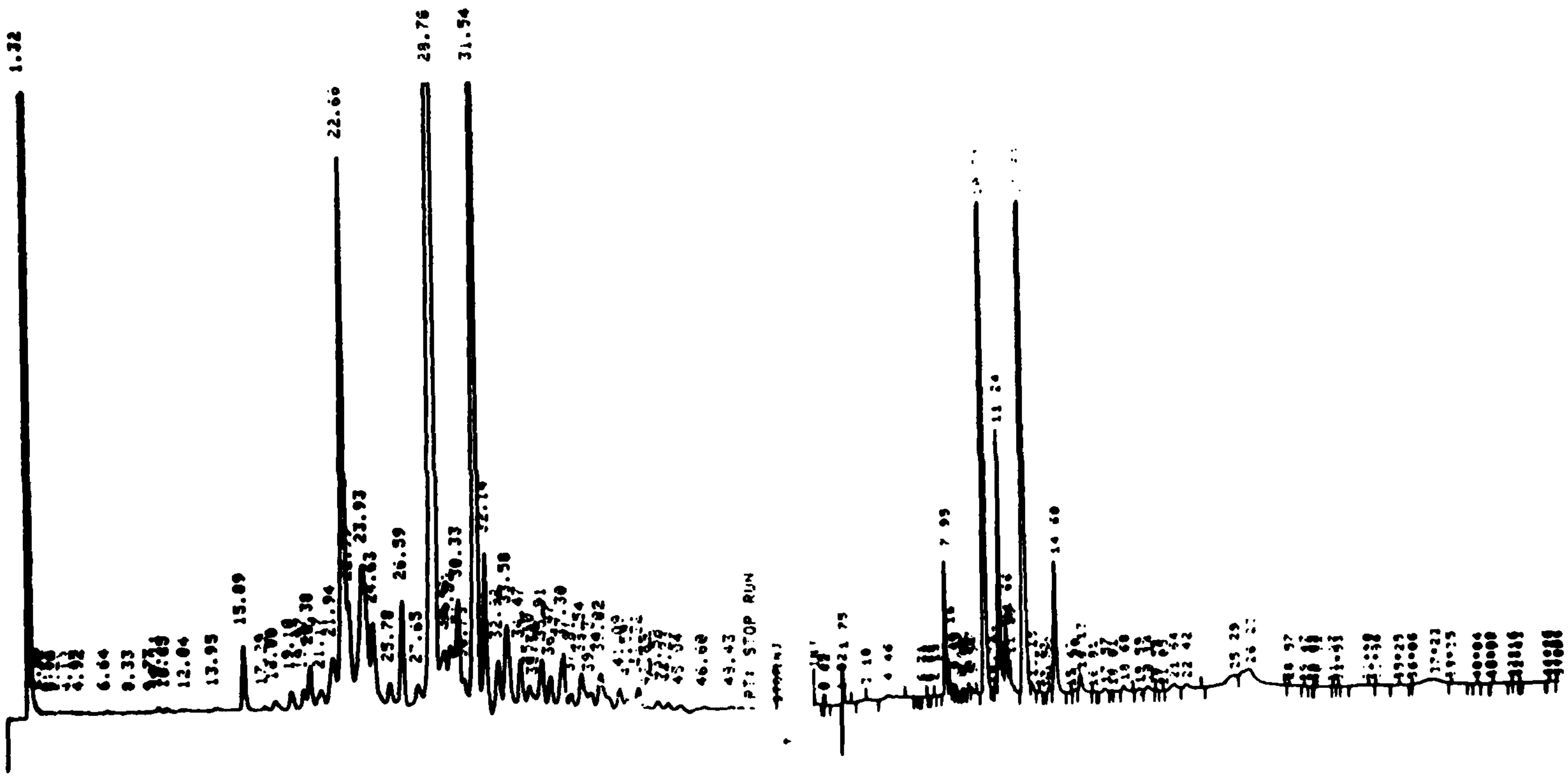
Because of improved acid numbers and obvious visual improvements in color, additional studies were warranted.

Two samples of a mixture of all 15 oils in the volume proportions received (see Figure 33 for HPLC and gas chromatograms) were distilled, one treated with sufficient NaOH to effect total neutralization and the other without treatment. Samples were taken throughout distillation for analysis. Figure 34 shows results for the mixture distilled without caustic treatment and Figure 35 gives the corresponding results for the mixture treated with NaOH. The circles represent vapor temperature vs. acid number and the squares represent cumulative percent recovery vs. vapor temperature.

There is virtually no difference between the plots of cumulative recovery vs. vapor temperature, suggesting there is no deleterious effect on recovery by NaOH treatment. The acid number data show significant differences. The total amount of distilled material having low acid numbers is much greater in the NaOH treated sample. These lower acid numbers may mean that less postdistillation treatment will be required. This plot might also be used as an accurate means of determining a proper distillation cut-off point. HPLC analyses show no differences between the treated vs. nontreated samples. The treated samples were lighter colored, having fewer visible degradation products present. Thin layer chromatography (TLC) analysis did show removal of additional material from the NaOH-treated samples.

3.4.2 Analysis of Distilled Neutralized Used Oils

Various analyses (GC, HPLC, acid number, and foam testing) were performed on oil samples distilled with and without NaOH treatment. A GC comparison of three equal (vapor temperatures) points on the recovery curves (Figures 36-38) showed no differences between the treated and nontreated samples. HPLC comparisons of combined



Gas Chromatogram

High Performance Liquid Chromatogram

Figure 33. Chromatograms of the mixture of 15 used oil samples.

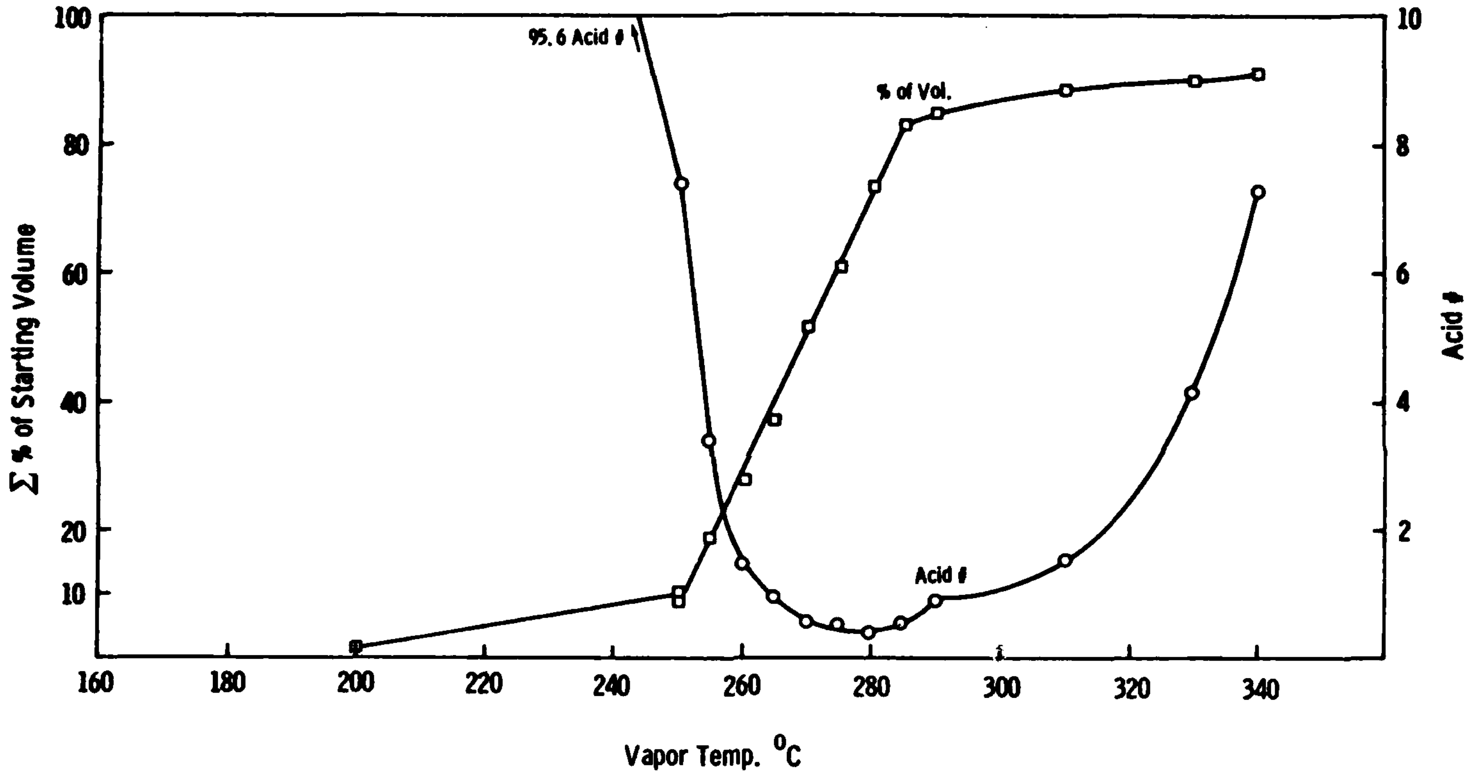


Figure 34. Sample 1568862, mixture of 15 used oils distilled with <u>no</u> NaOH (used oil starting acid number: 2.88).

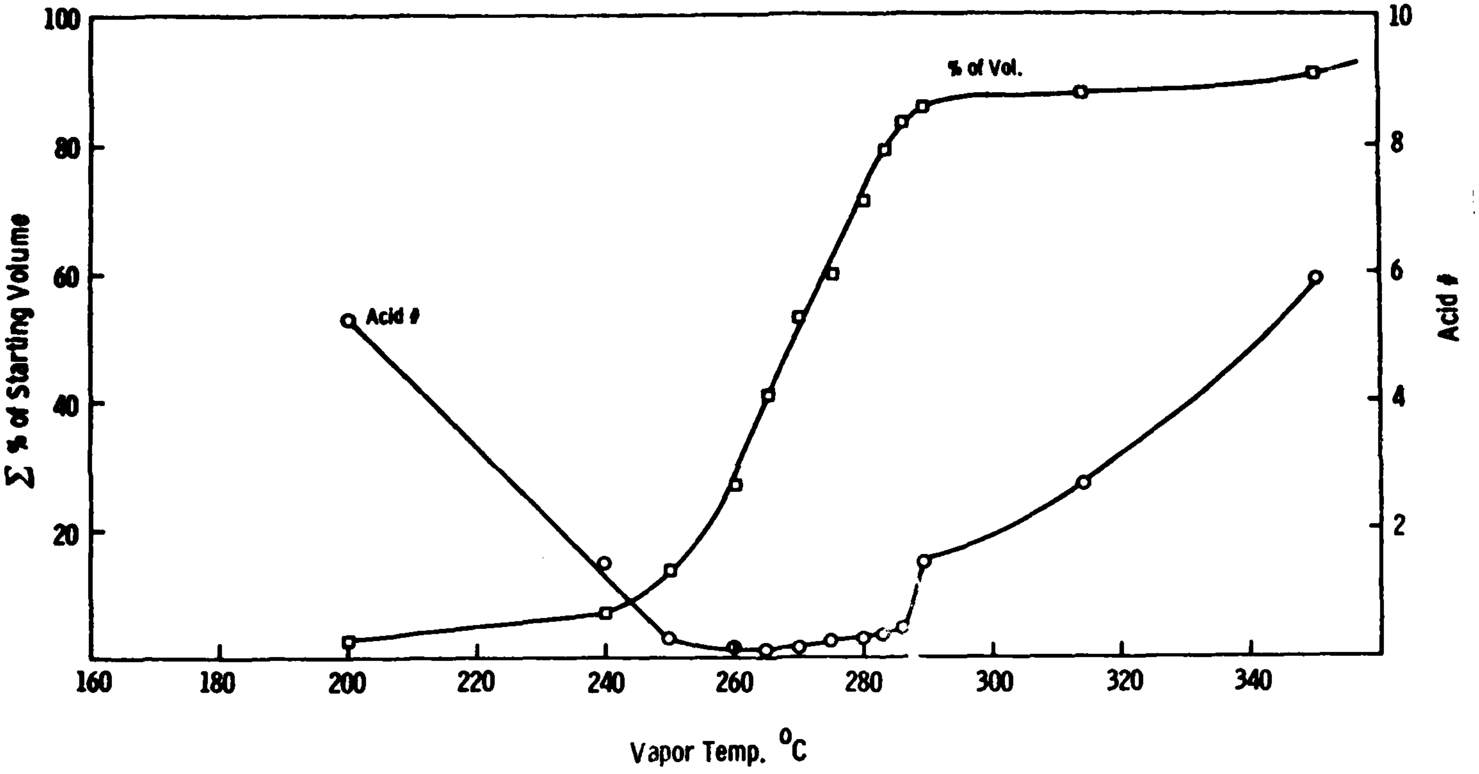
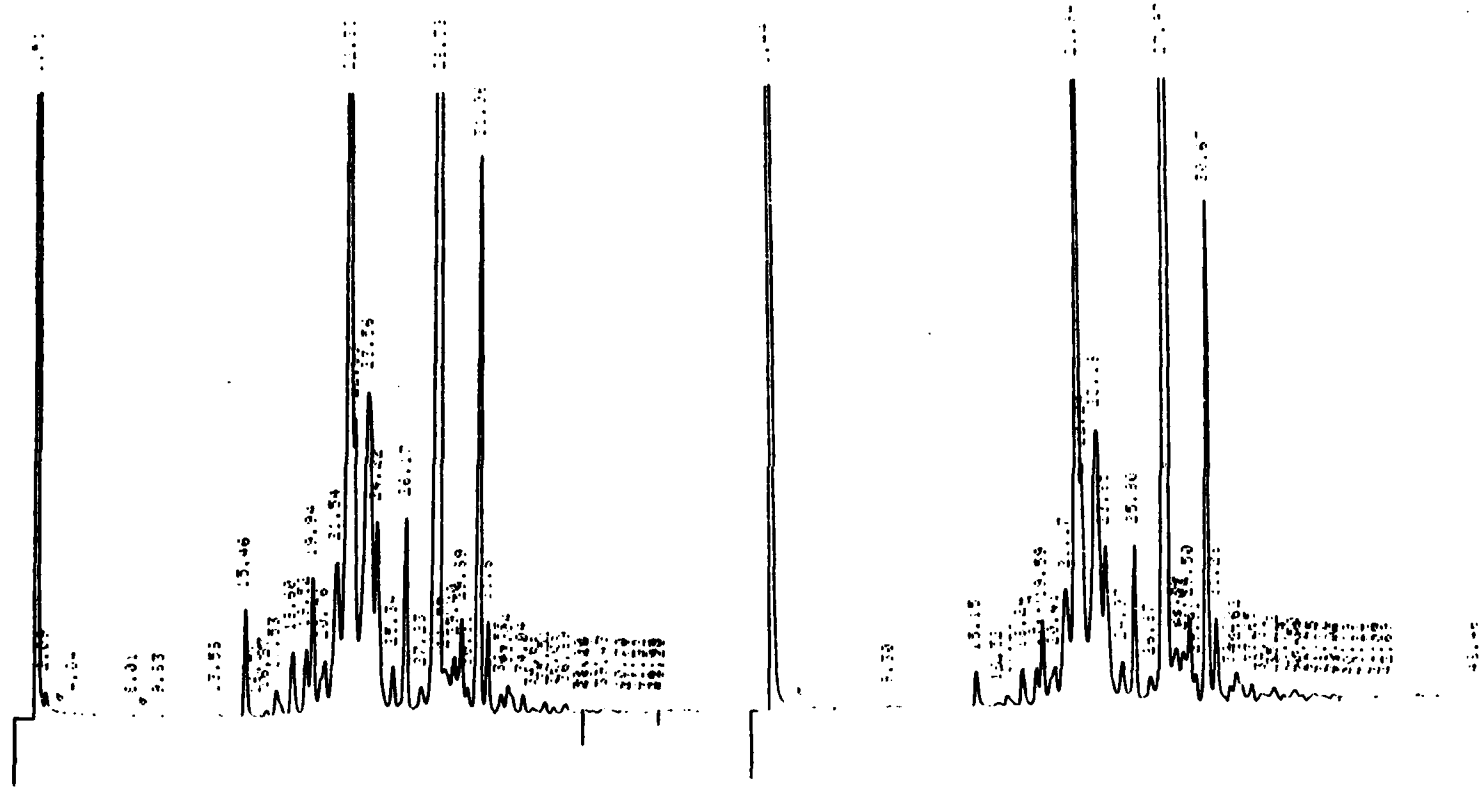


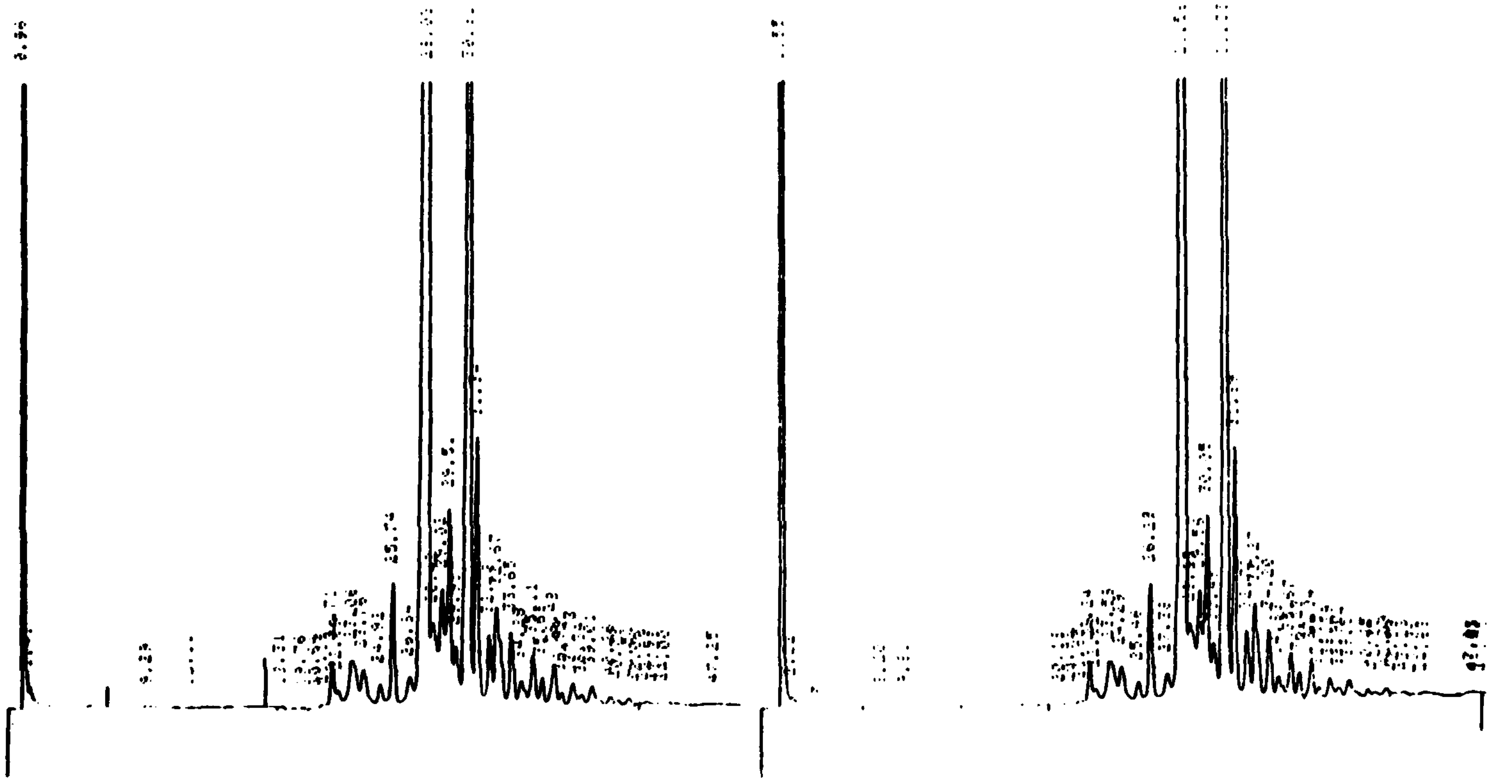
Figure 35. Sample 1568864, mixture of 15 used oils distilled with sufficient NaOH (added with water/isopropyl alcohol) for neutralization (used oil starting acid number: 2.88).



1568865-5 with NaOH

1568862-5 without NaOH

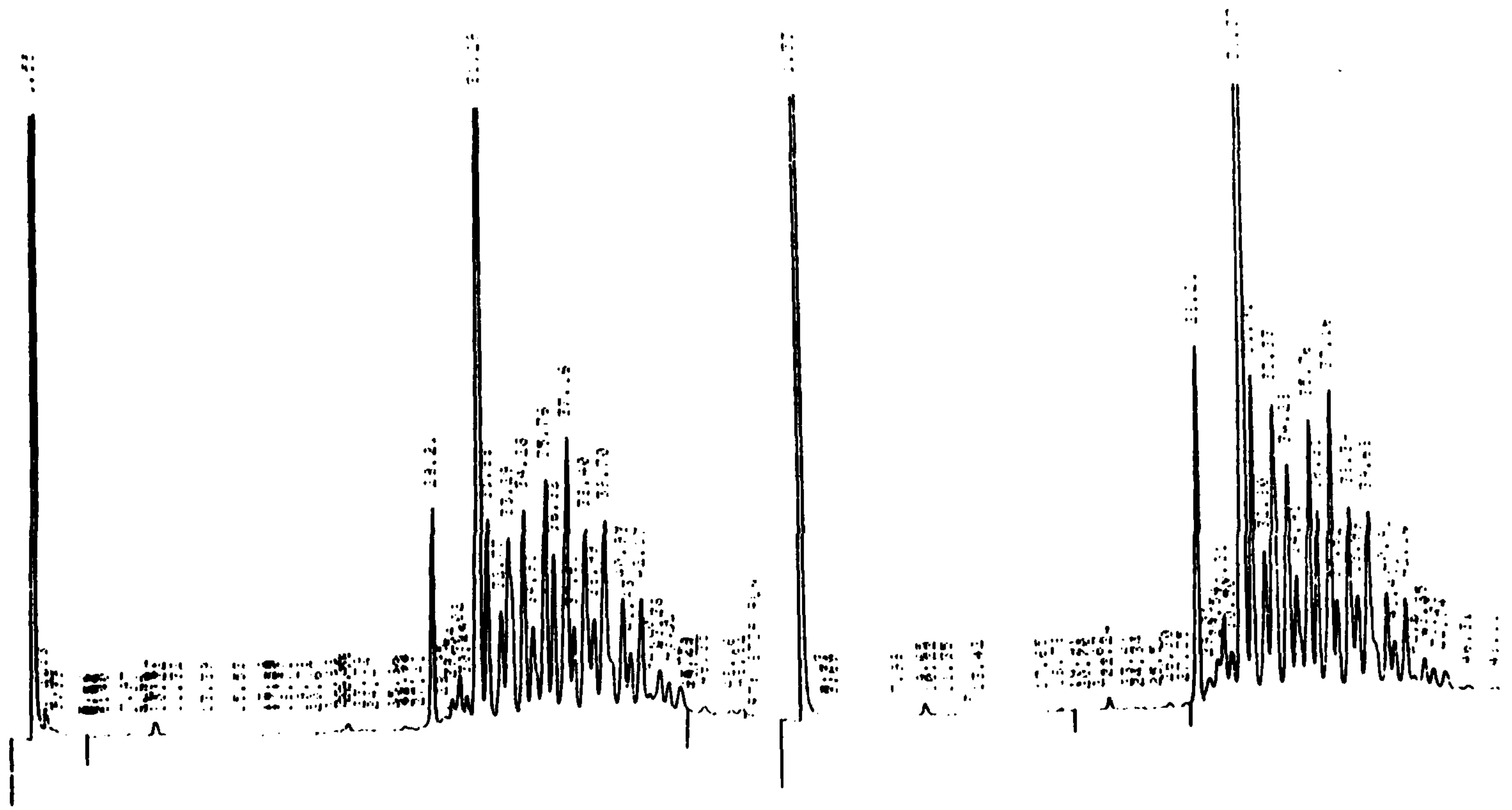
Figure 36. Gas chromatograms of distillation samples at 260°C vapor temperature.



1568865-9 with NaOH

1568862-9 without NaOH

Figure 37. Gas chromatograms of distillation samples at 280°C vapor temperature.



1568865-13 with NaOH

1568862-12 without NaOH

Figure 38. Gas chromatograms of distillation samples at 310°C vapor temperature.

distillates in the same vapor temperature ranges are shown in Figure 39. No differences are seen. These combined samples were foam tested and acid numbers were run with the following results:

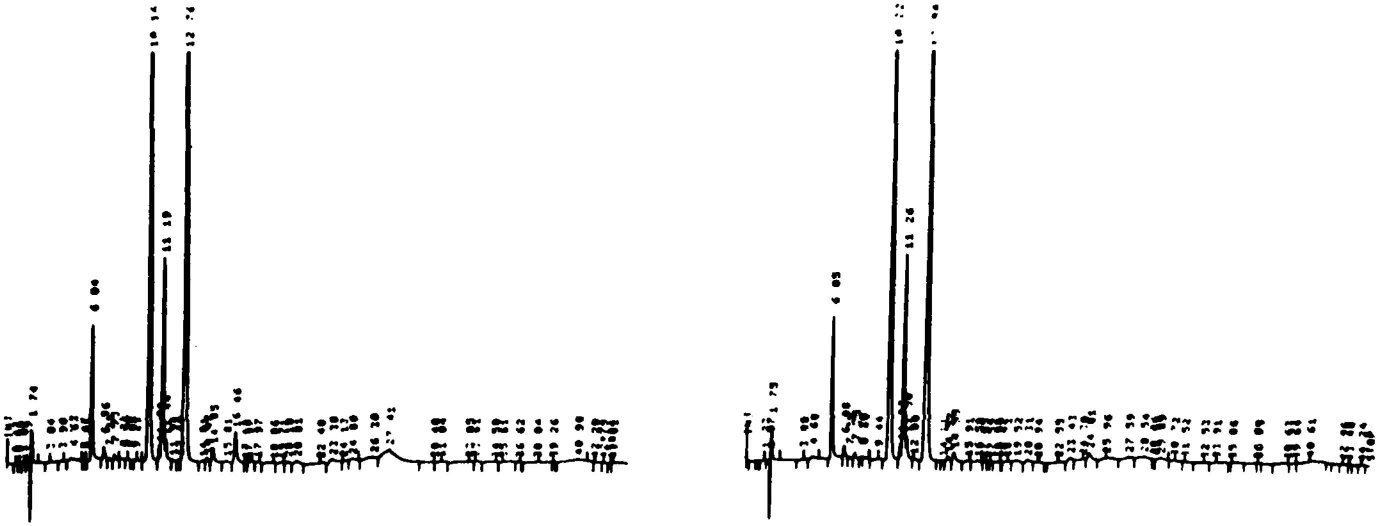
	Foam volume, mL	Acid number
1568887-A (156882 mixed fractions 3 through 11, distilled with no NaOH)	15	1.40
1568887-B (1568865 mixed fractions 4 through 11, distilled with NaOH)	10	0.35

Acid number was significantly improved by this treatment. Results show that NaOH (caustic) treatment does not adversely affect the combined distillates. In fact, the data suggest that such treatment improves acid number, color, and odor, and may eliminate some portions of posttreatment.

3.4.3 Substitution of Other Basic Material for Sodium Hydroxide

Because results of distillation with NaOH were so promising, we sought a more practical substitute. Since calcium hydroxide [$Ca(OH)_2$] can be added as a powder, its use would save total process time and energy. When $Ca(OH)_2$ was substituted, however, a solidified rubbery gel materialized in the still at 320°C, with a residue level of 13% of the original oil volume. These disappointing results terminated the study.

Other quantities of the mixture of the 15 used oils were distilled with NaOH/methanol, sodium carbonate, magnesium oxide, and a combination of 75:25 NaOH/methanol and magnesium oxide. Comparisons were made with previous distillations of NaOH/water:isopropyl alcohol. Figures 40 through 43 contain graphs showing acid number



1568887-A without NaOH

1568887-B with NaOH

Figure 39. High performance liquid chromatogram of combined distillation samples.

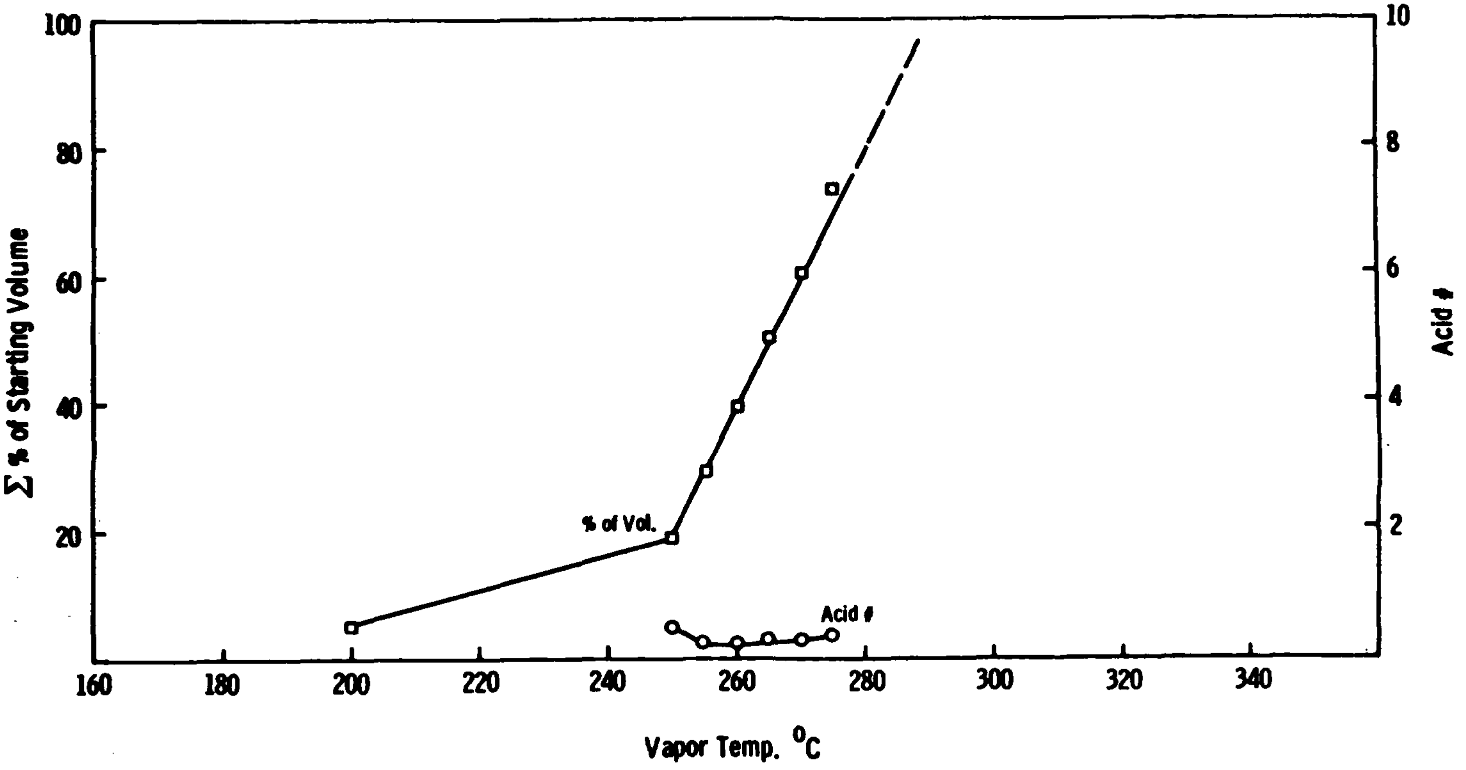


Figure 40. Sample 1732568, mixture of 15 used oils distilled with NaOH/methanol.

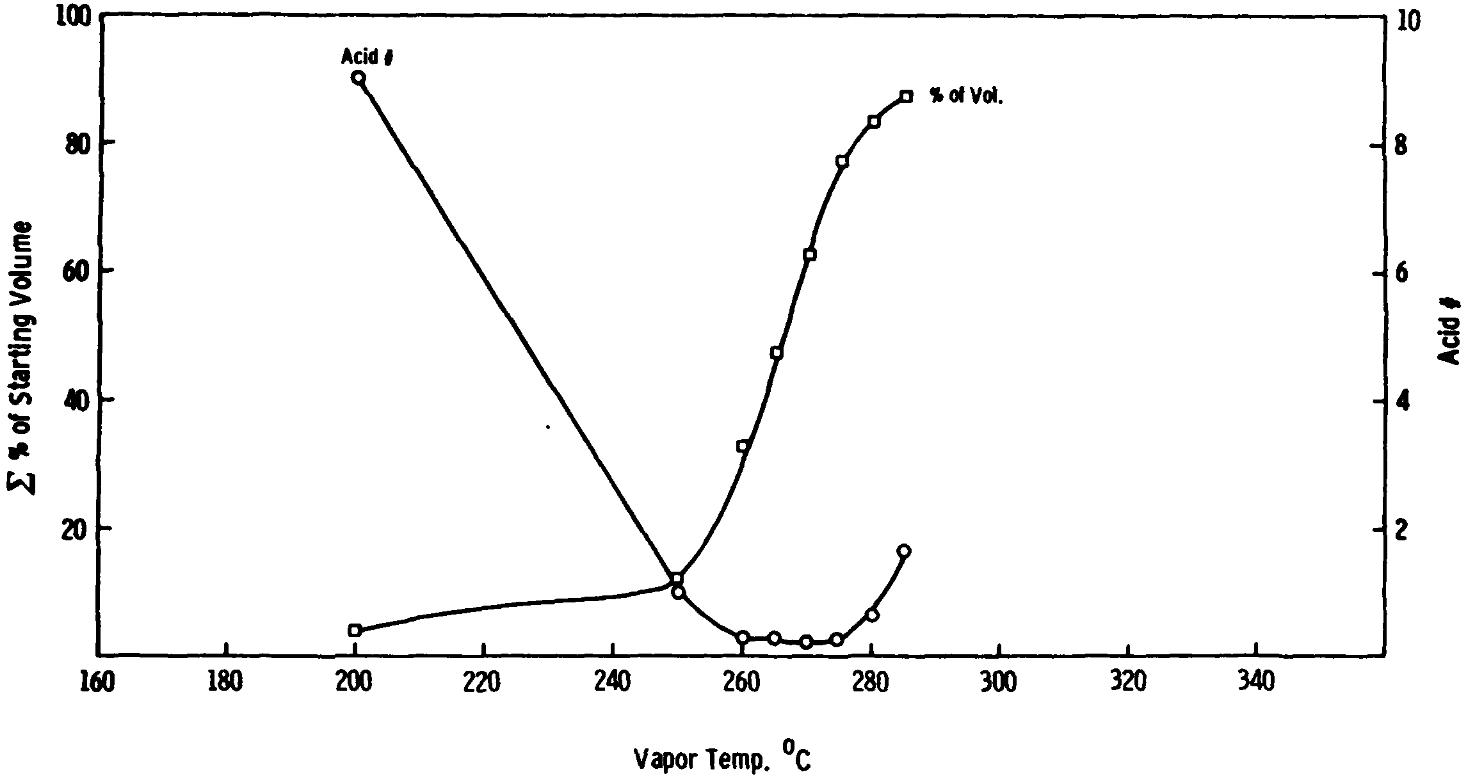


Figure 41. Sample 1732583, mixture of 15 used oils distilled with 75:25 NaOH/methanol:magnesium oxide.

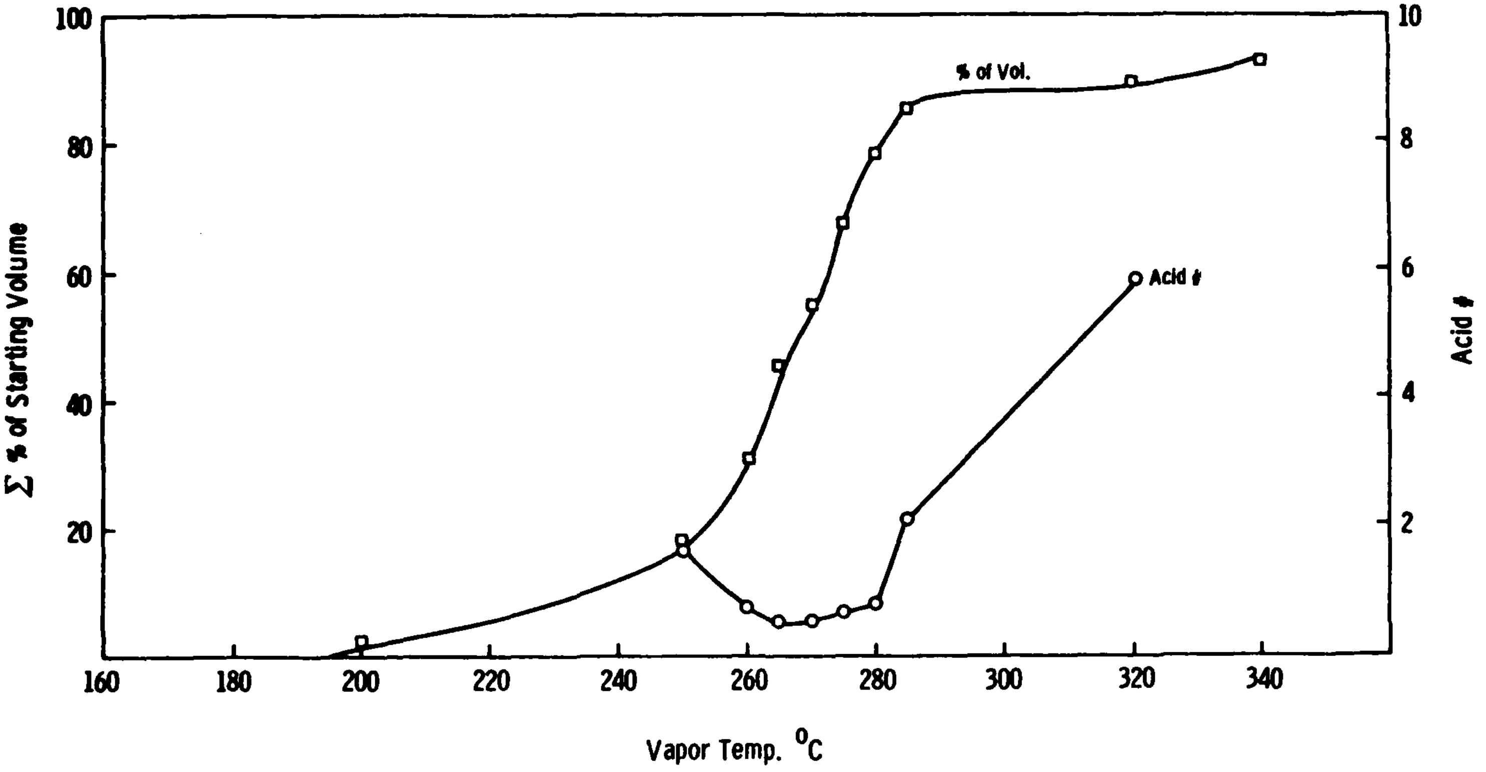


Figure 42. Sample 1732570, mixture of 15 used oils distilled with magnesium oxide.

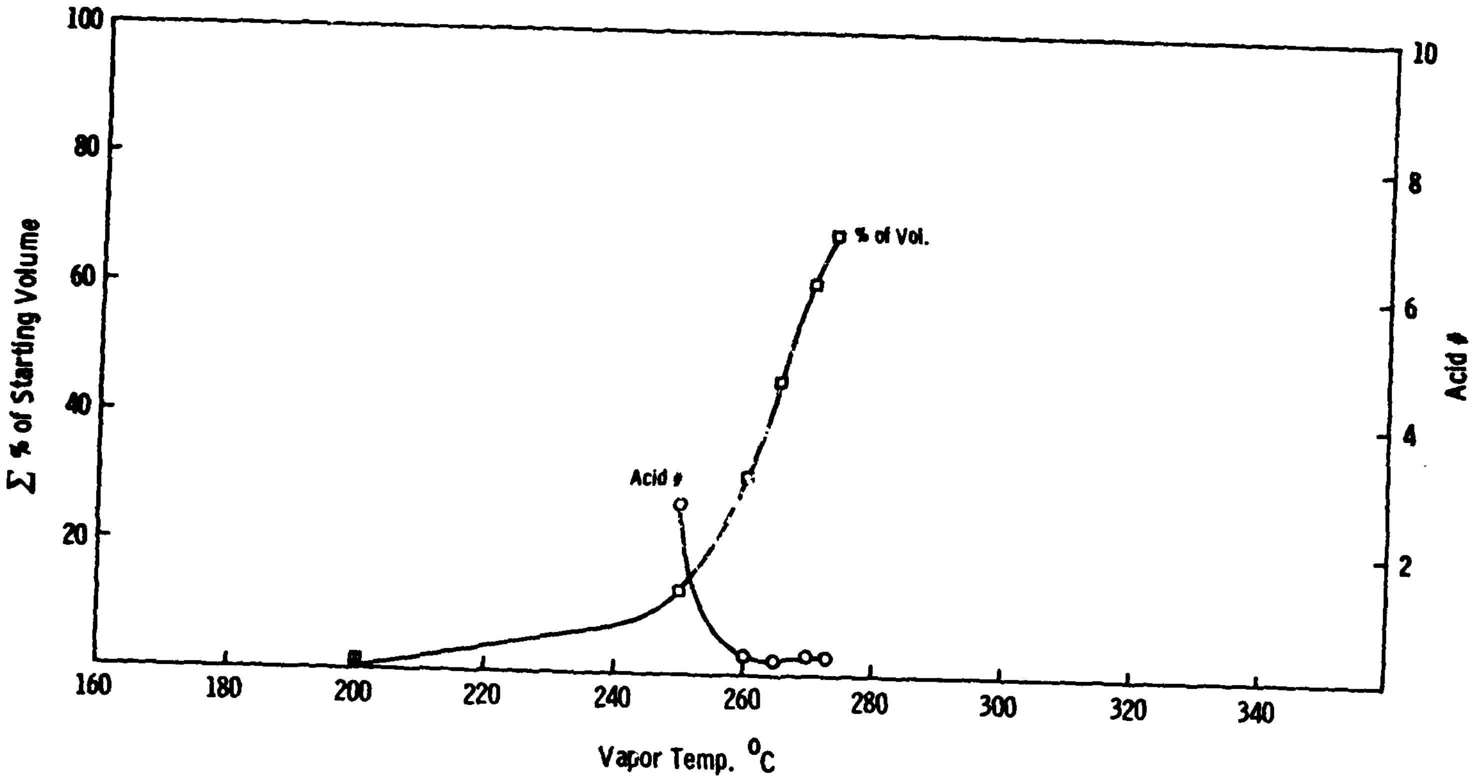


Figure 43. Sample 1732572, mixture of 15 used oils distilled with sodium carbonate.

vs. vapor temperature vs. cumulative volume percent of these distillations. HPLC's of distillates in the same vapor temperature range are shown in Figures 44 and 45. Examination of all data indicates the following decreasing order of effectiveness:

1. NaOH/methanol (Figure 40)
2. NaOH/methanol with magnesium oxide (Figure 41)
3. Magnesium oxide (Figure 42)
4. NaOH/water:isopropyl alcohol (Figure 35)
5. Sodium carbonate (Figure 43)

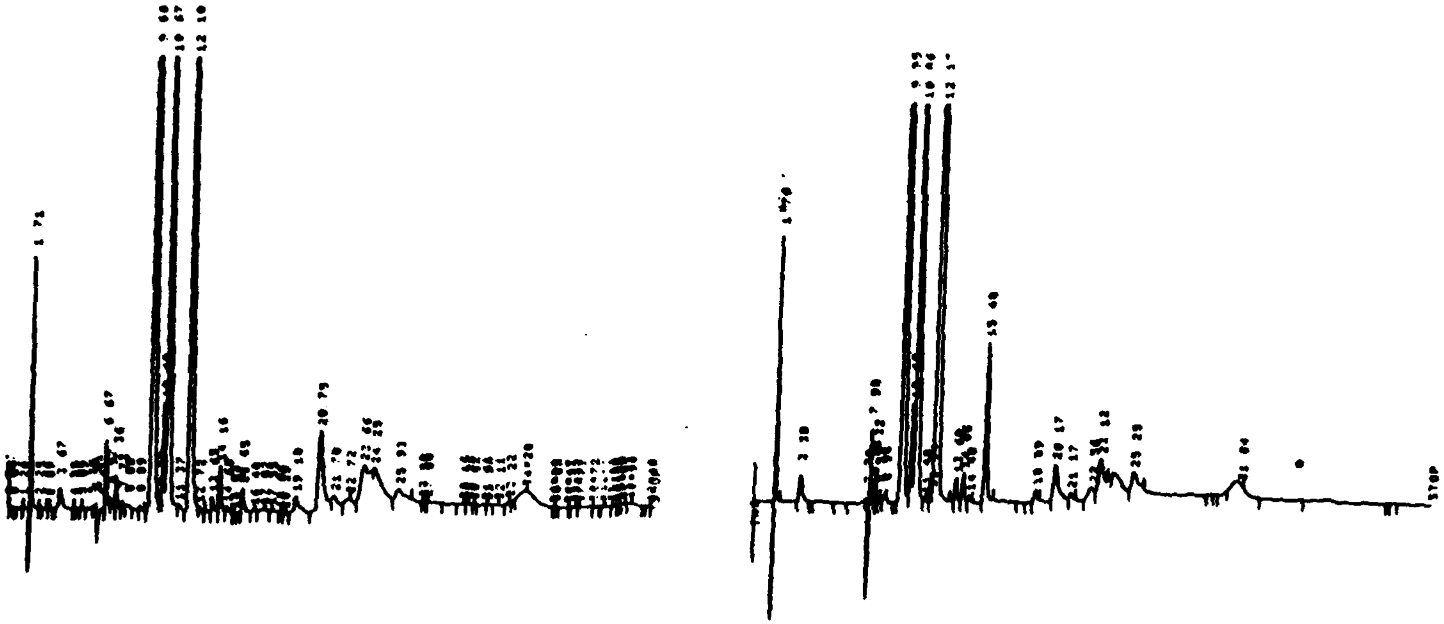
3.4.4 Comparison of NaOH Distillation of Used Oil and New Oil

Virgin oil containing MRC's proposed additive package was distilled with and without NaOH treatment to examine the distillation process with completely known additives. High performance liquid chromatograms (HPLC) of two selected distillate fractions, at the same vapor temperature range, are shown in Figure 46. It can be readily observed from the chromatograms that NaOH had removed material from the distillate. Thin layer chromatography studies of the same distillates confirmed the HPLC results. A typical chromatogram (HPLC) of MRC's additive package in a virgin base stock is shown in Figure 31.

Plots of acid number vs. vapor temperature vs. cumulative percent recovery of the virgin oil discussed above are shown in Figures 47 and 48. These two figures reemphasize the decrease in acid number with no deleterious effects on recovery by NaOH distillation.

3.4.5 Scaleup of Selected Distillations to 13-Liter Quantities

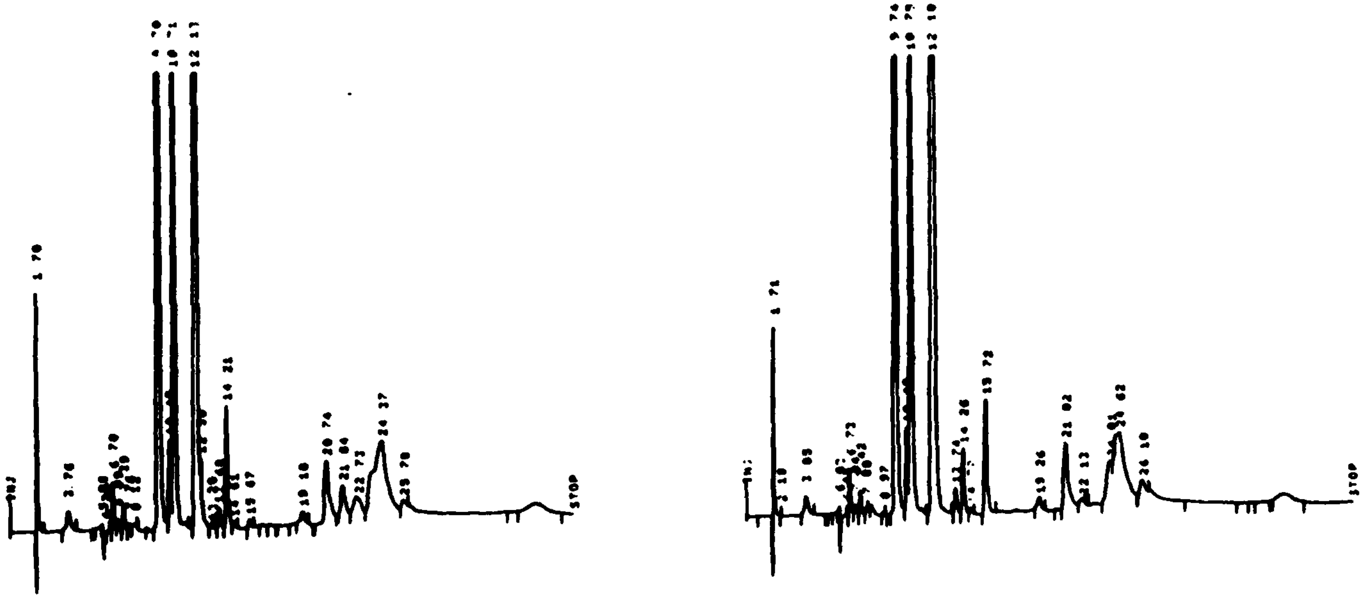
Results from previous small-scale (300-mL) distillations using various basic materials added to used oil warranted scaleup to 13-liter batch distillations with NaOH/methanol, 75/25 NaOH/magnesium oxide in methanol, NaOH/isopropyl alcohol:water, and



Sample 1732573(68),
fractions 4 through 7
distilled with NaOH/methanol

Sample 1732583,
fractions 3 through 6
distilled with 75:25 combination of
NaOH/methanol with magnesium oxide

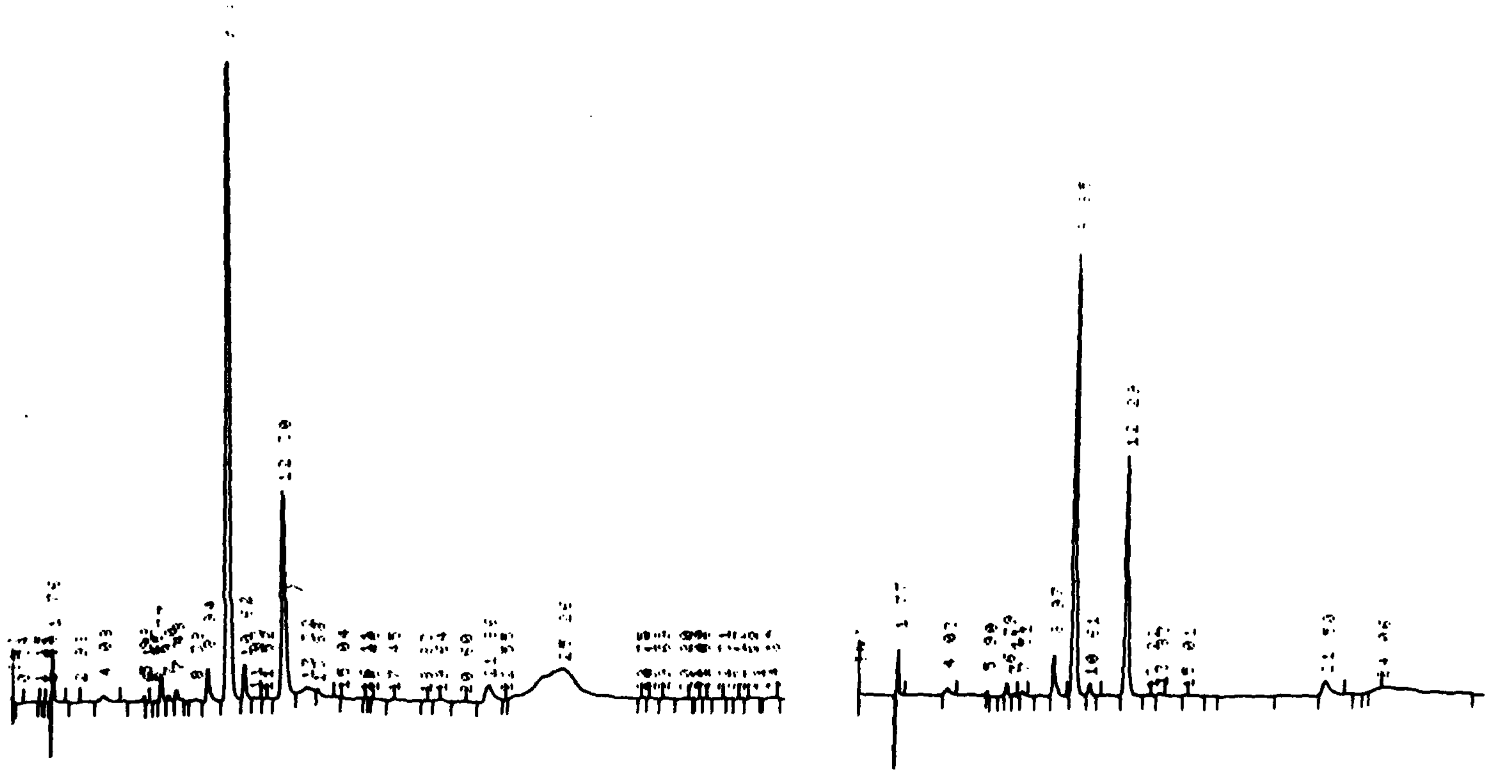
Figure 44. High performance liquid chromatograms of oil distillates in 260-275°C vapor temperature range.



Sample 1732573(70),
fractions 3 through 6
distilled with magnesium oxide

Sample 1732573(72),
fractions 3 through 6
distilled with sodium carbonate

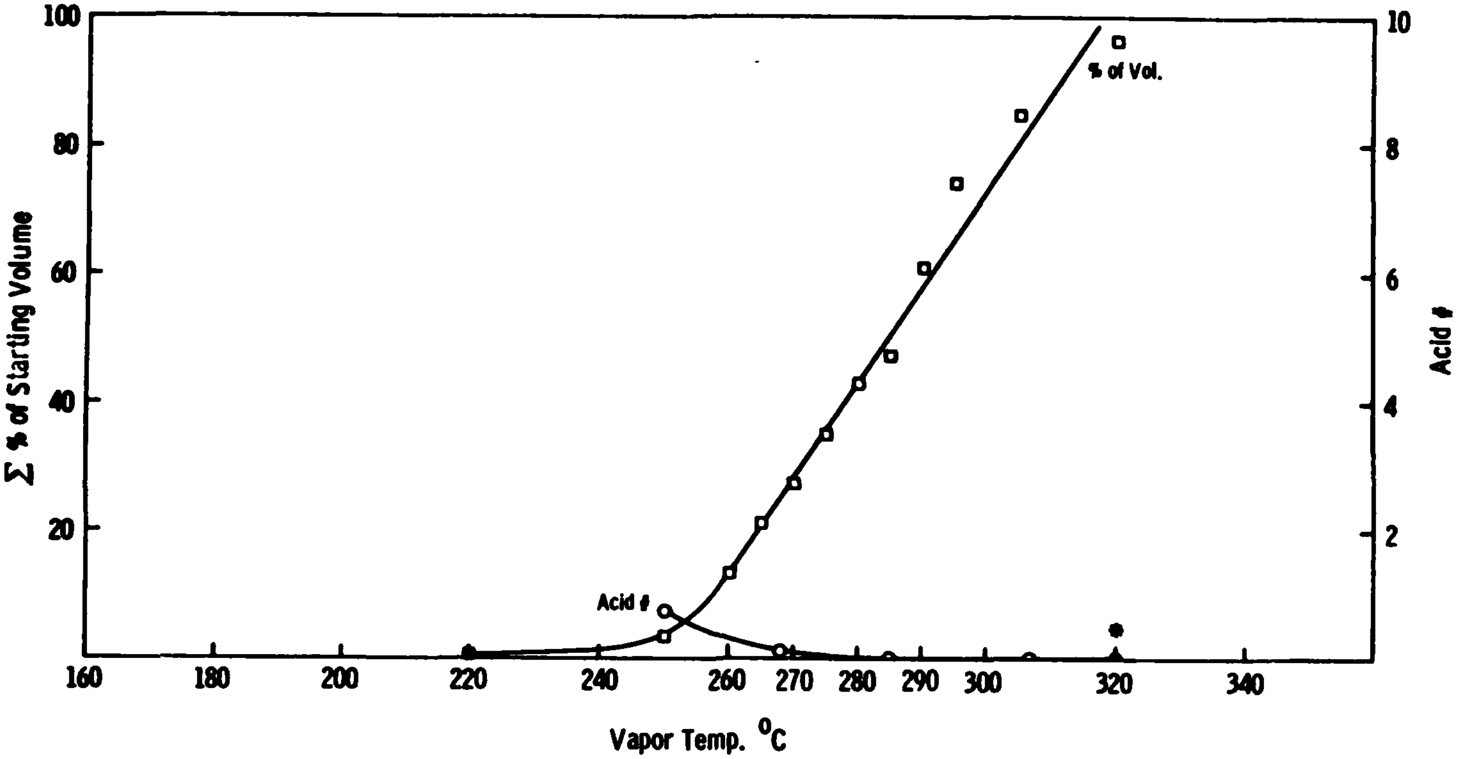
Figure 45. High performance liquid chromatograms of oil distillates in 260-275°C vapor temperature range.



Sample 1732518-8,
regular distillation

Sample 1732526-9,
NaOH distillation

Figure 46. HPLC's of two selected fractions of virgin oil containing MRC proposed additive package.



*Oil had Bumped over on this Fraction from Distillation Flask

Figure 47. Sample 1732526, Royal Lube base stock with MRC proposed additive package, distilled with sufficient NaOH for neutralization.

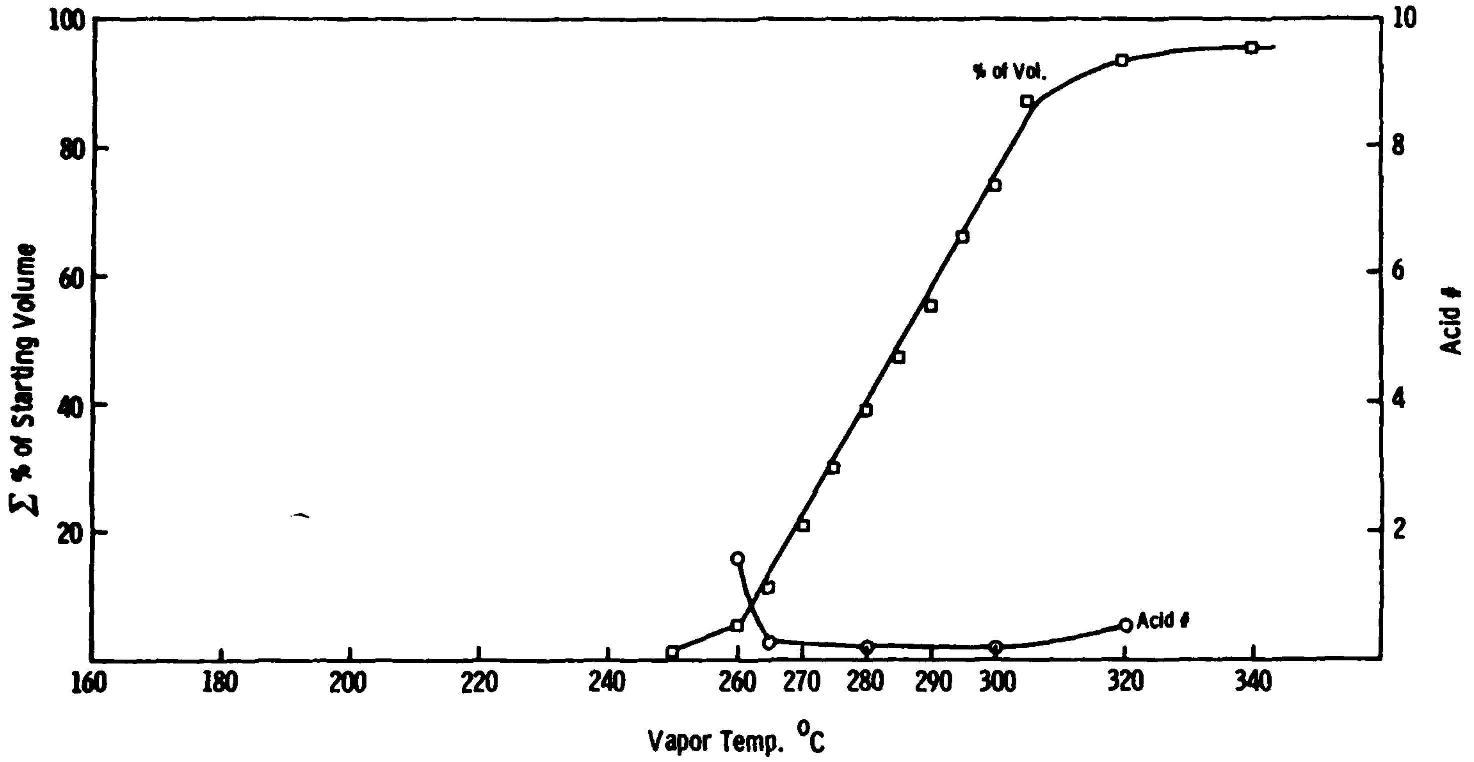


Figure 48. Sample 1732518, Royal Lube base stock with MRC proposed additive package.

regular distillation. Tables 5 and 6 summarize the intended and actual distillation conditions of the four batches. The intended distillation conditions listed in Tables 5 and 6 should be compared to prior distillation studies shown in Figures 34, 35, 40, and 41. Intended conditions were chosen by expected acid numbers and quantity recovered. The differences between the two sets of conditions were partially brought about by unfamilarity with the larger scale equipment, and by the extension of the distillation time (2 hr to 7-9 hr) caused by distilling larger oil quantities. Even with scaleup, and startup difficulties, NaOH distillation still improves acid numbers.

From these experiments, we produced sufficient quantities of distilled oil for adsorbent and other studies.

3.5 USE OF CALCIUM HYDROXIDE TO LOWER ACID NUMBERS

Our reclamation process will have to lower acid numbers to a level in which attapulgus clay is most effective in meeting MIL-L-7808H specifications. Data from earlier work in this program, described in Section 3.6, suggested the use of a slurry with sufficient $Ca(OH)_2$ to neutralize the acid number, but data from distillations with acid numbers around 0.50 or less did not support this idea. Results of a study initiated to determine the necessary level of $Ca(OH)_2$ are presented in Table 7. The data generally indicate 0.2% by weight $Ca(OH)_2$ as the minimum amount, unless a high acid number requires a larger amount for neutralization. In some instances treated samples of the same distillate do not have comparable acid numbers, but the numbers are still sufficiently lowered for reformulation. For our process, we will use a minimum of 0.3% by weight of $Ca(OH)_2$; The maximum will be the amount necessary to neutralize larger acid numbers. The time required to slurry the $Ca(OH)_2$ will be determined individually for each batch reclaimed in the pilot plant, and the resultant data will enable us to determine a minimum slurry time.

TABLE 5. LARGE-SCALE (13-LITER) DISTILLATION CONDITIONS

Batch identify	Intended distillation conditions[a]: Distillation temperature, °C	Intended distillation conditions[a]: Percent original volume	Intended distillation conditions[a]: Estimated acid number	Actual distillation conditions[a]: Distillation temperature, °C	Actual distillation conditions[a]: Percent original volume	Actual distillation conditions[a]: Acid number[b]
	1732588 with NaOH/methanol					
1st Fraction Precollection	200 PT[c]-240 VT[d]	16.0	1.5+	200 PT-240 VT	5.1	3.73
2nd Fraction Collected for intended reformulation	240 VT-285 VT	73.0	0.25	240 VT-285 VT	70.5	0.45
3rd Fraction Postcollection	285+ VT	6.0	1.5+	285 VT-305 VT	9.0	1.58
	1732591 with 75/25 NaOH/magnesium oxide in methanol					
1st Fraction Precollection	200 PT-250 VT	11.0	1.5+	200 PT-250 VT	7.0	2.57
2nd Fraction Collected for intended reformulation	250 VT-285 VT	76.0	0.40	250 VT-282 VT	65.5	0.32
3rd Fraction Postcollection	285+ VT	8.0	1.5+	282 VT-314 VT	20.0	1.31

[a] 14-15 mm pressure.

[b] Original acid number for oil before distillation = 2.45.

[c] PT = pot temperature.

[d] VT = vapor temperature.

TABLE 6. LARGE-SCALE (13-LITER) DISTILLATION CONDITIONS

	Intended distillation conditions[a]			Actual distillation conditions[a]		
Batch identity	Distillation temperature, °C	Percent original volume	Estimated acid number	Distillation temperature, °C	Percent original volume	Acid number[b]
	NaOH/isopropyl alcohol/water					
1st Fraction Precollection	200 PT[c]-240 VT[d]	15	1.5+	200 PT-240 VT	1.7	8.95
2nd Fraction Collected for intended reformulation	240-290 VT	71	0.3	240-290 VT	65.5	2.10
3rd Fraction Postcollection	290+ VT	5	1.5+	290-335 VT	27.2	1.70
	Regular distillation (without treatment)					
1st Fraction Precollection	200 PT-255 VT	19	3.4+	200 PT-260 VT	9.2	23.88
2nd Fraction Collected for intended reformulation	255-320 VT	71	1.0	260-310 VT	82	16.3
3rd Fraction Postcollection	320+ VT	2	2.7+	310-330 VT	5.2	7.3

[a] 14-15 mm pressure.

[b] Original acid number for oil before distillation = 2.69.

[c] PT = pot temperature.

[d] VT = vapor temperature.

TABLE 7. RESULTS OF VARYING $Ca(OH)_2$ TREATMENT LEVEL

Reference number	Treatment level of $Ca(OH)_2$	Acid number	Percent by weight $Ca(OH)_2$ to oil
1830378	Amount to neutralize acid number in 1732591-2[a]	0.39	0.04
1830378	5 times amount to neutralize acid number in 1732591-2	<.018	0.2
1830364	12.5 times amount to neutralize acid number in 1732591-2	.032	0.5
1830358	12.5 times amount to neutralize acid number in 1732591-2	.045	0.5
1830352	12.5 times amount to neutralize acid number in 1732591-2	.090	0.5
1830380	Amount to neutralize acid number in 1732588-4[b]	<.018	0.2
1830380	4 times amount to neutralize acid number in 1732588-4	<.018	0.8
1830380	12.5 times amount to neutralize acid number in 1732588-4	<.018	2.6
1830382	Amount to neutralize acid number in 1732588-3[c]	.40	0.06
1830382	4 times amount to neutralize acid number in 1732588-3	<.018	0.24
1830382	8 times amount to neutralize acid number in 1732588-3	<.018	0.48
1830385	5 times amount to neutralize acid number in 1732588-3	.090	0.3

[a] Main fraction of caustic:MgO/methanol distillation, acid number of 0.39.

[b] Post fraction of caustic/methanol distillation, acid number of 1.58.

[c] Main fraction of caustic/methanol distillation acid number of 0.45.

3.6 ADSORPTION TREATMENT STUDY

Another part of our reclamation process will be an adsorption treatment to remove surfactants, trace metals, and other material that distilled over and was not removed during $Ca(OH)_2$ treatment.

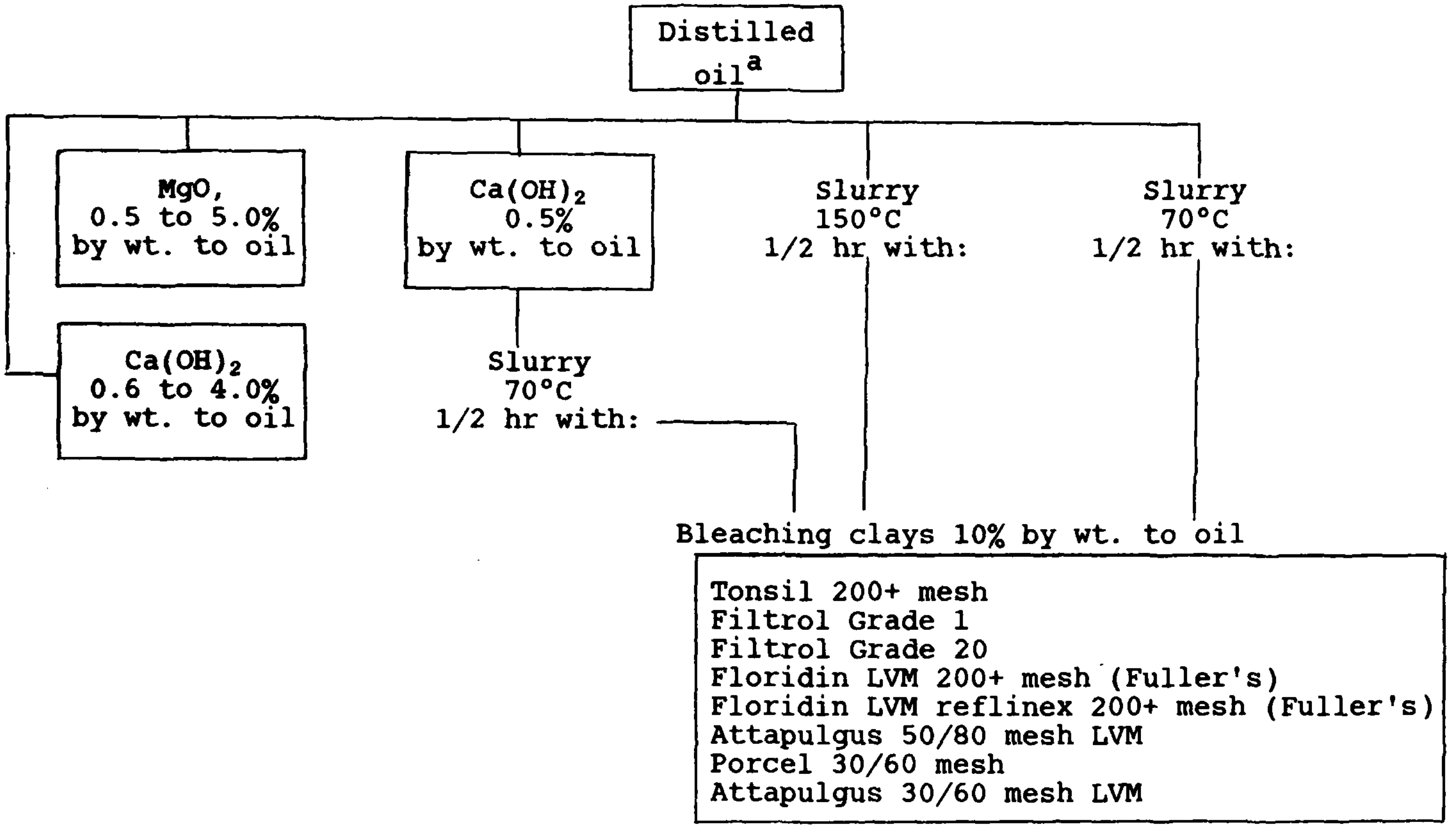
3.6.1 Slurry Treatment

Oil samples from the main distillate of the used oil distilled with NaOH/methanol (RF N/M = reformulation fraction NaOH/methanol distillation), were slurried at two different temperatures with eight adsorbents at 10% by weight to oil. Samples were also slurried with $Ca(OH)_2$ and magnesium oxide (MgO) at various concentrations to maximize lowering of the acid number. Oil slurried with 0.5% by weight $Ca(OH)_2$ was also slurried with bleaching clays for examination. Table 8 summarizes the adsorbent study scheme. Table 9 summarizes thin layer chromatography (TLC), high performance liquid chromatography (HPLC), and acid number analyses of the distillate treated with bleaching clays at two different temperatures (70°C and 150°C) to determine minimum treatment temperature. The data in Table 9 suggest the use of attapulgus or fuller's clay for additive/degradation product removal at 70°C.

Acid number lowering of the distillate with basic material was examined and the data are shown in Table 10. HPLC and TLC results indicate no differences in additive/degradation product removal by varying the basic material level or between $Ca(OH)_2$ and MgO. Data indicates use of $Ca(OH)_2$ as most effective in lowering the acid number.

In another study, the RF N/M distillate was treated with 0.5% by weight $Ca(OH)_2$ and then slurried with bleaching clays at 70°C. The data shown in Table 11 suggest the use of attapulgus or fuller's clay for treatment.

TABLE 8. ADSORBENT STUDY SCHEME



[a] Main fraction distillate of NaOH/methanol distillation.

TABLE 9. SUMMARY OF DISTILLATE TREATED WITH VARIOUS BLEACHING CLAYS[a]

Bleaching Clays 10% by wt. to Oil	Acid No. Slurry heated to 70°C	Acid No. Slurry heated to 150°C
Tonsil 200+ mesh	0.17	0.16
Filtrol Grade 1 200+ mesh	0.24	1.77
Filtrol Grade 20 200+ mesh	0.25	2.26
Floridin 200+ mesh (Fullers)	0.14	0.09
Floridin reflinex (Fullers) 200+ mesh	0.10	0.10
Attapulgus 50/80 mesh LVM	0.17	0.10
Porcel 30/60 mesh	0.10	0.15
Attapulgus 30/60 mesh LVM	0.11	0.18

Thin Layer Chromatography[b]

Decreasing removal of material ↓

Slurry heated to 70°C	
Filtrol 1	+
Filtrol 20	
Attapulgus 30/60	
Tonsil	0
All Fullers	
Attapulgus 50/80	
Porcel	-

Slurry heated to 150°C	
Tonsil	+
Floridin reflinex	
Attapulgus 30/60	0
Floridin 200+	
Attapulgus 50/80	
Filtrol 1	0^-
Filtrol 20	
Porcel	-

Clays rated + at 150°C are slightly better than clays rated + at 70°C.

High Pressure Liquid Chromatography[b]

Decreasing removal of material ↓

Slurry heated to 70°C	
6 clays	0
Filtrol 1	-
Filtrol 20	

Slurry heated to 150°C	
Attapulgus 50/80	+
Porcel	
4 clays	0
Filtrol 1	-
Filtrol 20	

Comparison of clays rated + at 150°C are equivalent to clays rated 0 at 70°C.

---

[a] Main fraction from NaOH/methanol distillation.

[b] Subjective test, with + meaning the greatest removal of material.

TABLE 10. USE OF BASIC MATERIAL TO LOWER ACID NUMBER AFTER DISTILLATION[a]

$Ca(OH)_2$ as a base		MgO as a base	
Level of addition	Resulting acid number of the treated oil[b]	Level of addition	Resulting acid number of the treated oil[b]
Stoichiometric amount for 0.0 acid number (0.06% by wt. to oil)	0.02	Stoichiometric amount for 0.0 acid number (3.0% by wt. to oil)	0.48
0.5% by wt. to oil	0.06	0.5% by wt. to oil	0.35
2.0% by wt. to oil	0.02	2.0% by wt. to oil	0.14
4.0% by wt. to oil	0.03	4.0% by wt to oil	0.10

[a] Slurry for 16 hours at room temperature; main fraction from NaOH/methanol distillation.

[b] Original acid number before treatment: 0.52.

TABLE 11. SUMMARY OF DISTILLATES[a] SLURRIED WITH 0.5% BY WEIGHT $Ca(OH)_2$ AND THEN WITH VARIOUS BLEACHING CLAYS

Bleaching Clays Slurried at 70°C	Acid No.
No Bleaching Clay treatment	<0.09
Porcel	<0.09
Attapulgus 30/60	<0.09
Attapulgus 50/80	0.00
Floridin (Fullers) 200+	<0.09
Floridin reflinex	<0.09
Tonsil	<0.09
Filtrol Grade 1	<0.08
Filtrol Grade 20	<0.09

High Pressure Liquid Chromatography[b]

Decreasing removal of material ↓

Attapulgus 50/80
Attapulgus 30/60
Floridin 200+ (Fullers)
} almost equal

Remaining clays equal to or worst than oil before treatment.

Thin Layer Chromatography

Tonsil Floridin reflinex	+
Floridin 200+ mesh Attapulgus 30/60 Attapulugus 50/80	0+
Filtrol Grade 1 Filtrol Grade 20	0
Porcel	-

---

[a] Main fraction from NaOH/methanol distillation.

[b] Subjective test, with + meaning greatest removal of material.

When acid number needs lowering, the data generated by this adsorbent study suggest a slurry at room temperature for 16 hr with the stoichiometric level of caustic to neutralize the acid number, followed by a slurry with fuller's or attapulgus bleaching clays at 70°C for 0.5 hour.

The adsorbent study scheme suggested by the data generated with the RF N/M distillate, which will be used with the distillates from the remaining three scaleup distillations is shown in Table 12.

Data presented in Table 13, for main distilled fraction (MDF) from NaOH/H_2O in isopropyl alcohol (IPA) distillation, suggest the use of enough $Ca(OH)_2$ to neutralize the acid number, followed by treatment with fuller's earth. Data in Table 14 for MDF from NaOH/MgO distillation indicate the use of the stoichiometric level of $Ca(OH)_2$ to neutralize the acid number followed by treatment with either fuller's earth or attapulgus clay.

Data in Table 15 (MDF from no treatment) suggest slurry with the stoichiometric amount of $Ca(OH)_2$ to neutralize, followed by reslurry with fuller's earth.

A comparison of acid number, HPLC, and TLC data for the reclaimed oil from the four large-scale distillations suggests the following decreasing order of effectiveness for the additive/degradation removal processes:

1. NaOH/MeOH - $Ca(OH)_2$ slurry - attapulgus clay slurry
2. NaOH:MgO/MeOH - $Ca(OH)_2$ slurry - fuller's or attapulgus clay slurry
3. Either NaOH/H_2O:IPA - $Ca(OH)_2$ slurry - fuller's earth slurry, or use of no basic material - $Ca(OH)_2$ slurry - fuller's earth slurry

TABLE 12. ADSORBENT STUDY SCHEME TO USE WITH DISTILLATES OF THE REMAINING 3 SCALE-UP DISTILLATIONS

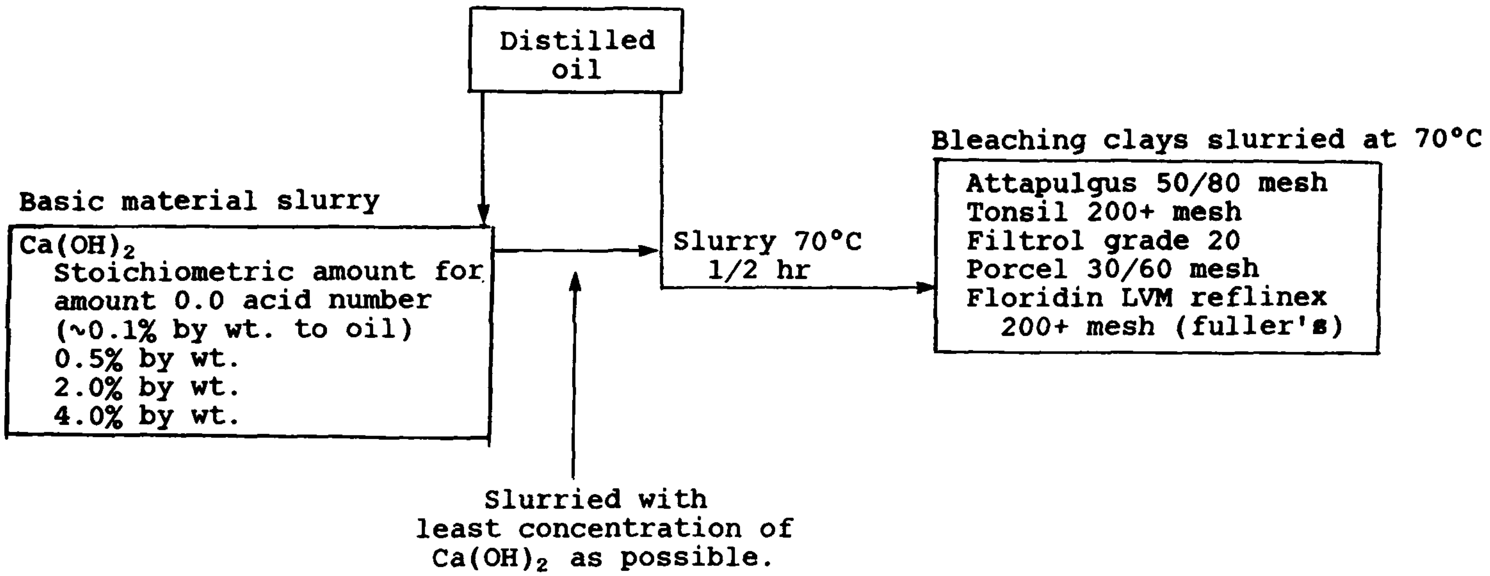


TABLE 13. SUMMARY OF MAIN FRACTION DISTILLATE FROM NaOH/ WATER: ISOPROPYL ALCOHOL DISTILLATION TREATED WITH VARIOUS BLEACHING CLAYS

Bleaching clays 10% by weight slurried at 70°C	Acid number oil treated with clay	Acid number of oil treated with 0.5% by weight Ca(OH)$_2$ and then with clay
No clay treatment	2.18	<0.06
Tonsil	1.47	>0.09 <0.18
Attapulgas	1.66	<0.09
Fullers (Floridin-reflinex)	1.18	<0.09
Filtrol 20	1.83	<0.09

Lowering of acid number with Ca(OH)$_2$	Acid number
Quantity to neutralize acid no. (0.28%)	<0.09
0.5% by weight Ca(OH)$_2$	<0.06
2.0% by weight Ca(OH)$_2$	<0.09

No difference in removal by changing Ca(OH)$_2$ treatment level by HPLC and TLC.

Thin Layer Chromatography

	Oil + adsorbents	Oil + Ca(OH)$_2$ + adsorbents
Decreasing removal of material ↓	Filtrol 20	Tonsil
	Tonsil	Fullers (reflinex)
	Attapulgas	Filtrol 20
	Fullers (reflinex)	Attapulgas

Ca(OH)$_2$ + bleaching clays better than bleaching clays only.

High Pressure Liquid Chromatography

	Oil + adsorbents	Oil + Ca(OH)$_2$ + adsorbents
Decreasing removal of material ↓	Attapulgas	Tonsil
	Tonsil	Fullers (reflinex)
	Fullers (reflinex)	Filtrol 20
	Filtrol 20	Attapulgas

Ca(OH)$_2$ + Tonsil better than attapulgas alone.

TABLE 14. SUMMARY OF MAIN FRACTION DISTILLATE FROM 75/25 NaOH/MgO IN METHANOL, DISTILLATION TREATED WITH VARIOUS BLEACHING CLAYS

Bleaching clays 10% by weight slurried at 70°C	Acid number oil treated with clay	Acid number of oil treated with 0.5% by weight $Ca(OH)_2$ and then with clay
No clay treatment	0.35	<0.08
Tonsil	0.12	<0.09
Filtrol 20	0.18	0.11
Fullers (reflinex)	0.09	<0.09
Attapulgas	0.13	<0.09

Lowering of acid number with $Ca(OH)_2$	Acid number
Quantity to neutralize acid no. (0.042%)	<0.080
0.5% by weight	<0.080
2.0% by weight	<0.085

No difference in removal by changing $Ca(OH)_2$ treatment level by HPLC and TLC.

Thin Layer Chromatography[a]

	Oil + adsorbents		Oil + $Ca(OH)_2$ + adsorbents	
Decreasing removal of material ↓	Tonsil	same	Tonsil	+
	Attapulgas		Fullers	+
	Fullers (reflinex)		Attapulgas	0
	Filtrol 20	-	Filtrol 20	-

Treatment with $Ca(OH)_2$ + clay better than clay alone.

High Pressure Liquid Chromatography[a]

	Oil + adsorbents	Oil + $Ca(OH)_2$ + adsorbents
Decreasing removal of material ↓	Fullers (reflinex)	Fullers (reflinex)
	Tonsil	Attapulgas
	Attapulgas	Tonsil
	Filtrol 20	Filtrol 20

Treatment with $Ca(OH)_2$ + clay slightly better than clay alone.

---

[a] Subjective test, with + meaning greatest removal of material.

TABLE 15. SUMMARY OF MAIN FRACTION DISTILLATE FROM DISTILLATION TREATED WITH NO BASIC MATERIAL, TREATED WITH VARIOUS BLEACHING CLAYS

Bleaching clays 10% by weight slurried at 70°C	Acid number oil treated with clay	Acid number of oil treated with 3% by weight $Ca(OH)_2$ and then with clay
No bleaching clay treatment	1.84	0.17
Tonsil 200+ mesh	1.24	0.24
Porcel	0.60	0.22
Fullers (Floridin-reflinex)	0.73	0.22
Attapulgas 50/80 mesh	1.40	0.17
Filtrol grade 20	1.43	0.17

Lowering of acid number with $Ca(OH)_2$	Acid number
0.5% by weight	0.22
2% by weight	0.17
Quantity to neutralize acid no. (2.1%)	0.17
3% by weight	0.17
4% by weight	0.16

No difference in removal by changing $Ca(OH)_2$ treatment level by HPLC and TLC.

Thin Layer Chromatography[a]

Decreasing removal of material ↓	Oil + adsorbents		Oil + $Ca(OH)_2$ + adsorbents	
	Filtrol grade 20	+		
	Fullers (reflinex)	0+	Tonsil	+
	Tonsil		Filtrol grade 20	0+
	Attapulgas	0	Fullers (reflinex)	
	Porcel	-	Attapulgas	0
			Porcel	-

Oil + $Ca(OH)_2$ + adsorbents better than oil + adsorbents.

High Pressure Liquid Chromatography[a]

Decreasing removal of material ↓	Oil + adsorbents		Oil + $Ca(OH)_2$ + adsorbents	
	Tonsil	+	Fullers	+
	Fullers	0	Tonsil	
	Attapulgas		Filtrol 20	0
	Filtrol 20	-	Attapulgas	
	Porcel		Porcel	-

Oil + $Ca(OH)_2$ + adsorbents = oil + adsorbents.

[a] Subjective test, with + meaning greatest removal of material.

We recommend NaOH/MeOH - $Ca(OH)_2$ slurry - attapulgus clay slurry as a viable reclamation procedure on which to base our future studies.

Studies had shown that attapulgus clay slurried in oil at approximately 70°C was the ideal treatment for additive/degradation product removal. We further defined the optimum slurry temperature through the use of HPLC, TLC, and acid number. Results are presented in Table 16. The data show a wide range of temperatures that could be used, but to keep energy costs low and oil viscosity down (to aid in filtration), we will clay treat at 50°C for 30 min to 1 hr.

The attapulgus clay-to-oil ratio will be determined individually for each batch processed in the pilot plant; the results will enable us to determine a general clay-to-oil ratio.

TABLE 16. VARYING ATTAPULGUS CLAY TREATMENT TEMPERATURE

Conditions (slurry for 30 min)	Acid number	TLC[a]	HPLC[a]
90-105°C	<0.018	0^+	0^-
70-77°C	<0.018	0	0
50-55°C	<0.018	0	0
30-40°C	<0.018	0	0

1830373 - Main fraction NaOH:MgO/methanol distillate treated with $Ca(OH)_2$ and 10% by weight clay to oil.

[a] Subjective test, with + meaning the greatest removal of material.

3.6.2 Chromatographic Adsorbent Studies

We examined the use of a column (93 cm x 1 cm) packed with 50/80 mesh attapulgus clay heated from 70-100°C for comparison with the 10% by weight clay-to-oil slurry procedure. The MDF from NaOH/MeOH treated with 0.5% by weight $Ca(OH)_2$ was used, to provide a direct comparison with the slurry studies. Acid number data presented in Figure 49 for both procedures show that the slurry treatment is more efficient; HPLC and TLC data bear out this conclusion.

We extended this study by varying column temperature and oil retention time. Figures 50, 51, and 52 present sample acid number vs. total volume through column by varying column conditions. The data suggest that a ≤7.5-min retention time and a column temperature of 65-80°C will treat (determined by HPLC and TLC) a greater volume of oil than a slurry of 10% by weight clay to oil. Nevertheless, the 10% by weight clay presently used for slurrying is probably an excess, and column adsorption is not as attractive as the data suggest because of the extra work involved in packing columns on a large scale and the need for high pressure pumps. We will therefore use the slurry adsorption procedure in our reclamation process.

3.7 USE OF ACTIVATED CHARCOAL AS AN ADSORBENT

The original reclamation process included an activated charcoal treatment step of questionable value. We again examined the use of charcoal in this program. A sample of a distillate treated with $Ca(OH)_2$ and attapulgus clay was treated with 6% by weight charcoal to oil for 30 min at 70°C and examined by HPLC and TLC. The only perceptible change to the oil was a very slight color improvement, which may not improve the total reclamation process.

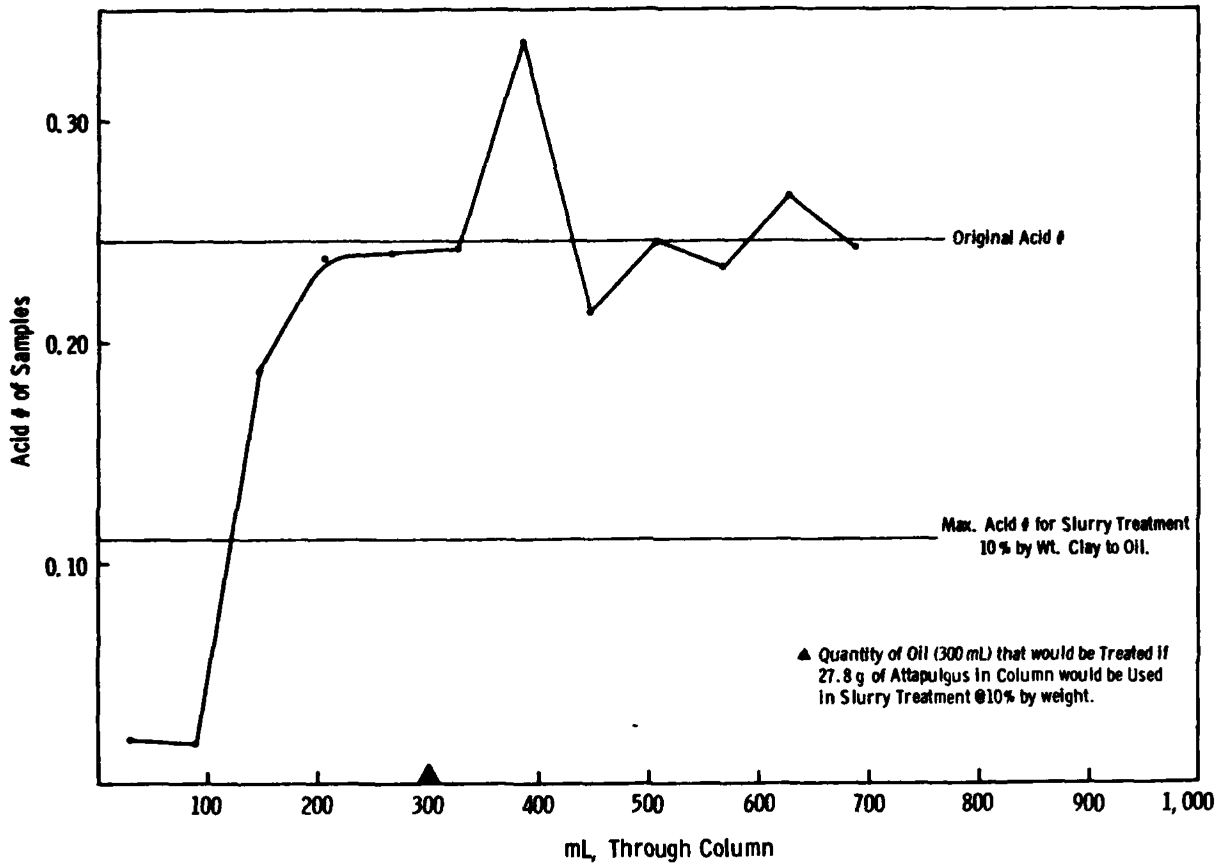


Figure 49. Main fraction from NaOH/MeOH distillation, pretreated with $Ca(OH)_2$, followed by chromatographic treatment with attapulgus clay.

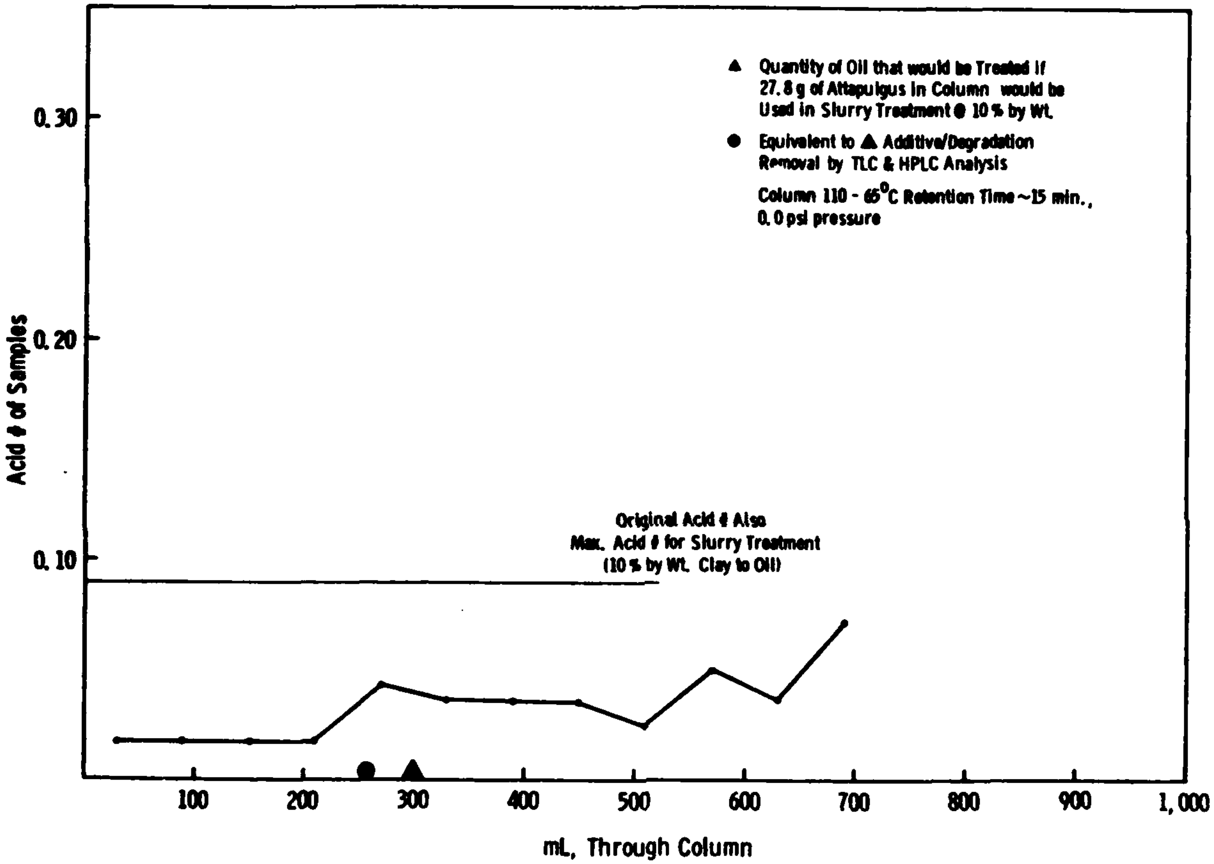


Figure 50. Main fraction from NaOH:MgO/MeOH distillation, pretreated with $Ca(OH)_2$, followed by chromatographic treatment with attapulgus clay.

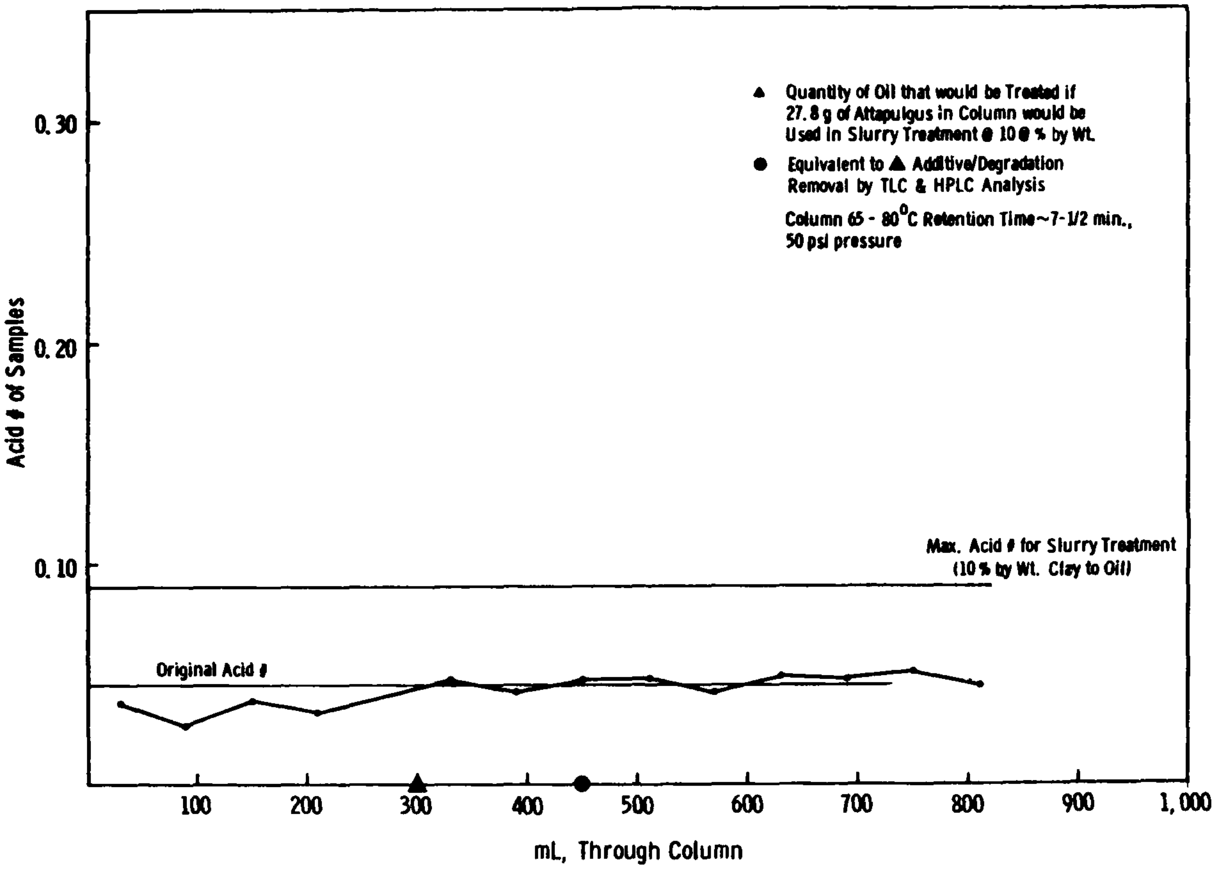


Figure 51. Main fraction from NaOH:MgO/MeOH distillation, pretreated with $Ca(OH)_2$, followed by chromatographic treatment with attapulgus clay.

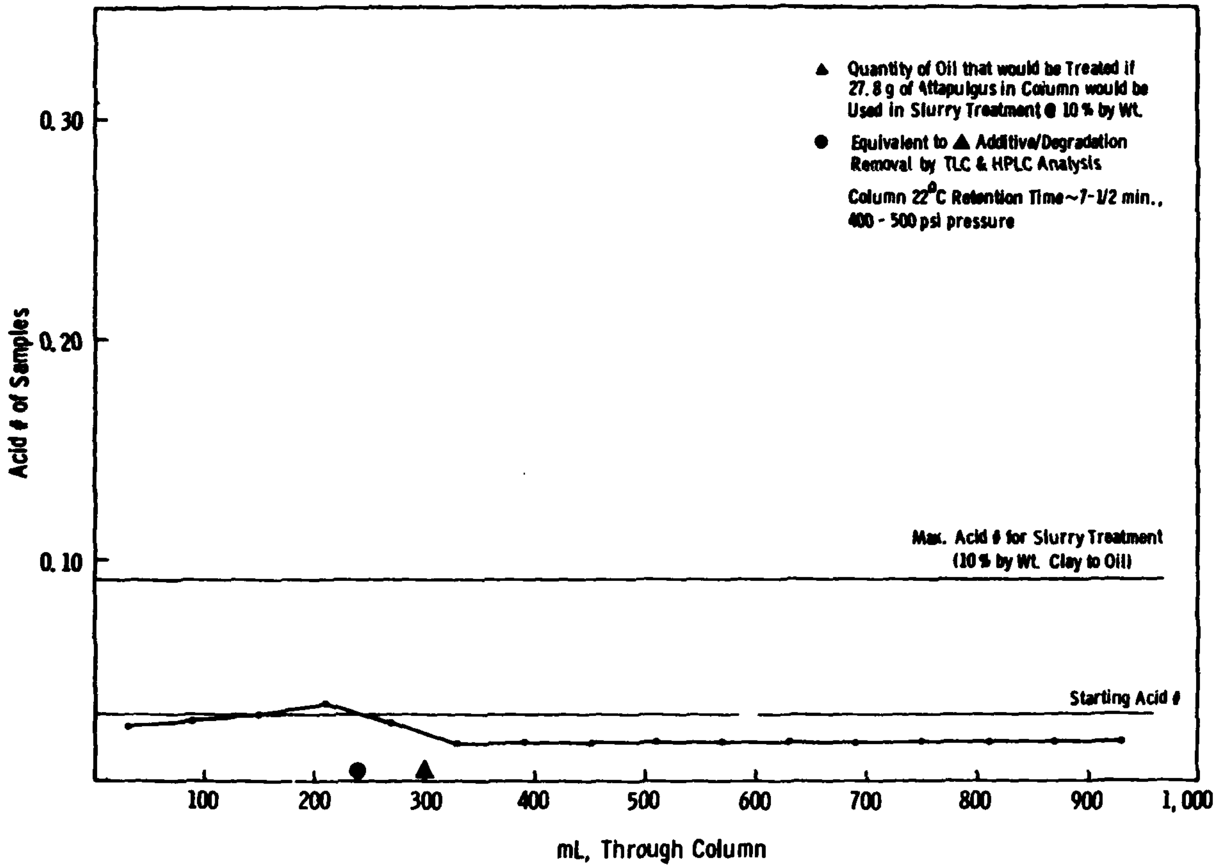


Figure 52. Main fraction from NaOH:MgO/MeOH distillation, pretreated with $Ca(OH)_2$, followed by chromatographic treatment with attapulgus clay.

3.8 RECLAIMED BASE STOCK EVALUATION

In the last few months we have concentrated on identifying a distillation procedure, selecting a clay adsorbent for additive/degradation removal with a treatment procedure, and identifying the level of $Ca(OH)_2$ treatment required to lower the acid number. The next step was to reclaim a small quantity of oil with our modified procedure and reformulate it with additives to perform a few selective tests to verify our overall process. Table 17 presents our reclaimed oil test scheme.

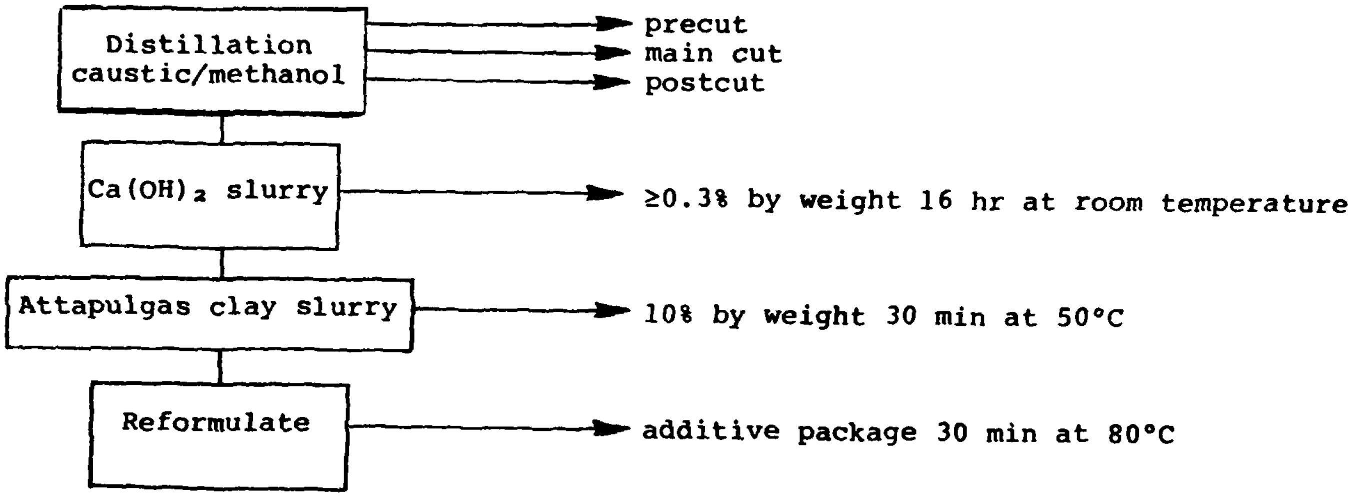
To determine if precut, main cut, and postcut distillates could be combined as reclaimed base stock, distillates from NaOH/methanol distillation were combined, reformulated and foam tested. Table 18 lists the resulting foam test volumes, which suggest that it may be possible to combine all fractions for recovery. To further verify the reclamation process and the idea of combining the distillate fractions, two 2.6-liter samples had been reclaimed. They were reformulated with additives and sent to Alcor Testing Laboratory for tests outlined in our reclaimed oil test scheme.

The two reclaimed samples of combined NaOH/methanol distillates had the vapor temperature ranges shown in Table 19.

The results of the selected MIL-L-7808H tests by Alcor are included in Appendix B.

In general, the reclaimed/reformulated (RR) samples performed as well as the formulated virgin base stocks from various manufacturers used earlier to verify the additive package. We have shown by experimentation in the laboratory that the 100-120 mL foam volumes of the RR samples were due to inadvertent addition of excess (3%) PANA additive. In the corrosion and oxidation

TABLE 17. RECLAIMED OIL TEST SCHEME



Foam test 3 formulated samples - main cut
- main cut + appropriate percent of precut
- main cut + appropriate percent of pre- and postcut

Alcor testing of 2-2.6 liter samples - main cut + precut
- main cut + precut and postcut

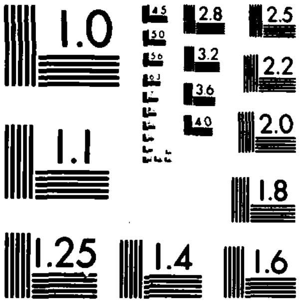
Tests:

Acid number
Viscosities at 210°F and -65°F
Static foaming
Lead corrosion, 1 hr @ 325°F
Silver and bronze corrosion, 50 hr @ 450°F
Deposition number test
Corrosion and oxidation 48 hr @ 392°F

AD-A112 098   MONSANTO RESEARCH CORP DAYTON OHIO DAYTON LAB   F/G 11/8
TURBINE ENGINE LUBRICANT RECLAMATION.(U)
DEC 81 G L BEEMSTERBOER, R J BRUNS   F33615-79-C-2052
UNCLASSIFIED   MRC-DA-1057   AFWAL-TR-81-2053   NL

2 of 2
AD
A112098

END
DATE
FILMED
4 82
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

TABLE 18. REFORMULATED BASE STOCK FOAM VOLUMES

Sample	Distilled oil sample numbers	Foam volume
1	Reclaimed 1732588-3 (main cut)	10 mL
2	Reclaimed 1732588-3+ 6% (1732588-2) (precut)	15 mL
3	Sample 2 reformulated	15 mL
4	Sample 3 + reformulated 1732588-4 (postcut)	15 mL

TABLE 19. VAPOR TEMPERATURE RANGES OF COLLECTED DISTILLATES IN THE ALCOR TESTED SAMPLES

Sample	Vapor temperature range
1830396-C/M-23	135-285°C
1830397-C/M-234	135-305°C

stability test, the RR samples do not meet the MIL-L-7808H requirements with respect to percent change in viscosity and total acid number change. However, this is attributed to the probable presence of MIL-L-7808G oils in the samples which do not meet these requirements even as new oils. This deficiency could be corrected by dilution with a MIL-L-7808 virgin base stock if necessary. In conclusion, we feel that the developed reclamation process is viable.

4. CONCLUSIONS

1. A feasible process for reclamation of synthetic ester turbine engine oils was developed in the earlier program. The main features of the process consist of distillation to recover base stock, treatment with adsorbents to remove degradation products, and addition of additives to upgrade the oil to meet specifications.

2. Two samples of a reclaimed oil mixture met selected MIL-L-7808H tests. The samples had been distilled with NaOH, treated with $Ca(OH)_2$ and attapulgus clay, and reformulated with additives.

3. MRC's proposed additive package has been shown to work in seven different base stock formulations.

4. Treatment with $Ca(OH)_2$ to lower the acid number depends on the following rule of thumb: $\geq 0.3\%$ by weight $Ca(OH)_2$ to oil. (A greater amount of $Ca(OH)_2$ may be required to neutralize larger acid numbers.)

5. Attapulgus clay was found to be the most effective bleaching material.

6. Activated charcoal adsorption was found unnecessary.

5. PLANS FOR REMAINDER OF PROGRAM

1. Start large-scale reclamation as soon as possible.
2. Determine optimum level of adsorbent for effective treatment on pilot plant batches.
3. Determine $Ca(OH)_2$ treatment time on pilot plant batches.
4. Develop cost estimates for the reclamation process.

BIBLIOGRAPHY

Gunderson, R. C.; Hart, A. W.; et al. Synthetic Lubricants, New York, Reinhold Publishing Corp. 1962.

"Reclamation of Synthetic Turbine Engine Oil Mixtures," Technical Report AFAPL-TR-78-50, AF Aero Propulsion Lab, AF Wright Aeronautical Laboratories, AF Systems Command, Wright-Patterson Air Force Base, OH 43433.

Ronney, W. M. Lubricant Additives, Chemical Technology Review No. 104, Park Ridge, NJ, Noyes Data Corp. 1978.

Ronney, W. M. Synthetic Oils and Greases for Lubricants, Chemical Technology Review No. 72, Park Ridge, NJ, Noyes Data Corp. 1976.

APPENDIX A

MIL-L-7808H TEST RESULTS FOR SELECTED FORMULATED VIRGIN BASE STOCKS

1732506 (Hatco base stock)
1732510 (Stauffer base stock)
1732511 (Rohm and Haas base stock) (Plexol)
1732508 (APL-furnished ATL 9148 base stock)
1732509 (APL-furnished ATL 9149 base stock)

ADDITIVE LEVELS USED IN VIRGIN BASE STOCKS

Additives	Percent by weight
Tricresyl phosphate	2.0
4,4'-Dioctyldiphenylamine	1.0
Phenyl-α-naphthylamine	1.0
Benzotriazole	0.1
Triphenyl phosphite	0.1
Quinizarin	0.05
Antioxidant 703	0.1

ALCOR, INC.
10130 Jones Maltsberger Road
San Antonio, Texas
(512) 349-3771

SAMPLE Monsanto #1732511 Date 4/07/80

	Specification	Results
PHYSICAL & CHEMICAL PROPERTIES		
Neutralization Number	0.30 Max.	0.14
Viscosity @ 210°F, cs	3.0 Min.	3.0
Viscosity @ 100°F, cs	Report	11.5
VISCOSITY STABILITY @ -65°F		
Original Oil, 35 Min., cs	17,000 Max.	11,341
After 3 Hours, cs	17,000 Max.	11,633
Viscosity Change, %	6.0 Max.	+2.6
FOAMING CHARACTERISTICS, STATIC		
176°F, Vol. after 30 Min. Aeration, ml	100 Max.	35
Collapse time, seconds	60 Max.	6.8
FOAMING CHARACTERISTICS, DYNAMIC		
176°F		
Volume @ 1000 cc air, cc	100 Max.	10
Collapse time, minutes	60 Max.	24.6 sec.
Volume @ 1500 cc air, cc	150 Max.	20
Collapse time, minutes	60 Max.	38.9 sec.
Volume @ 2000 cc air, cc	Report	20
Collapse time, minutes	60 Max.	33.8 sec.
230°F		
Volume @ 1000 cc air, cc	100 Max.	10
Collapse time, minutes	60 Max.	31.8 sec.
Volume @ 1500 cc air, cc	150 Max.	10
Collapse time, minutes	60 Max.	31.8 sec.
Volume @ 2000 cc air, cc	Report	20
Collapse time, minutes	60 Max.	35.5 sec.

Sample Monsanto #1732511

	Specification	Results
FA ELASTOMER COMPATIBILITY, 72 HOURS @ 347°F		
% Swell	2.0 - 25.0	+15.8
Tensile Strength, % Change	50 Max.	-14.0
Elongation, % Change	50 Max.	+15.6
Hardness, No. Change	20 Max.	-5
LEAD CORROSION, 1 Hour @ 325°F		
Weight Change, mg/in^2	6 Max.	0.0
SILVER & BRONZE CORROSION, 50 HOURS @ 450°F		
Silver Weight Change, mg/in^2	3.0 Max.	-0.1
Bronze AMS4616, mg/in^2	3.0 Max.	0.0
DEPOSITION NUMBER (see attached data sheet)		
Deposit Number	1.5 Max.	0.67
Viscosity Change, %	Report	55.6
TAN Change	Report	22.88
Oil Consumption	Report	175 cc
RYDER GEAR TEST (see attached data sheet)		
2 Determinations, ppi	2400 Min.	2631

Sample Monsanto # 1732511

CORROSION AND OXIDATION STABILITY, 96 HOURS @ 392°F

	Specification	Results
Corrosion:		
Steel, mg/cm^2	Report	-0.030
Silver, mg/cm^2	Report	-0.148
Aluminum, mg/cm^2	Report	+0.010
Magnesium, mg/cm^2	Report	-12.247
Bronze AMS4616, mg/cm^2	Report	+0.053
Titanium, mg/cm^2	Report	+0.050
M50 Steel, mg/cm^2	Report	+0.060
Appearance of Metal Specimens:		
Pitting	Report	None
Etching	Report	None
Corrosion	Report	Mg
Staining	Report	None

Oxidation:	Specification	16	24	40	48	64	72	88	96
Viscosity @ 100°F, % Change	Report	+4.3	+5.2	+13.0	+24.3	+56.5	+74.8	+113.9	+129.6
Viscosity @ 210°F, % Change	Report								+73.3
Total Acid Number, Change	Report	0.64	1.16	5.58	12.26	24.30	27.46	38.26	40.74
Evaporation Loss, %	Report								5.9
Sludge, Volume, %	Report								0.2

ALCOR, INC.
10130 Jones Maltsberger Road
San Antonio, Texas
(512) 349-3771

SAMPLE Monsanto #1732509 Date 4/07/80

	Specification	Results	
PHYSICAL & CHEMICAL PROPERTIES			
Neutralization Number	0. 30 Max.	0. 17	
Viscosity @ 210°F, cs	3. 0 Min.	3. 5	
Viscosity @ 100°F, cs	Report	14. 8	
VISCOSITY STABILITY @ -65°F			
Original Oil, 35 Min., cs	17,000 Max.	16,642	
After 3 Hours, cs	17,000 Max.	16,954	
Viscosity Change, %	6. 0 Max.	+1. 9	
FOAMING CHARACTERISTICS, STATIC			
176°F, Vol. after 30 Min. Aeration, ml	100 Max.	115	
Collapse time, seconds	60 Max.	7. 4	
FOAMING CHARACTERISTICS, DYNAMIC			
176°F			
Volume @ 1000 cc air, cc	100 Max.	10	
Collapse time, minutes	60 Max.	12. 7	sec.
Volume @ 1500 cc air, cc	150 Max.	30	
Collapse time, minutes	60 Max.	14. 7	sec.
Volume @ 2000 cc air, cc	Report	30	
Collapse time, minutes	60 Max.	18. 9	sec.
230°F			
Volume @ 1000 cc air, cc	100 Max.	10	
Collapse time, minutes	60 Max.	13. 1	sec.
Volume @ 1500 cc air, cc	150 Max.	20	
Collapse time, minutes	60 Max.	14. 2	sec.
Volume @ 2000 cc air, cc	Report	20	
Collapse time, minutes	60 Max.	14. 7	sec.

Sample Monsanto #1732509

	Specification	Results
FA ELASTOMER COMPATIBILITY, 72 HOURS @ 347°F		
% Swell	2.0 - 25.0	+15.8
Tensile Strength, % Change	50 Max.	-11.4
Elongation, % Change	50 Max.	+35.9
Hardness, No. Change	20 Max.	0
LEAD CORROSION, 1 Hour @ 325°F		
Weight Change, mg/in^2	6 Max.	0.0
SILVER & BRONZE CORROSION, 50 HOURS @ 450°F		
Silver Weight Change, mg/in^2	3.0 Max.	0.0
Bronze AMS4616, mg/in^2	3.0 Max.	0.1
DEPOSITION NUMBER (see attached data sheet)		
Deposit Number	1.5 Max.	0.56
Viscosity Change, %	Report	112.8
TAN Change	Report	14.41
Oil Consumption	Report	150 cc
RYDER GEAR TEST (see attached data sheet)		
2 Determinations, ppi	2400	3282

Sample Monsanto #1735209

CORROSION AND OXIDATION STABILITY, 96 HOURS @ 392°F

	Specification	Results							
Corrosion:									
Steel, mg/cm^2	Report	-0.024							
Silver, mg/cm^2	Report	-0.059							
Aluminum, mg/cm^2	Report	0.000							
Magnesium, mg/cm^2	Report	-0.036							
Bronze AMS4616, mg/cm^2	Report	+0.010							
Titanium, mg/cm^2	Report	-0.020							
M50 Steel, mg/cm^2	Report	+0.030							
Appearance of Metal Specimens:									
Pitting	Report	None							
Etching	Report	None							
Corrosion	Report	None							
Staining	Report	None							
Oxidation:		16	24	40	48	64	72	88	96
Viscosity @ 100°F, % Change	Report	+6.1	+7.4	+9.5	+10.1	+12.2	+12.8	+14.2	+14.2
Viscosity @ 210°F, % Change	Report								+8.6
Total Acid Number, Change	Report	0.51	0.83	1.17	1.23	1.57	1.69	1.91	2.30
Evaporation Loss, %	Report								3.8
Sludge, Volume, %	Report								0.0

ALCOR, INC.
10130 Jones Maltsberger Road
San Antonio, Texas
(512) 349-3771

SAMPLE Monsanto #1732510 Date 4/07/80

	Specification	Results
PHYSICAL & CHEMICAL PROPERTIES		
Neutralization Number	0.30 Max.	0.25
Viscosity @ 210°F, cs	3.0 Min.	3.1
Viscosity @ 100°F, cs	Report	12.8
VISCOSITY STABILITY @ -65°F		
Original Oil, 35 Min., cs	17,000 Max.	13,925
After 3 Hours, cs	17,000 Max.	13,484
Viscosity Change, %	6.0 Max.	+3.1
FOAMING CHARACTERISTICS, STATIC		
176°F, Vol. after 30 Min. Aeration, ml	100 Max.	30
Collapse time, seconds	60 Max.	3.8
FOAMING CHARACTERISTICS, DYNAMIC		
176°F		
Volume @ 1000 cc air, cc	100 Max.	10
Collapse time, minutes	60 Max.	9.1 sec.
Volume @ 1500 cc air, cc	150 Max.	10
Collapse time, minutes	60 Max.	9.3 sec.
Volume @ 2000 cc air, cc	Report	10
Collapse time, minutes	60 Max.	10.3 sec.
230°F		
Volume @ 1000 cc air, cc	100 Max.	10
Collapse time, minutes	60 Max.	8.5 sec.
Volume @ 1500 cc air, cc	150 Max.	10
Collapse time, minutes	60 Max.	8.2 sec.
Volume @ 2000 cc air, cc	Report	10
Collapse time, minutes	60 Max.	8.9 sec.

Sample Monsanto #1732510 Page 2.

	Specification	Results
FA ELASTOMER COMPATIBILITY, 72 HOURS @ 347°F		
% Swell	2.0 - 25.0	+17.6
Tensile Strength, % Change	50 Max.	-11.9
Elongation, % Change	50 Max.	+17.2
Hardness, No. Change	20 Max.	-5
LEAD CORROSION, 1 Hour @ 325°F		
Weight Change, mg/in^2	6 Max.	-0.1
SILVER & BRONZE CORROSION, 50 HOURS @ 450°F		
Silver Weight Change, mg/in^2	3.0 Max.	-0.1
Bronze AMS4616, mg/in^2	3.0 Max.	-0.2
DEPOSITION NUMBER (see attached data sheet)		
Deposit Number	1.5 Max.	0.40
Viscosity Change, %	Report	82.0
TAN Change	Report	14.85
Oil Consumption	Report	125 cc
RYDER GEAR TEST (see attached data sheet)		
2 Determinations, ppi	2400 Min.	2671

Sample Monsanto # 1732510

CORROSION AND OXIDATION STABILITY, 96 HOURS @ 392°F

	Specification	Results							
Corrosion:									
Steel, mg/cm^2	Report	+0.069							
Silver, mg/cm^2	Report	-0.040							
Aluminum, mg/cm^2	Report	+0.016							
Magnesium, mg/cm^2	Report	+0.030							
Bronze AMS4616, mg/cm^2	Report	+0.115							
Titanium, mg/cm^2	Report	+0.050							
M50 Steel, mg/cm^2	Report	-0.028							
Appearance of Metal Specimens:									
Pitting	Report	None							
Etching	Report	None							
Corrosion	Report	None							
Staining	Report	None							
Oxidation:		16	24	40	48	64	72	88	96
Viscosity @ 100°F, % Change	Report	+6.3	+7.0	+7.0	+9.4	+10.7	+11.7	+14.1	+14.8
Viscosity @ 210°F, % Change	Report								+9.7
Total Acid Number, Change	Report	0.71	0.87	1.43	1.61	1.77	2.05	2.33	2.89
Evaporation Loss, %	Report								5.2
Sludge, Volume, %	Report								0.0

ALCOR, INC.
10130 Jones Maltsberger Road
San Antonio, Texas
(512) 349-3771

SAMPLE Monsanto #1732506 Date 4/07/80

	Specification	Results
PHYSICAL & CHEMICAL PROPERTIES		
Neutralization Number	0.30 Max.	0.20
Viscosity @ 210°F, cs	3.0 Min.	3.0
Viscosity @ 100°F, cs	Report	12.5
VISCOSITY STABILITY @ -65°F		
Original Oil, 35 Min., cs	17,000 Max.	12,136
After 3 Hours, cs	17,000 Max.	12,561
Viscosity Change, %	6.0 Max.	3.5
FOAMING CHARACTERISTICS, STATIC		
176°F, Vol. after 30 Min. Aeration, ml	100 Max.	15
Collapse time, seconds	60 Max.	3.2
FOAMING CHARACTERISTICS, DYNAMIC		
176°F		
Volume @ 1000 cc air, cc	100 Max.	10
Collapse time, minutes	60 Max.	7.9 sec.
Volume @ 1500 cc air, cc	150 Max.	10
Collapse time, minutes	60 Max.	8.8 sec.
Volume @ 2000 cc air, cc	Report	10
Collapse time, minutes	60 Max.	8.5 sec.
230°F		
Volume @ 1000 cc air, cc	100 Max.	10
Collapse time, minutes	60 Max.	8.4 sec.
Volume @ 1500 cc air, cc	150 Max.	10
Collapse time, minutes	60 Max.	8.5 sec.
Volume @ 2000 cc air, cc	Report	10
Collapse time, minutes	60 Max.	7.6 sec.

Sample Monsanto #1732506

	Specification	Results
FA ELASTOMER COMPATIBILITY, 72 HOURS @ 347°F		
% Swell	2.0 - 25.0	+12.4
Tensile Strength, % Change	50 Max.	+2.1
Elongation, % Change	50 Max.	+9.3
Hardness, No. Change	20 Max.	-5
LEAD CORROSION, 1 Hour @ 325°F		
Weight Change, mg/in^2	6 Max.	0.0
SILVER & BRONZE CORROSION, 50 HOURS @ 450°F		
Silver Weight Change, mg/in^2	3.0 Max.	0.0
Bronze AMS4616, mg/in^2	3.0 Max.	-0.2
DEPOSITION NUMBER (see attached data sheet)		
Deposit Number	1.5 Max.	0.52
Viscosity Change, %	Report	48.8
TAN Change	Report	13.10
Oil Consumption	Report	110 cc
RYDER GEAR TEST (see attached data sheet)		
2 Determinations, ppi	2400 Min.	2919

Sample Monsanto # 1732506

CORROSION AND OXIDATION STABILITY, 96 HOURS @ 392°F

	Specification	Results
Corrosion:		
Steel, mg/cm^2	Report	+0.010
Silver, mg/cm^2	Report	-0.069
Aluminum, mg/cm^2	Report	-0.030
Magnesium, mg/cm^2	Report	-0.022
Bronze AMS4616, mg/cm^2	Report	-0.032
Titanium, mg/cm^2	Report	-0.026
M50 Steel, mg/cm^2	Report	-0.020
Appearance of Metal Specimens:		
Pitting	Report	None
Etching	Report	None
Corrosion	Report	None
Staining	Report	None

Oxidation:		16	24	40	48	64	72	88	96
Viscosity @ 100°F, % Change	Report	+5 6	+6.4	+8.8	+8.8	+10.4	+11.2	+12.0	+12.8
Viscosity @ 210°F, % Change	Report								+16.7
Total Acid Number, Change	Report	0.24	0.42	1.14	1.38	1.82	2.04	2.44	2.91
Evaporation Loss, %	Report								3.8
Sludge, Volume, %	Report								0.0

ALCOR, INC.
10130 Jones Maltsberger Road
San Antonio, Texas
(512) 349-3771

SAMPLE Monsanto #1732508 Date 4/07/80

	Specification	Results
PHYSICAL & CHEMICAL PROPERTIES		
Neutralization Number	0. 30 Max.	0. 22
Viscosity @ 210°F, cs	3. 0 Min.	3. 4
Viscosity @ 100°F, cs	Report	14. 2
VISCOSITY STABILITY @ -65°F		
Original Oil, 35 Min., cs	17,000 Max.	14,462
After 3 Hours, cs	17,000 Max.	14,799
Viscosity Change, %	6. 0 Max.	+2. 3
FOAMING CHARACTERISTICS, STATIC		
176°F, Vol. after 30 Min. Aeration, ml	100 Max.	100
Collapse time, seconds	60 Max.	5. 1
FOAMING CHARACTERISTICS, DYNAMIC		
176°F		
Volume @ 1000 cc air, cc	100 Max.	10
Collapse time, minutes	60 Max.	18. 9 sec.
Volume @ 1500 cc air, cc	150 Max.	20
Collapse time, minutes	60 Max.	16. 4 sec.
Volume @ 2000 cc air, cc	Report	20
Collapse time, minutes	60 Max.	19. 5 sec.
230°F		
Volume @ 1000 cc air, cc	100 Max.	10
Collapse time, minutes	60 Max.	12. 9 sec.
Volume @ 1500 cc air, cc	150 Max.	10
Collapse time, minutes	60 Max.	15. 2 sec.
Volume @ 2000 cc air, cc	Report	20
Collapse time, minutes	60 Max.	13. 9 sec.

Sample Monsanto #1732508 Page 2.

	Specification	Results
FA ELASTOMER COMPATIBILITY, 72 HOURS @ 347°F		
% Swell	2.0 - 25.0	+16.1
Tensile Strength, % Change	50 Max.	-12.1
Elongation, % Change	50 Max.	+12.5
Hardness, No. Change	20 Max.	-5
LEAD CORROSION, 1 Hour @ 325°F		
Weight Change, mg/in^2	6 Max.	0.0
SILVER & BRONZE CORROSION, 50 HOURS @ 450°F		
Silver Weight Change, mg/in^2	3.0 Max.	0.1
Bronze AMS4616, mg/in^2	3.0 Max.	0.1
DEPOSITION NUMBER (see attached data sheet)		
Deposit Number	1.5 Max.	0.51
Viscosity Change, %	Report	118.3
TAN Change	Report	11.96
Oil Consumption	Report	135 cc
RYDER GEAR TEST (see attached data sheet)		
2 Determinations, ppi	2400 Min	2815

Sample Monsanto #1732508

CORROSION AND OXIDATION STABILITY, 96 HOURS @ 392°F

	Specification	Results							
Corrosion:									
Steel, mg/cm^2	Report	+0.020							
Silver, mg/cm^2	Report	-0.099							
Aluminum, mg/cm^2	Report	-0.010							
Magnesium, mg/cm^2	Report	-0.030							
Bronze AMS4616, mg/cm^2	Report	-0.010							
Titanium, mg/cm^2	Report	0.000							
M50 Steel, mg/cm^2	Report	+0.030							
Appearance of Metal Specimens:									
Pitting	Report	None							
Etching	Report	None							
Corrosion	Report	None							
Staining	Report	None							
Oxidation:		16	24	40	48	64	72	88	96
Viscosity @ 100°F, % Change	Report	+5.6	+6.3	+8.5	+8.5	+9.8	+11.2	+11.9	+11.9
Viscosity @ 210°F, % Change	Report								+5.9
Total Acid Number, Change	Report	0.42	0.46	0.74	0.84	1.08	1.24	1.36	1.60
Evaporation Loss, %	Report								4.6
Sludge, Volume, %	Report								0.0

APPENDIX B

MIL-L-7808H TEST RESULTS FOR RECLAIMED OIL

1830396-C/M-23 (Reclaimed oil, NaOH/methanol, vapor temperature distillation 135-285°C)

1830397-C/M-234 (Reclaimed oil, NaOH/methanol, vapor temperature distillation 135-305°C)

ADDITIVE LEVELS USED IN RECLAIMED BASE STOCK

Additives	Percent by weight
Tricresyl phosphate	2.0
4,4'-Dioctyldiphenylamine (DODPA)	1.0
Phenyl-α-naphthylamine (PANA)	1.0[a]
Benzotriazole	0.1
Triphenyl phosphite	0.1
Quinizarin	0.05
Antioxidant 703	0.10

[a] Both samples inadvertently had more (3%) than 1% PANA added.

ALCOR, INC.
10130 Jones Maltsberger Road
San Antonio, Texas
(512) 349-3771

CUSTOMER Monsanto Research Corporation Date 10/16/80

	Specification	Results 183039-6C/M-23	 183039-7C/M-234
PHYSICAL & CHEMICAL PROPERTIES			
Neutralization Number (T.A.N.)	0.30 Max.	0.22	0.20
Viscosity @ 210°F, cs	3.0 Min.	3.0	3.1
VISCOSITY STABILITY @ -65°F			
Original Oil, 35 Minutes, cs	17,000 Max.	9,515	10,428
After 3 Hours, cs	17,000 Max.	9,777	10,340
Viscosity Change, %	6.0 Max.	+2.8	-0.8
FOAMING CHARACTERISTICS, STATIC			
176°F, Volume after 30 Min. Aeration, ml	100 Max.	100	120
Collapse Time, seconds	60 Max.	4.2	5.1
LEAD CORROSION, 1 HOUR @ 325°F			
Weight Change, mg/in^2	6 Max.	+0.1	+0.1
SILVER & BRONZE CORROSION, 50 HOURS @ 450°F			
Silver Weight Change, mg/in^2	3.0 Max.	-0.1	-0.1
Bronze AMS4616, mg/in^2	3.0 Max.	-0.3	-0.5
DEPOSITION NUMBER (see attached data sheets)			
Deposit Number	1.5 Max.	0.53	0.41
Viscosity Change, %	Report	+119.3	+38.3
T.A.N. Change	Report	25.04	11.42
Oil Consumption	Report	100 cc	50 cc

	Specification	Results 183039- 6C/M-23	 183039- 7C/M-234
CORROSION & OXIDATION STABILITY, 48 HOURS @ 392°F			
Corrosion:			
Steel, mg/cm^2	±0.2	-0.010	-0.099
Silver, mg/cm^2	±0.2	-0.139	-0.050
Aluminum, mg/cm^2	±0.2	-0.073	-0.040
Magnesium, mg/cm^2	±0.4	-0.050	-0.030
Bronze AMS4616, mg/cm^2	±0.4	-0.119	-0.010
Titanium, mg/cm^2	±0.2	-0.040	-0.080
M-50 Steel, mg/cm^2	±0.2	-0.080	-0.046
Appearance of Metal Specimens:			
Pitting	Report	None	None
Etching	Report	None	None
Corrosion	Report	None	None
Staining	Report	None	None
Oxidation:			
Viscosity @ 100°F, Initial	Report	11.4	12.0
Viscosity @ 100°F, % Change	-5 to +25	+25.4	+23.3
Viscosity @ 210°F, Initial	Report	3.0	3.1
Viscosity @ 210°F, % Change	Report	+13.3	+12.9
Total Acid Number, Initial	Report	0.22	0.20
Total Acid Number, Change	4.0 Max.	5.03	4.80
Evaporation Loss, %	Report	2.5	2.1
Sludge, Volume, %	Report	0.0	0.0

APPENDIX C

ANALYTICAL CONDITIONS

Gas Chromatography

High Performance Liquid Chromatography

Thin Layer Chromatography

ANALYTICAL CONDITIONS

GAS CHROMATOGRAPHY

Column:	3% Dexsil 300 on Chromasorb W 80/100 0.125 in. OD 12 ft length acid washed and silanized
Sample:	10% in cyclohexane
Sample size:	1 µL
Helium flow rate:	40 cc/min
Inlet temperature:	300°C
FID temperature:	400°C
Temperature program:	180-350°C at 4°C/min

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

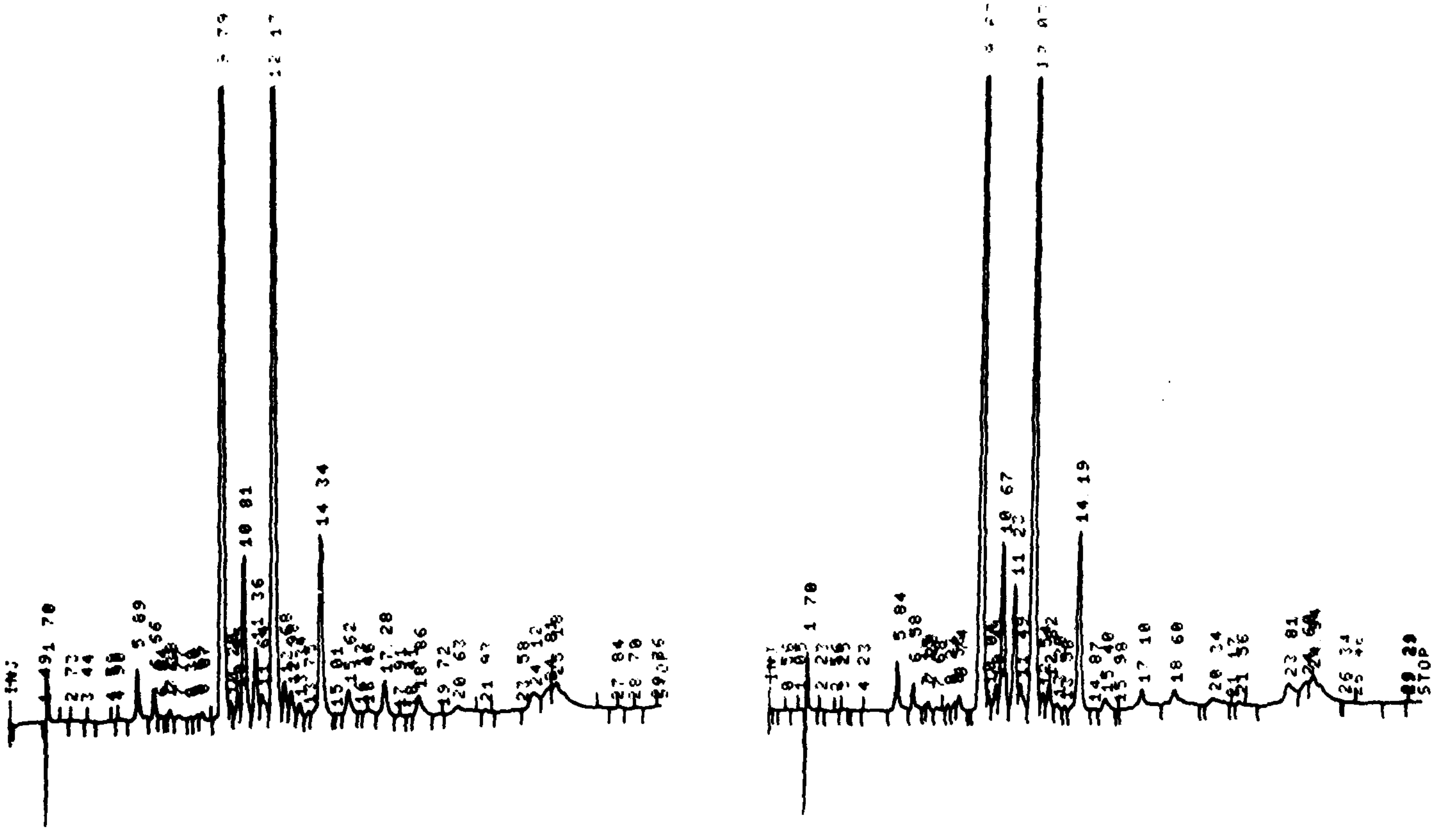
Column:	Partisil PXS 10/25 PAC
Sample:	10% in cyclohexane
Sample size:	10 µL
Mobile phase:	100% isooctane TO 70/30 methylene chloride/isooctane
Program:	Linear, 20 min
Detector:	UV @ 254 nm
Chart:	0.5 cm/min

THIN LAYER CHROMATOGRAPHY

Plate:	Silica gel F-254 activated at 100°C for 1 hr
Sample:	30 µL 10% solution oil in cyclohexane
Mobile phase:	30/70 heptane/toluene
Lamp:	254 nm UV

APPENDIX D

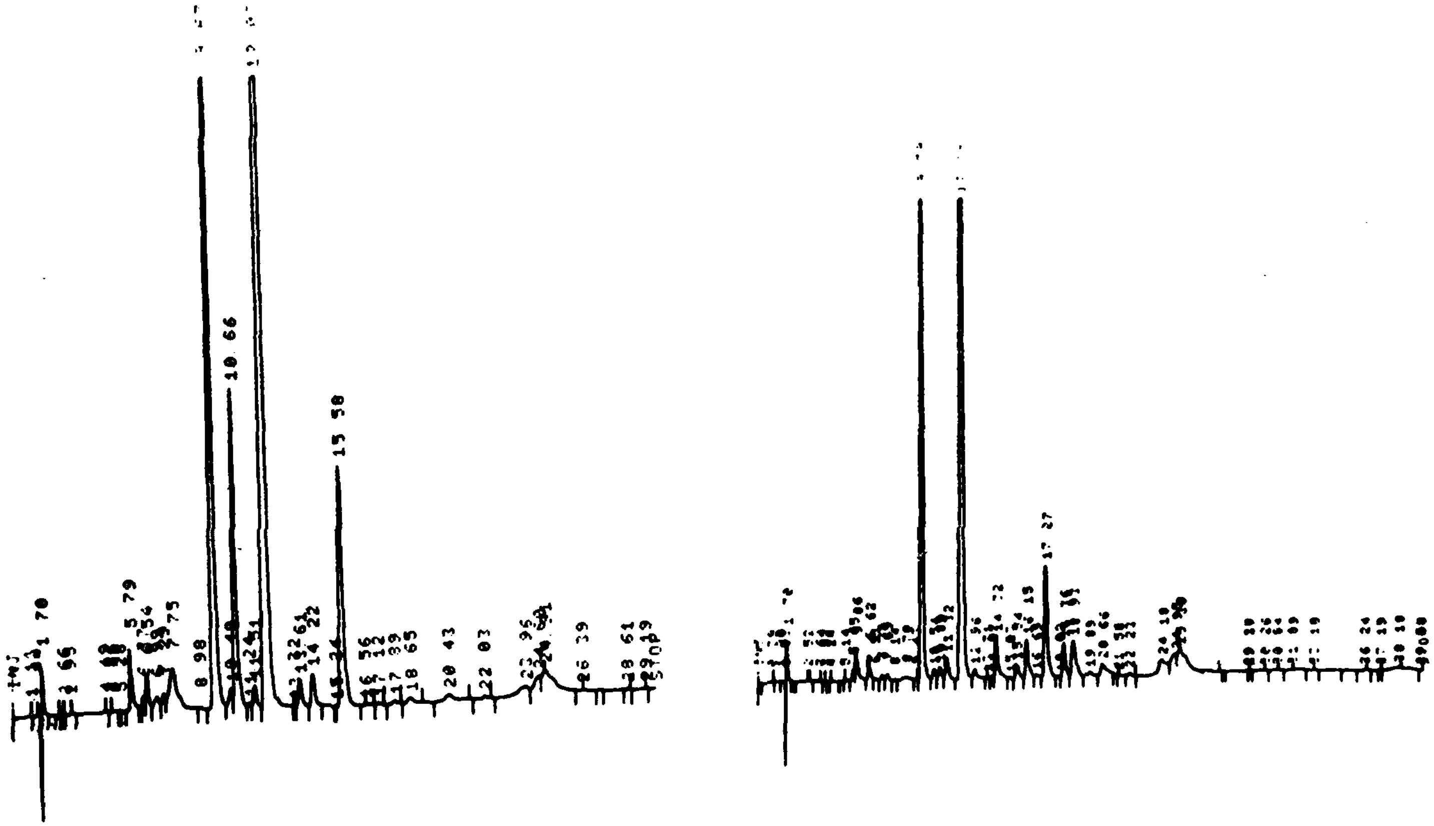
HIGH PERFORMANCE LIQUID CHROMATOGRAMS OF 15 USED OILS AS RECEIVED



0-79-1

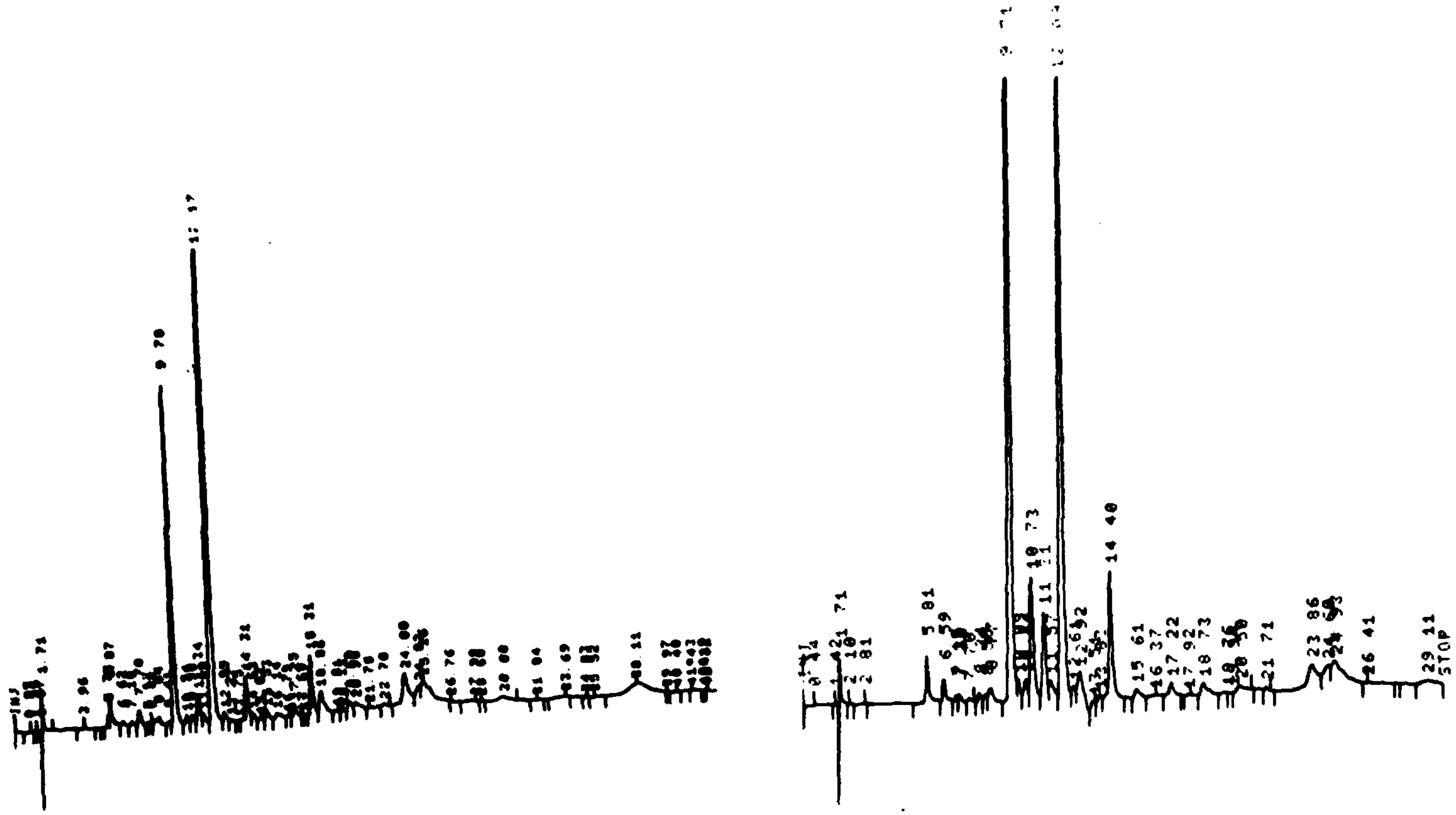
0-79-2

Figure D-1. High performance liquid chromatograms of used oil as received.



0-79-3　**0-79-4**

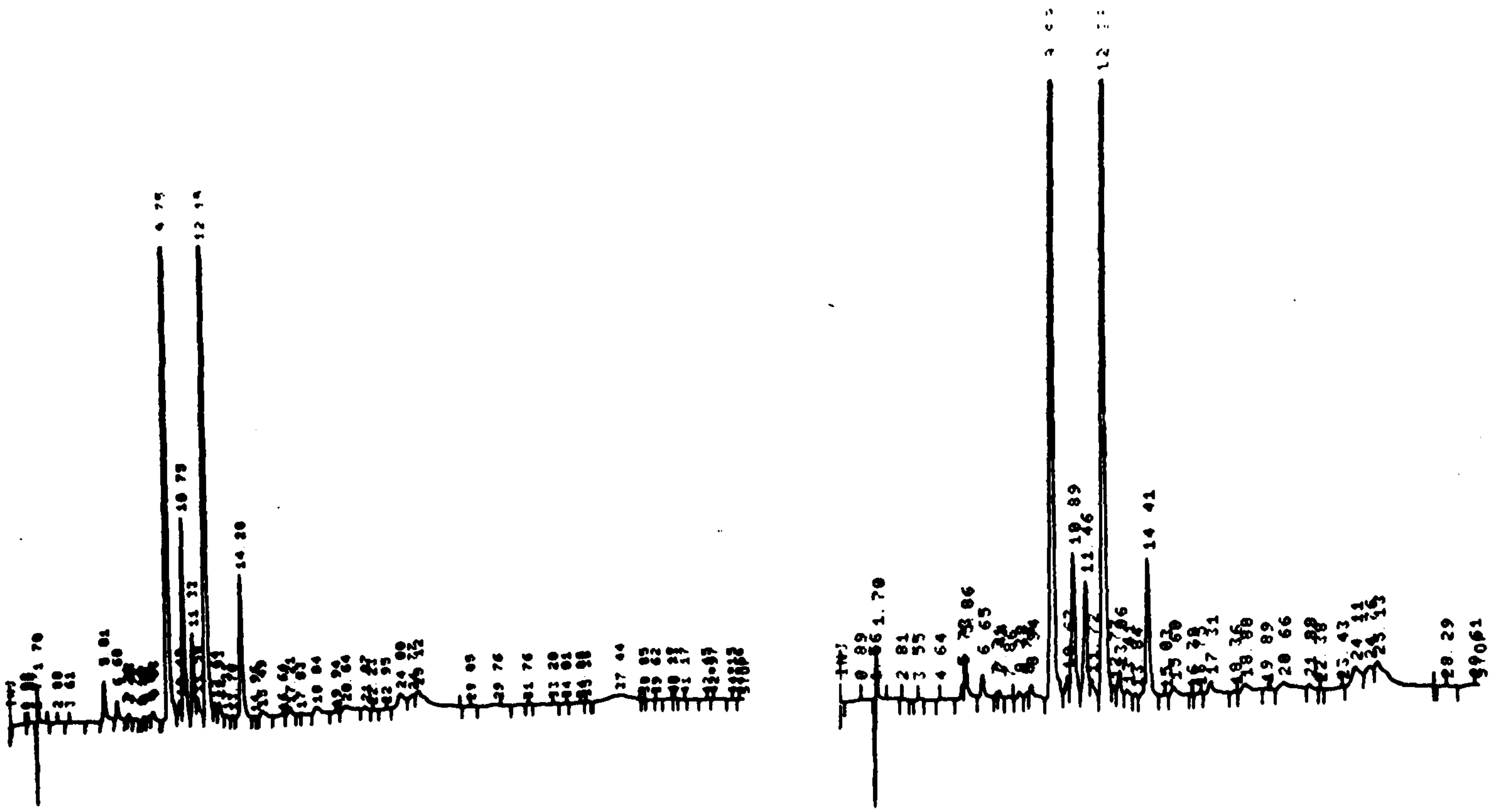
Figure D-2. High performance liquid chromatograms of used oil as received.



0-79-5

0-79-6

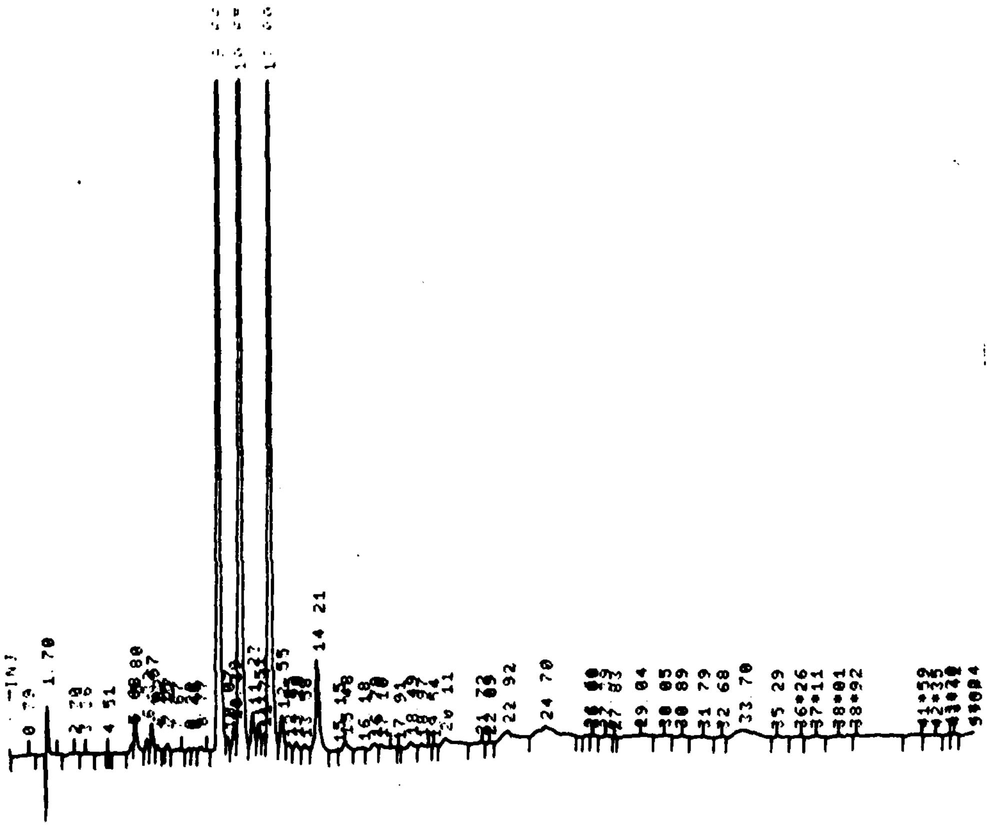
Figure D-3. High performance liquid chromatograms of used oil as received.



0-79-7

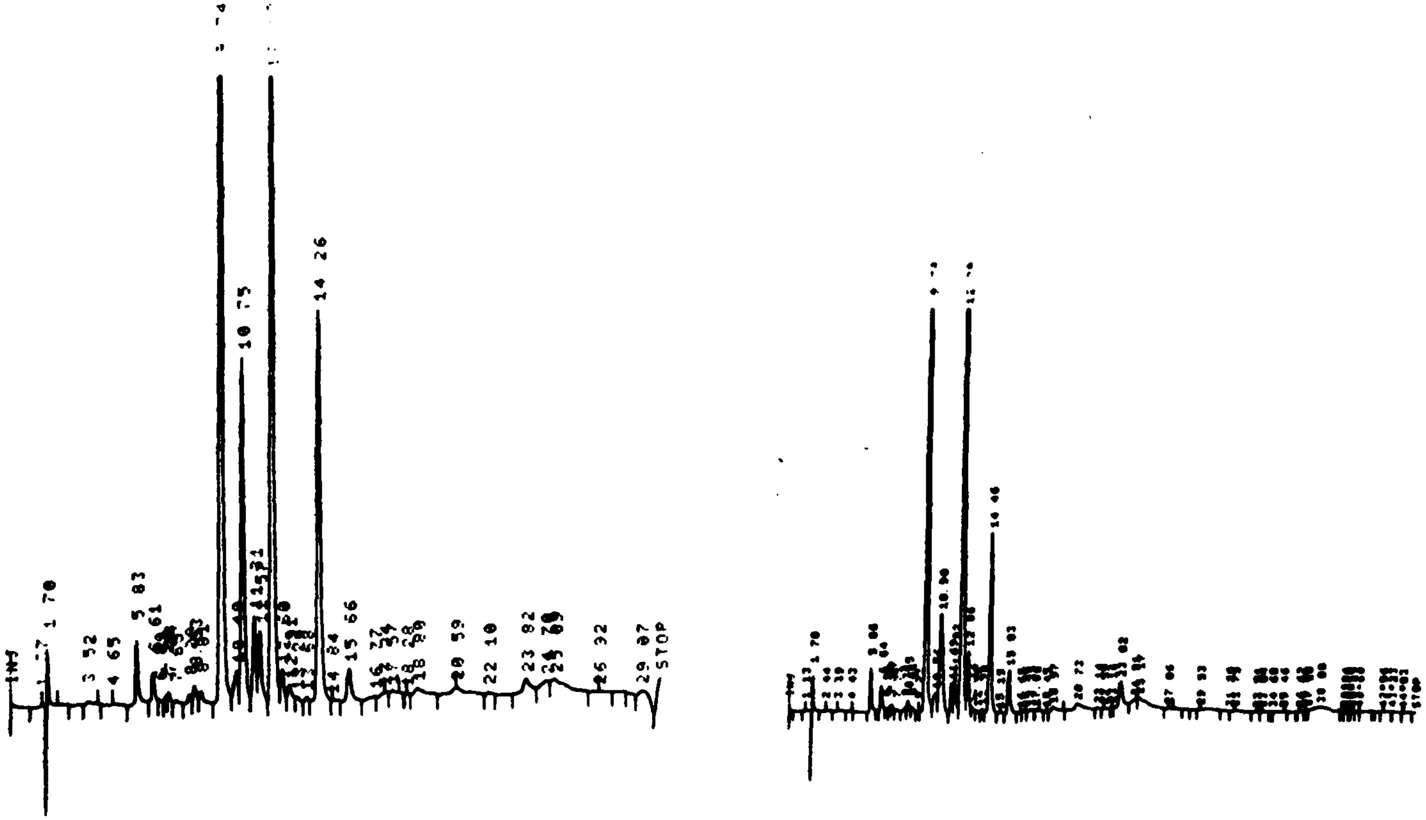
0-79-8

Figure D-4. High performance liquid chromatograms of used oil as received.



0-79-9

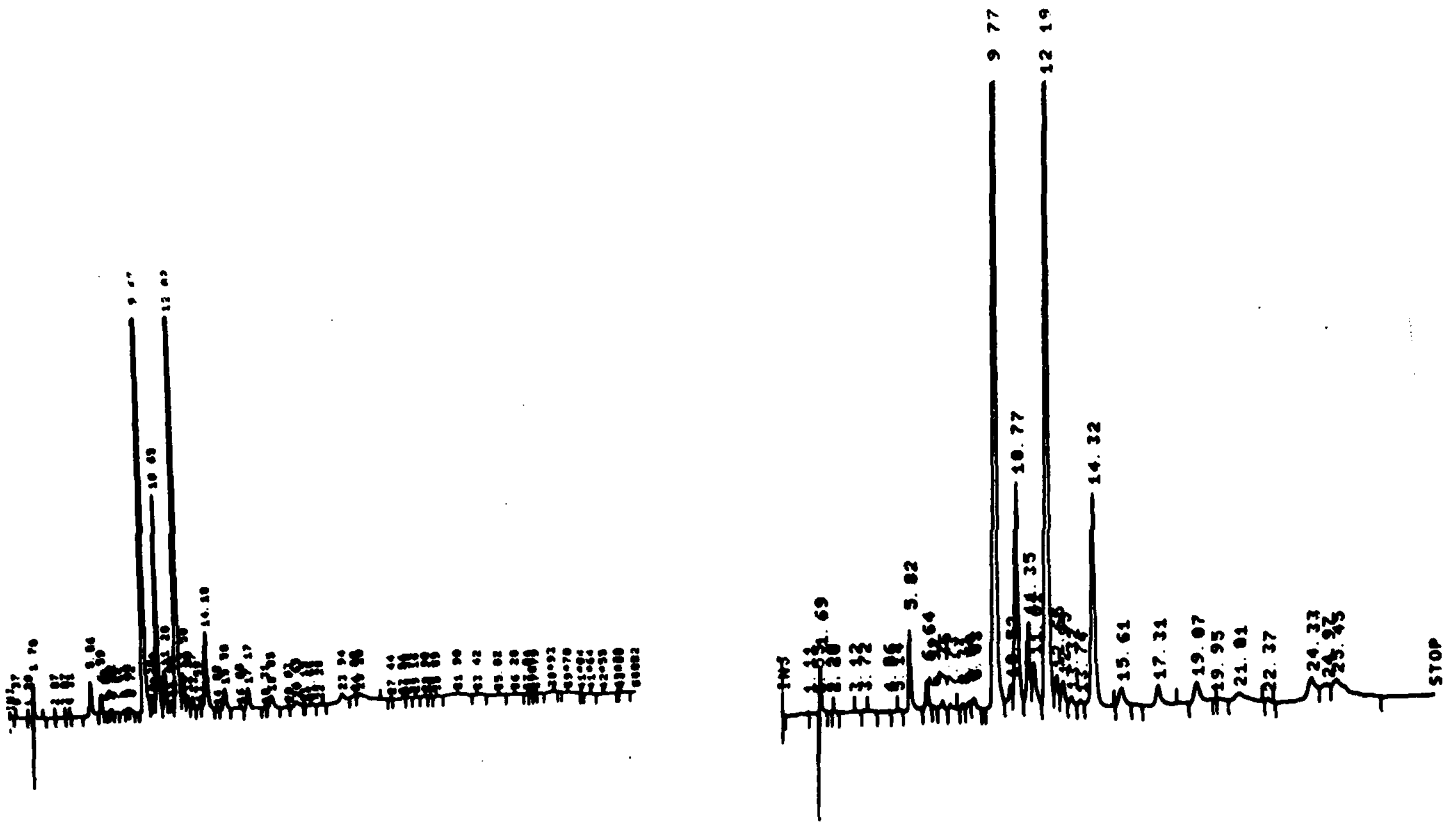
Figure D-5. High performance liquid chromatogram of used oil as received.



0-79-10

0-79-11

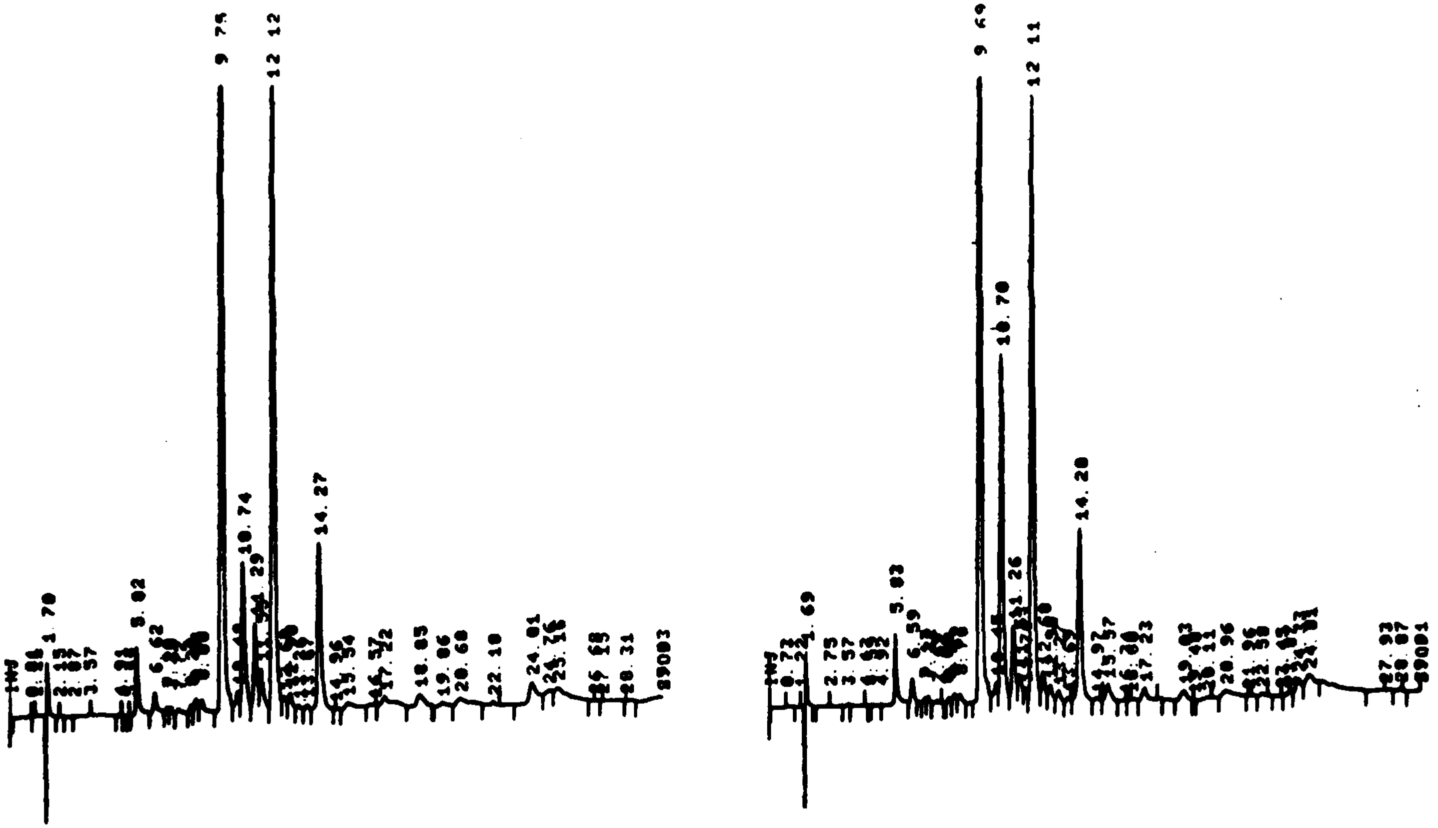
Figure D-6. High performance liquid chromatograms of used oil as received.



0-79-12

0-79-13

Figure D-7. High performance liquid chromatograms of used oil as received.



0-79-14

0-79-15

Figure D-8. High performance liquid chromatograms of used oil as received.

ATE

LMED

8