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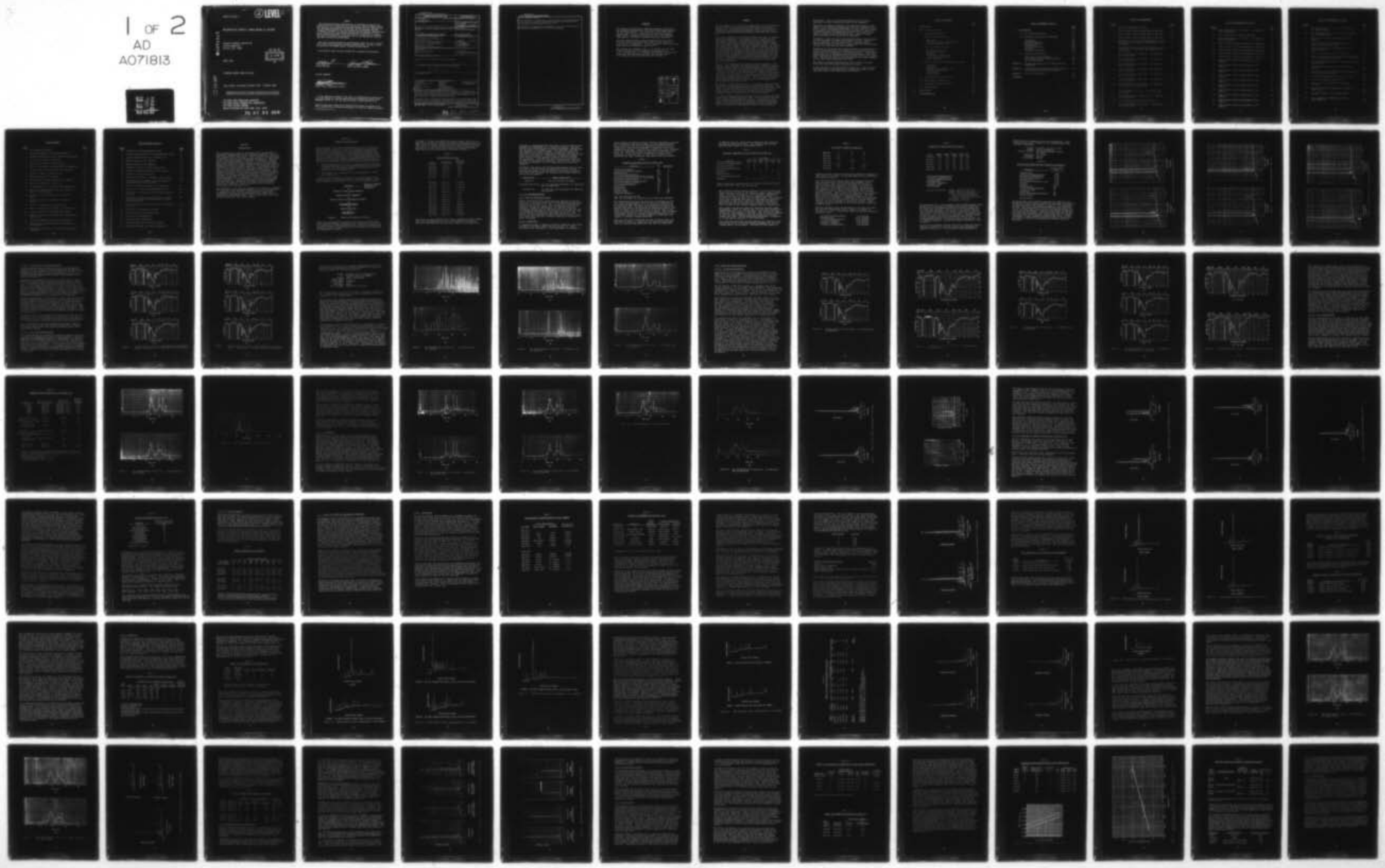

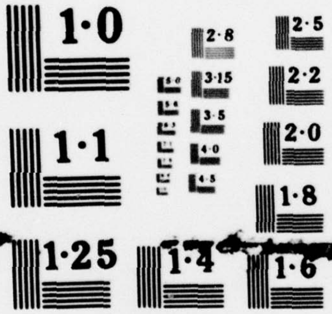
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AFAPL-TR-78-50 √

RECLAMATION OF SYNTHETIC TURBINE ENGINE OIL MIXTURES

MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO 45407

APRIL 1979

TECHNICAL REPORT AFAPL-TR-78-50

FINAL REPORT FOR PERIOD 15 MARCH 1976 - 15 MARCH 1978

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G A Beane IV
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Project Engineer

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Chief, Lubrication Branch

FOR THE COMMANDER

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The objective of this program was to develop a technique for reclaiming used synthetic turbine engine oil mixtures and to demonstrate the technical feasibility of the developed reclamation technique by restoring a limited number of used MIL-L-7808 oils to a satisfactory performance level.

Reclamation process studies based on approaches utilized by the natural oil and fat refining industry resulted in the development of a reclamation process applicable to synthetic ester turbine engine oils. The components of a reclamation

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No. 20. ABSTRACT (cont'd)

Process applicable to a broad range of used MIL 7808G oil mixtures were defined and the technical feasibility established by reclamation and evaluation (via qualification tests) of two batches of used oils.

Recommendations for improvement and refinement of the process and approaches to more extensive documentation of its viability were made.

FOREWORD

This report was prepared by Monsanto Research Corporation, 1515 Nicholas Road, Dayton, Ohio 45407 under USAF Contract No. AF33615-76-C-2037. The contract was initiated under Project 3048, "Fuels, Lubrication and Fire Protection", Task 304806, "Aerospace Lubrication", Work Unit 30480686, "Reclamation of Synthetic Turbine Engine Oil Mixtures."

The work reported herein was performed during the period 15 March 1976 to 15 March 1978, under the direction of G. A. Beane IV (AFAPL/SFL), project engineer. The report was submitted by the authors in April 1978.

The authors are indebted to Dr. J. M. Butler for his many helpful suggestions and stimulating discussions, to J. V. Pustinger and P. L. Sherman under whose direction the analytical methods were developed and applied, and to C. M. Moscowitz who performed the cost analysis.

SUMMARY

The development of a process for reclamation of a used synthetic turbine engine oil meeting MIL-L-7808G specifications was carried out. Techniques for characterization of new and used 7808G oils were developed and applied. The components of a reclamation process were defined and optimization was carried out.

New turbine engine oils supplied by AFAPL were used to develop analytical techniques for characterization of additives and base stock components. Most additives were identified by a literature search and confirmed by thin layer chromatography (TLC) and high pressure liquid chromatography (HPLC). Several were quantified by HPLC. TLC was a useful technique for following qualitative changes in aromatic additive levels occurring during reclamation studies on used oils. A gas chromatographic (GC) technique was developed which characterized each new oil and was useful for estimating relative proportions of new oils found in used oil mixtures. A modified GC technique was used to identify an additive, tris(β-chloroethyl)phosphate, in one new oil. Infrared spectrophotometry (IR) was useful in qualitative identifcation of the oil for presence of diester and triester components.

Used oils were characterized using the above analytical techniques. Four additives, dioctyldiphenylamine (DODPA), N-phenyl-α-naphthylamine (PANA), tricresyl phosphate (TCP) and quinizarin, were detected in all used oils supplied for reclamation studies. Two types of contamination were found in used oils. A methanol insoluble phase identified as polymerized base stock was present at low levels in oils with long service histories. Volatiles obtained from the supplied used oils were mostly water and toluene (foreign contaminates). The only potential base stock degradation product detected was 2-ethylhexanol and it was present at less than 0.03%.

Reclamation studies were carried out following leads developed by a review of the natural oil and fat refining industry. Six types of processes were studied; adsorbents, distillation, oxidation, treatment with strong acids, solvent partitioning and precipitation. The latter two techniques were given very limited evaluation as they did not show much promise.

A study of several adsorbents results in the selection of three types, basic alumina, an acidic clay (Fuller's earth) and charcoal, for use in a reclamation process. Evaluation of both vacuum steam distillation and vacuum distillation showed the latter to be quite useful in separating the bulk of the base stock from additives, degradation products and polymerized

base stock. Late in the program substitution of calcium hydroxide for basic alumina was found to be necessary.

Oxidation of aromatic non-base stock materials present in the used oils was evaluated extensively using four different oxidants. Use of potassium permanganate in acid solution followed by treatment with absorbents was very effective in removal of aromatic materials as determined by HPLC. The oxidation processes do present some difficulties with respect to large scale operation due to formation of emulsions.

Treatment of used oils with concentrated sulfuric acid followed by lime was shown to remove some aromatic amines. However, other treatments, such as distillation, also effectively removed the amines in addition to other materials thus negating the need for the sulfuric acid treatment.

Evaluation of reclaimed base stocks was done by determination of foaming characteristics, acid numbers and viscosities as well as utilizing the analytical tests mentioned above. These tests showed that use of adsorbents and distillation was a more reliable technique for reclamation than oxidation and use of adsorbents. The concentration of trace metals was well below specification limits when adsorbents were used.

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

A cost analysis of the process was carried out. This analysis indicates that a continuous batch reclamation process at the 5000 gallon batch size would be cost effective.

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SECTION I

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 basestocks and additive packages are normally mixed in service. An estimated total of one to four million quarts of used ester based oils are generated per year which 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 in addition to being 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.

The objective of this two-year program is to develop a technique for reclaiming used synthetic turbine engine oil mixtures and to demonstrate the technical feasibility of the developed reclamation technique by restoring used MIL-L-7808 oils to a satisfactory performance level. This is the final report and covers the work for the entire program.

SECTION II

RESULTS AND DISCUSSION

The development of a general reclamation process for used synthetic turbine engine oils that can potentially be applied to a wide variety of mixtures of not only oils from different manufactures but with unknown foreign contamination requires some carefully selected techniques. The approach taken in this project is to assume that there is only a very small number of lots of used oil that would be heavily contaminated with foreign materials that could not be readily separated from the base stock. Based on this assumption, the efforts have been concentrated on:

(1) characterization of the oils to identify potential reclamation problems and also to identify approaches to analytical techniques for determining whether or not a given lot of used oil could be reclaimed and

(2) development of a reclamation process applicable to large scale operation.

A general flow diagram for a reclamation process based on the above assumption is shown in Figure 1. The most difficult task in the project is development of a process for removal of the additives and degradation products that gives a reclaimed base stock capable of being reformulated with additives to obtain an oil meeting MIL-L-7808G specifications. Ideally it would be desirable to obtain a virgin base stock after removal of additives and degradation products.

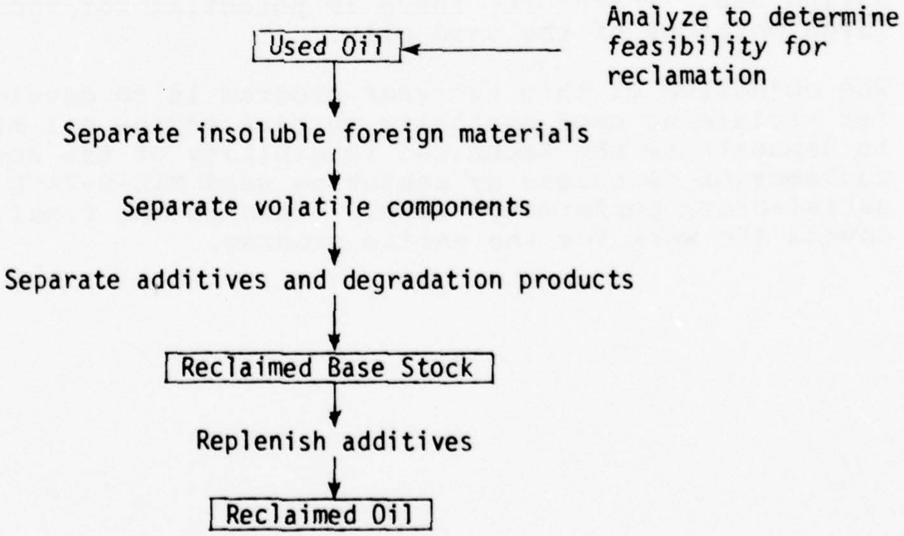


Figure 1. Idealized Reclamation Process

In order to develop a reclamation process general enough to be applicable to used oils whose compositions could range from those that had been severely stressed to those containing some appreciable levels of foreign contamination, a series of used oils was supplied by the Air Force Aero Propulsion Laboratory (AFAPL). These oils and their description are given in Table 1.

Table 1

OILS SUPPLIED BY AFAPL

Oil	Description	Quantity Available
ATL-6021	new oil	pint
ATL-6022	new oil	pint
ATL-6023	new oil	pint
ATL-6024	new oil	pint
ATL-6025	new oil	pint
ATL-6026	new oil	pint
ATL-5051	used oil	10 gallon
ATL-5052	used oil	10 gallon
ATL-7069	used oil	50 gallon
ATL-7071	used oil	50 gallon
ATL-6027	used oil	pint
ATL-6028	used oil	pint
ATL-6029	used oil	pint
ATL-6030	used oil	pint
ATL-6031	used oil	pint
ATL-6059	used oil	gallon
ATL-6060	used oil	gallon
ATL-6061	used oil	gallon
ATL-6100	used oil	5 gallon
ATL-6101	used oil	5 gallon

The first six oils, ATL-6021 thru 6026, represent new MIL-L-7808G that could ultimately be found in current used oil mixtures. The oils coded ATL-5051 and 5052 were samples of the used oils available in large quantities that were to be utilized in this program for development of a reclamation process. ATL-7069 and 7071 were large batches of used oil provided to demonstrate the process at a 50 gallon level. Oils ATL-6027 thru 6031 and 6100/6101 are smaller samples of used oil available to help define the various contamination problems that potentially could be encountered in a large scale reclamation process where used oil of many unknown histories could be blended for processing. Oils ATL-6100 and 6101 have known histories of 1800 and 1000 hours of operation. ATL-6059 thru 6061 were supplied as reference oils for standardizing our foam test equipment.

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

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

2.1 OIL CHARACTERIZATION

2.1.1 New Oil Characterization

Several characterization techniques were applied to new and used oils to determine their utility for detecting differences occurring as a result of oil use. Analytical techniques are needed to follow the changes occurring during evaluation of different reclamation techniques, for characterizing the contaminant present and for determination of the advisability for attempting reclamation of any given lot of used oil. The various analytical techniques developed and used in this project will be discussed as their application occurs in the text rather than devoting a separate section to discussion of these techniques.

2.1.1.1 Additives

A literature survey to identify potential additives that could be found in new MIL-L-7808G oils was carried out. This information was necessary to allow development of methods to insure removal of additives and/or additive degradation products. This information was also necessary to allow quantification of any additives that were not completely removed during reclamation so that proper adjustment in additive level could subsequently be done. The additives identified in the literature survey are presented in Table 2 along with a reference citing their use. This list may not be complete and may contain materials not actually used in 7808 oils at present but it represents the best information developed during the program.

Table 2

POTENTIAL ADDITIVES FOR MIL-L-7808G OILS

Additive	R_f	Reference
tricresyl phosphate	0	1
tris(β-chloroethyl)phosphate	ND[1]	2
phenothiazine	2.9	3
3,7-dioctylphenothiazine	4.8	3
2,6-di-tert-butyldimethylamino-*p*-cresol	0	4
Dow Corning 200 silicone oil (60,000 MW)	ND	5
N-phenyl-α-naphthylamine	4.0	6
N-(4-octylphenyl)-α-naphthylamine	NA[2]	7
4,4'-dioctyldiphenylamine	5.8	8
salicylaminoquanidine	NA	8
quinizarin	2.7	8
Primene-JM-t	ND	9
benzotriazole	0	10a
propyl gallate	3.2	10b
triphenyl phosphite	0	11

[1] ND, not detectable by TLC
[2] NA, not available for evaluation when study was conducted

We investigated the use of UV detection in conjunction with thin layer chromatography (TLC) to follow the depletion of any potential additives that can be separated and detected by this technique. Following the technique outlined in the experimental section we obtained the retardation factors (R_f) given in Table 2 on activated silica F-254 for many of the additives identified in the literature search. This technique is extremely useful for allowing quick determination of the qualitative effects of various reclamation techniques with respect to removal of known additives.

Additives that were identified via TLC in specific new oils are given in Table 3. Along with the identified additives each oil contains some additives that were not identified.

In addition each oil could contain additives that cannot be detected by ultraviolet light. For example, the silicone antifoam agent would not be detected with UV.

Table 3

ADDITIVES DETECTED IN MIL-L-7808G OILS USING TLC

Additive	Oil ATL- 6021	6022	6023	6024	6025	6026
4,4'-dioctyldiphenylamine	X	X	X	X	X	X
tricresylphosphate	X	X		X		
N-phenyl-α-naphthylamine	X	X		X		
quinizarin			X		X	X
phenothiazine						X
3,7-dioctylphenothiazine						X
unknowns[1]	1	1	3	2	3	3

[1] Number represents minimum number of unknown materials detected with ultraviolet light (254 and 366 nm).

The literature survey and TLC analysis of new oils led to the identification of many of the additives used in these formulations. However, the identity of the probable load bearing additives in three of the new oils supplied by AFAPL, i.e. in ATL-6023, 6025 and 6026, was not established. This information could ultimately have been of value when reformulation work began in the event a different load bearing additive would be required for diesters and triesters. The lack of TCP in either of the diesters suggests this as a possibility.

Since known load bearing additives generally contain either phosphorous, sulfur or chlorine the new oils were analyzed for these elements by x-ray fluorescence. The results are shown in Table 4. The numbers in the table refer to relative amounts of the individual elements using the lowest level of each element as a base. Tris(2-chloroethyl)phosphate is suggested as a load bearing additive in the literature.

Since ATL-6025 contained both phosphorous and chlorine it was analyzed by GC for tris(2-chloroethyl)phosphate and found to contain about 0.7% by weight. ATL-6023 and 6026 appear to

Table 4

P, S and Cl Content of New Oils

New Oil	P	S	Cl
ATL-6021	1.45	--	--
ATL-6022	1.56	--	--
ATL-6023	--	1.00	--
ATL-6024	2.38	--	--
ATL-6025	1.00	--	1.00
ATL-6026	--	1.82	--

contain a sulfur containing load bearing additive although at least some of the sulfur in ATL-6026 comes from the phenothiazine additive present.

Once the known and potential additives discussed above had been identified and a satisfactory high pressure liquid chromatography (HPLC) procedure developed for analysis of many of the aromatic additives (see below), the new oils were analyzed. The purpose was to identify and determine the concentrations of the six most probable additives used in commercial oils to assist in formulation of an optimum additive package. Table 5 gives the results of this analysis. One of the six possible additives screened that could have been detected (UV detector), triphenylphosphite, was not found in the oil samples. In addition to the above materials detected in the new oils ATL-6023 contains one and ATL-6025 contains two major unknowns as determined by HPLC. These unknowns did not correspond to any of the potential additives listed in Table 2.

The high pressure liquid chromatograms of the new oils under the operating conditions given in Table 5 are shown in Figures 2, 3, and 4. The elution times for specific additives are given below.

p,p-Dioctyldiphenylamine	7.51 minutes
phenothiazine	14.12 minutes
3,7-dioctylphenothiazine	10.47 minutes
tricresyl phosphate	22.00 minutes
triphenyl phosphite	7.80 minutes
N-phenyl-α-naphthylamine	9.89 minutes

Table 5

ADDITIVES IN NEW MIL-L-7808G OILS, %

Oil	DODPA[1]	PANA[2]	DOPTA[3]	PTA[4]	TCP[5]
ATL-6021	0.83	1.01	PT[6]	ND[7]	0.95
ATL-6022	1.37	0.57	ND	ND	1.11
ATL-6023	1.70	ND	ND	ND	ND
ATL-6024	1.12	1.13	ND	ND	1.39
ATL-6025	2.08	ND	ND	ND	ND
ATL-6026	2.12	ND	1.01	0.29	0.21

[1] 4,4'-dioctyldiphenylamine

[2] N-phenyl-α-naphthylamine

[3] 3,7-dioctylphenothiazine

[4] phenothiazine

[5] tricresyl phosphate

[6] possible trace

[7] not detected

Analysis conditions:
column, Partisil 10/25 PAC
sample, ~8% in cyclohexane, 4 μl
elution solvent, isooctane to 50/50 isooctane/methylene-chloride over 20 minute period
flow rate, 20 ml/min
UV detector, 254 nm

The development of a high pressure liquid chromatography (HPLC) technique for detecting and quantifying aromatic additives was done using a Micromeritics Model 7115-24 instrument and an ultraviolet detector. The use of an UV detector permits very accurate measurements of aromatic materials at low concentrations, e.g. ppm levels in most cases. Development work carried out early in the project resulted in several changes in the procedure occurring at different times so that chromatograms obtained at different times in the project are not always comparable. The best procedure developed is given in Table 5.

During this development process the elution times for several additives available at the time and two known degradation products of TCP (i.e. *m*- and *p*-cresol) were determined to demonstrate that separation could be accomplished. These elution times, given in Table 6, were obtained under the following conditions:

Column:	μ-Porasil, 25 cm x 4.7 mm
Sample:	∿8% in cyclohexane
Elution Solvent:	isooctane/isopropyl alcohol (97.5/2.5)
Flow Rate:	1.0 cc/min
Pressure:	750 psi
UV Detector:	280 nm

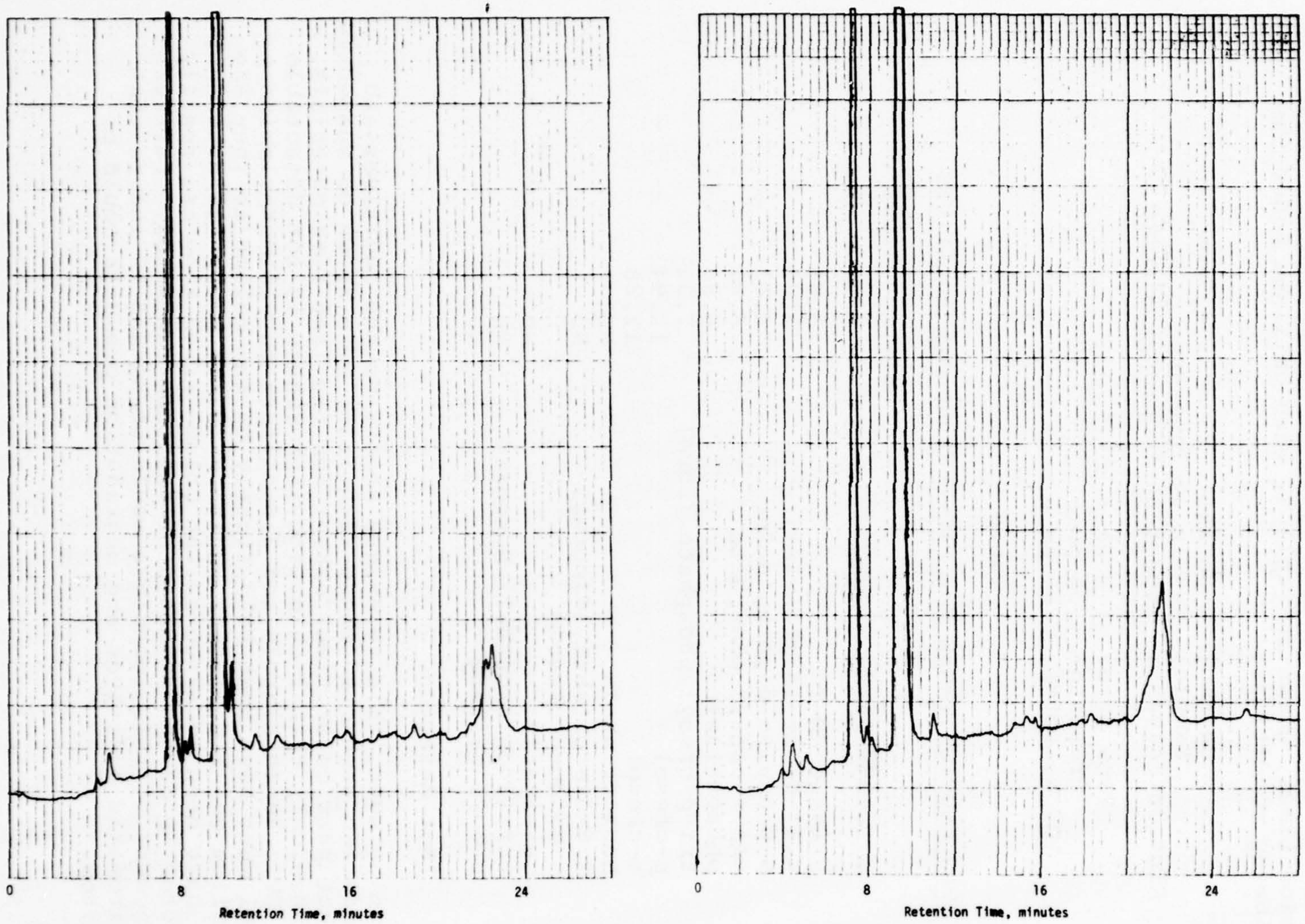
Table 6

HPLC ELUTION TIMES FOR MIL-L-7808G OIL ADDITIVES

Additive	Eluting Time, min
Primene JM-T	3.65
4,4'-dioctyldiphenylamine	3.98
N-phenyl-α-naphthylamine	4.53
tri-*m*-cresyl phosphate	6.42
phenothiazine	6.90
tri-*p*-cresyl phosphate (pure)	7.32
p-cresol	12.94
m-cresol	12.88
benzotriazole	ND[1]
2,6-di-tert-butyldimethyl-amino-*p*-cresol	ND
quinizarin	ND
tris(2-chloroethyl)phosphate	ND
propyl gallate	ND

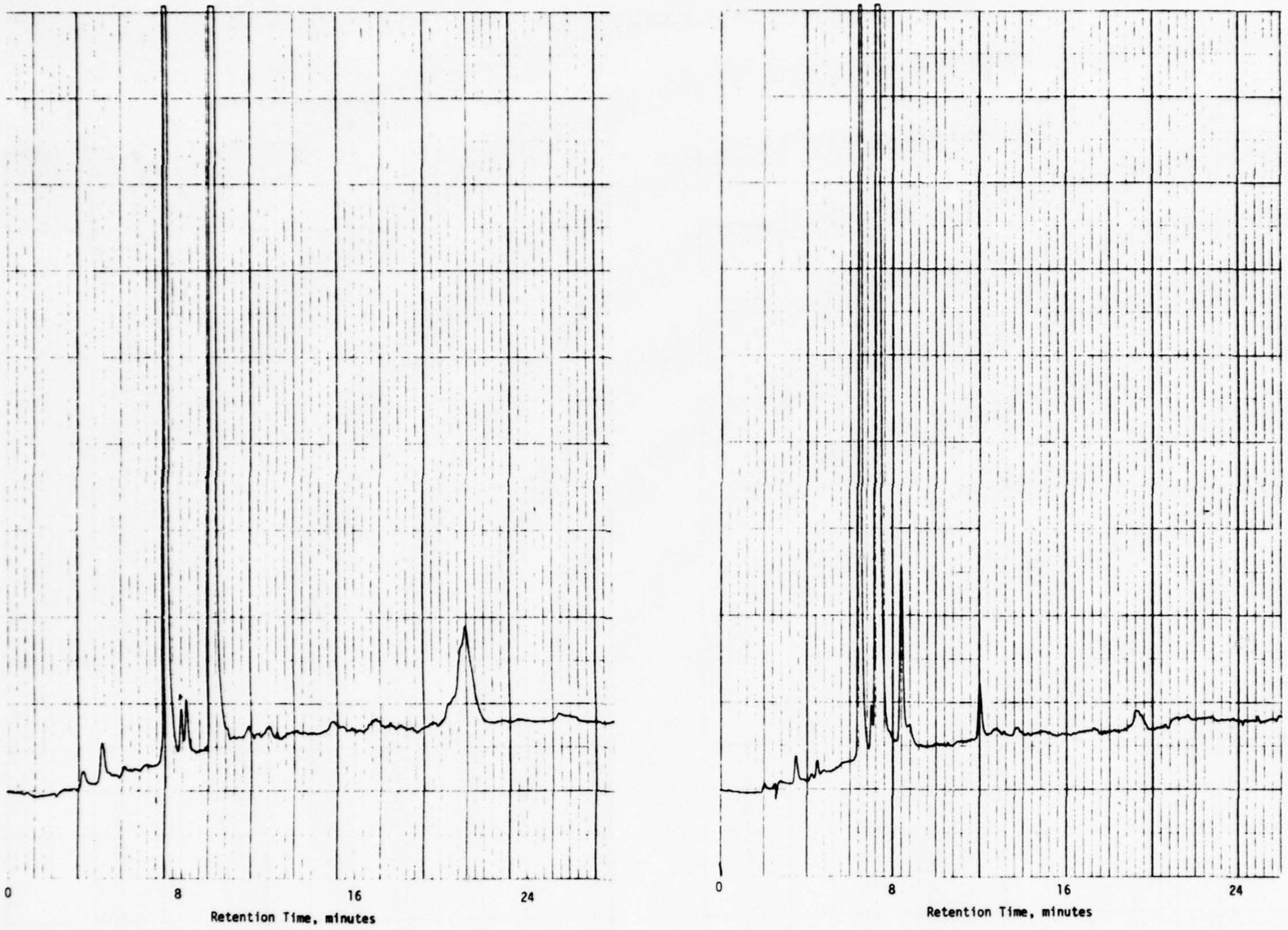
[1] Not detected

As can be seen, this technique separates the additives and degradation products (whose identities were known or suspected at that particular time) except for the last five materials. Of these only tris(2-chloroethyl)phosphate is not detectable with UV. Benzotriazole and 2,6-di-tert-butyldimethylamino-*p*-cresol must have been held tightly on the column as they are on silica gel TLC plates. Quinizarin and propyl gallate must also have been retained on the column since they are readily detected by UV and no detector response was noted. Further refinement of this technique would be needed to insure that all aromatic additives and degradation products could be detected.



ATL-6021 ATL-6024

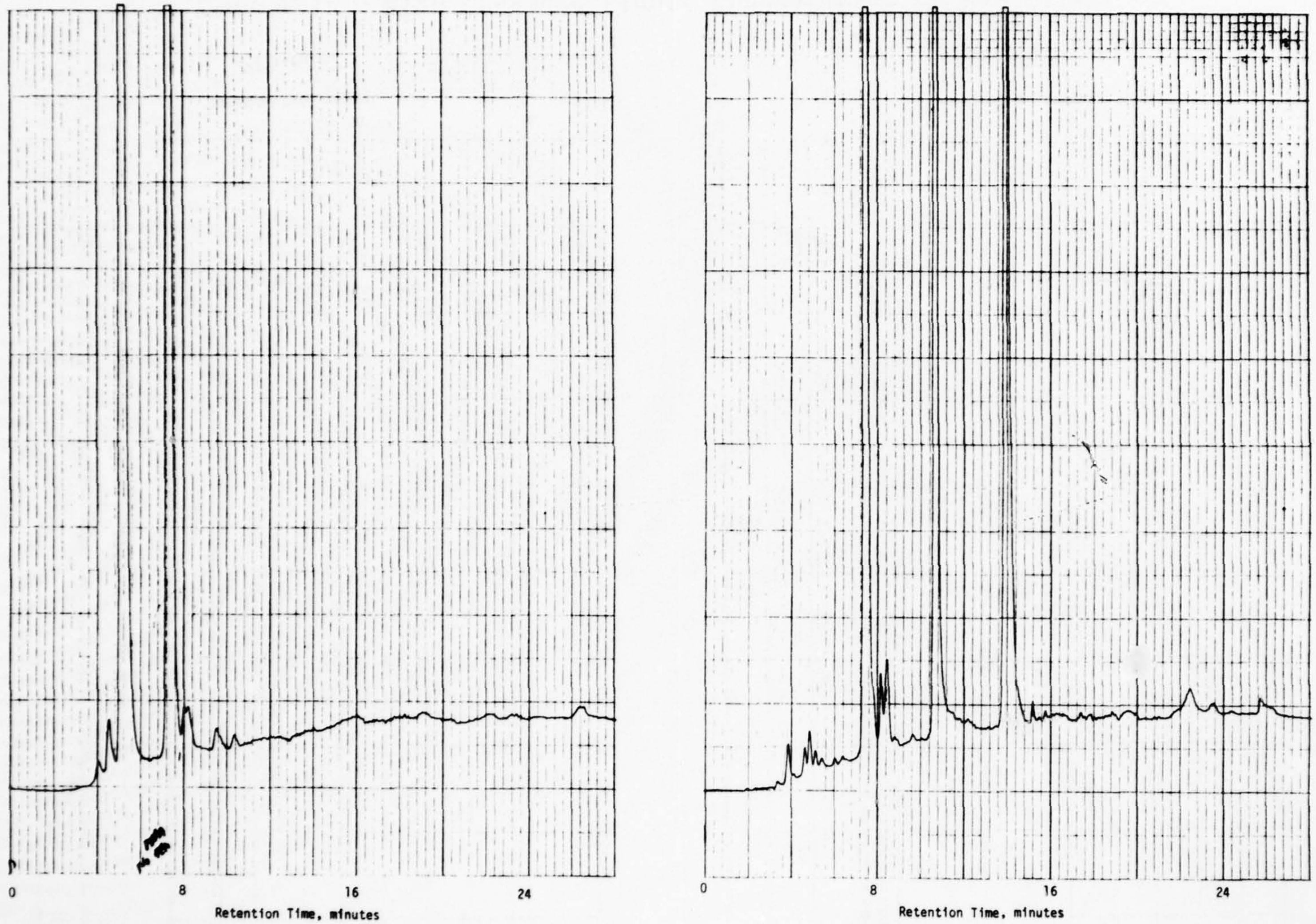
Figure 2. High Pressure Liquid Chromatogram of New Oils



ATL-6022

ATL-6025

Figure 3. High Pressure Liquid Chromatogram of New Oils



ATL-6023

ATL-6026

Figure 4. High Pressure Liquid Chromatogram of New Oils

2.1.1.2 Infrared (IR) Spectrophotometry

Infrared analyses were performed on samples of new synthetic lubricants to see if spectral differences could be observed between oils of different types and commercial sources. Infrared analyses are useful only as a qualitative tool to characterize used oil samples with respect to the presence of diesters or triesters.

Examination of the spectra of the new oils in Figure 5 and 6 reveals a characteristic pattern for a diester and a triester oil. Oils ATL-6021, 6022, 6024 and 6025 are all based on triesters. This conclusion is based on the fact that these oils have a much stronger absorption at 720 cm^{-1} (the absorption due to four or more methylene groups in a linear chain) than do the other two oils. A typical triester structure, e.g. the pelargonate ester of trimethylolpropane, has a much higher percentage of methylene groups in chains of four or more than for example di-2-ethylhexyl sebacate, a typical diester oil structure.

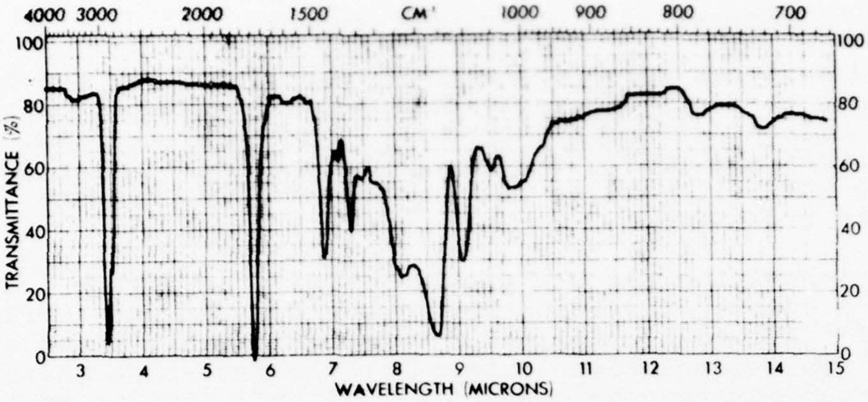
Another characteristic of the ATL-6021, 6022, 6024 and 6025 oils is an absorption at about 1100 cm^{-1}. This absorption is quite strong in ATL-6021 and 6024, is present to a lesser degree in ATL-6025 and to a still lesser degree in ATL-6022. It is undoubtedly associated with C-O-C bond in the ester and its shape is influenced by the type of acid structure in the ester. More detailed study would be required to establish the effect of acid structure on this peak but such work would be outside the scope of this project.

A characteristic feature evident in ATL-6023 and 6026 oils (i.e. the diester oils) is an absorption at 1350 cm^{-1}. This may be characteristic of the alcoholic portion of the ester since it is in a region normally associated with methyl group absorptions.

It is interesting to note the distinct similarity of the IR spectra of ATL-6021 and 6024 and ATL-6023 and 6026. Based on IR evidence alone these oils would be expected to have very similar base stocks.

2.1.1.3 Gas Chromatography (GC)

Gas chromatography was studied as a potential means of analysis to assist in characterizing used oils with respect to removal of additives and degradation products. Development of a suitable separation via GC would permit us to potentially identify each component in an oil mixture by analysis via a Gas Chromatography/Mass Spectrometer/Data System. It is unlikely that total identification of the components of an oil mixture would be attempted. However, degradation products and additives identification could be done to insure their removal during development of a reclamation process.



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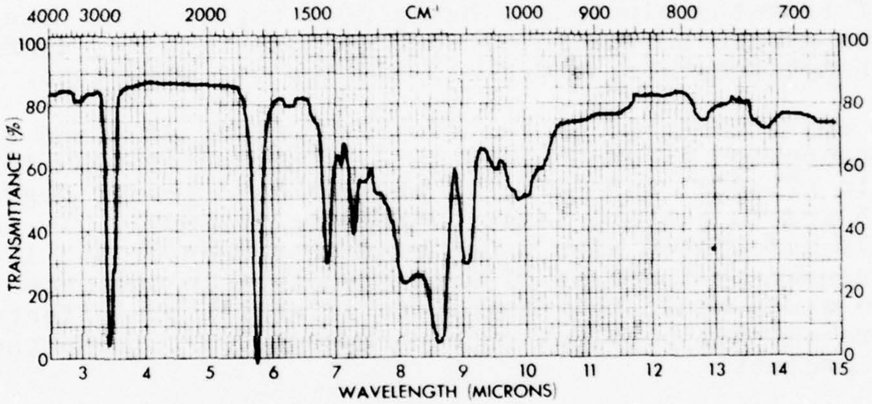

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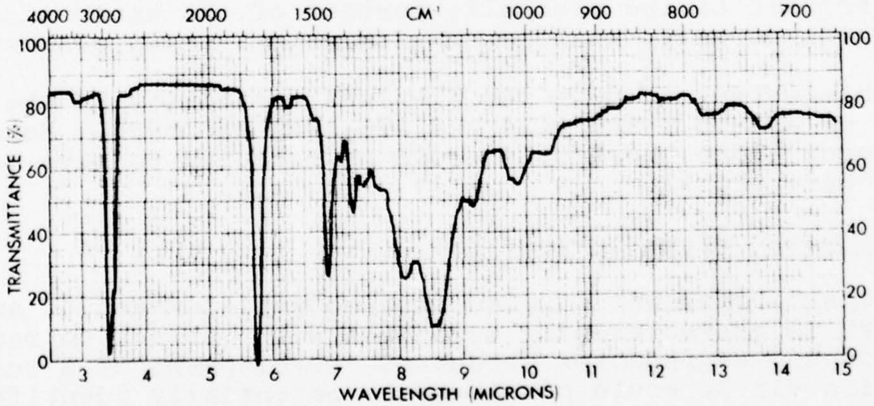


(C)

Figure 5. Infrared Spectra of MIL-L-7808G Synthetic Ester Lubricants: (A) ATL-6021, (B) ATL-6024 and (C) ATL-6022

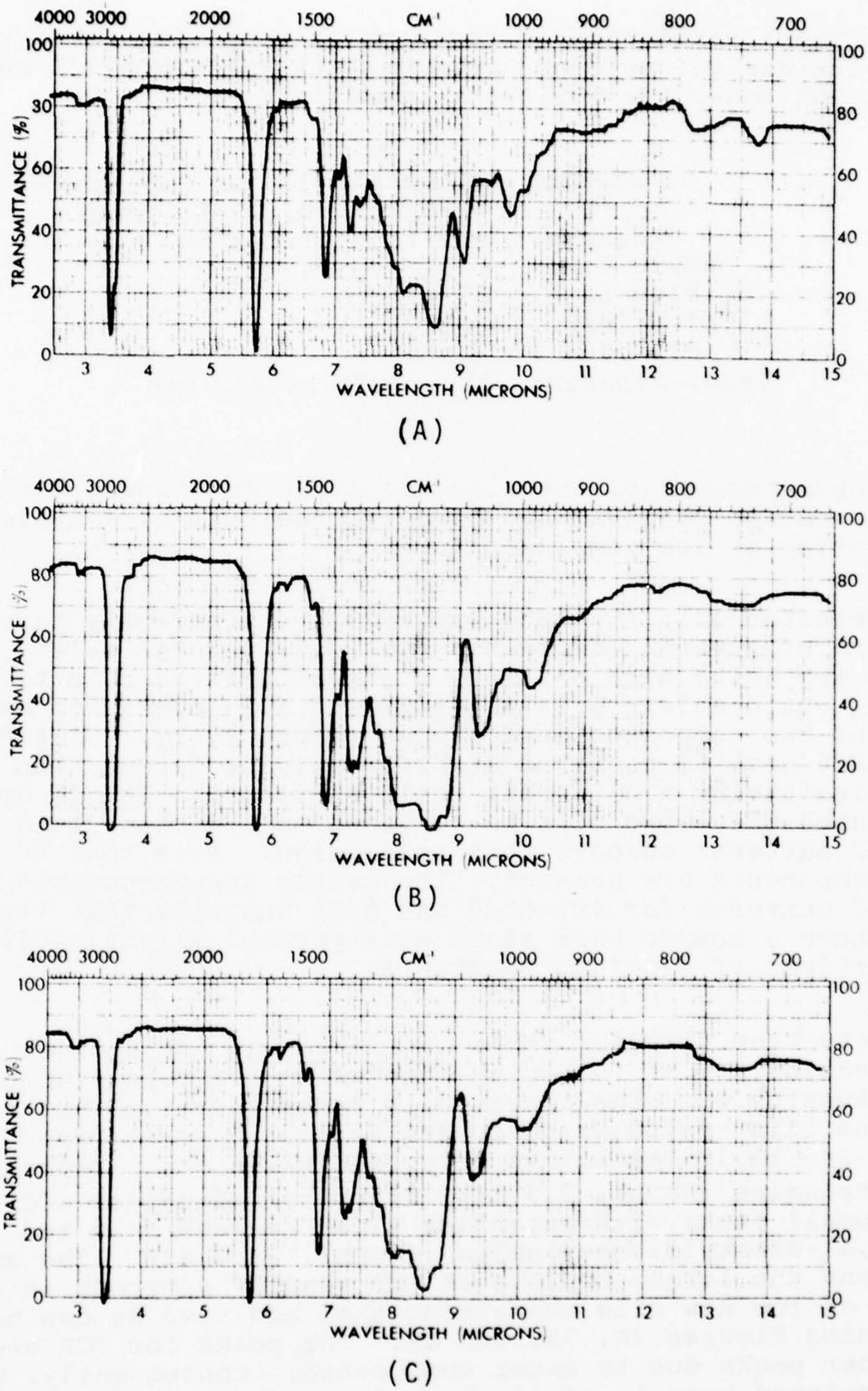


Figure 6. Infrared Spectra of MIL-L-7808G Synthetic Ester Lubricants: (A) ATL-6025, (B) ATL-6023 and (C) ATL-6026

Significant resolution of the complex compositions of the six new oils was accomplished on a Hewlett-Packard 5710A gas chromatograph under the following conditions:

Column: 3% Dexsil 300 on Chromasorb W, 0.25-in. OD, 12-ft length
Sample: ∿8% in cyclohexane
Sample Size: 1 μl
He Flow Rate: 25 ml/min
Inlet Temp.: 300°C
FID Temp.: 350°C
Temp. Program: 180-350°C at 4°C/min

The chromatograms of the oils are shown in Figures 7 through 9. It is readily obvious that each oil has a chracteristic pattern indicative of its complex nature.

The triester oils ATL-6021 and 6024 are apparently based on a mixture of several components (possibly several acids) some of which are quite high boiling, a characteristic of a triester of a long chain acid. Oils ATL-6022 and 6025 appear to be basically one and two component base stocks respectively. Oils ATL-6023 and 6026 have GC patterns significantly different than the other four indicating a different basic structure. The IR analysis indicated these two oils to be based on a diester base stock and the GC patterns support this conclusion. Note that no high boiling components are present. The nearly superimposable nature of the GC patterns for ATL-6023 and 6026 indicate that these two oils have a common base stock with perhaps slightly different proportions of original reactants.

The retention time for three additives was determined to examine the feasibility of following changes in concentration of these additives by GC. The presence of these additives had been detected in some oils by TLC as discussed earlier in this report. The additives and their respective retention times are: N-phenyl-α-naphthylamine (PANA), 7.5 min; tricresyl phoshpate (TCP), a group of 4 small peaks with retention times between 24.2 and 27.8 min; and 4,4'-dioctyldiphenylamine (DODPA), 34.8 min. The small PANA peak and the larger DODPA peak are readily apparent in chromatograms of the new oils containing that additive as can be seen by examining Figures 7A, 7B, and 8A. The peaks for TCP are masked by other peaks due to ester components. Consequently, GC analysis as developed here is of little value in general characterization of additive levels.

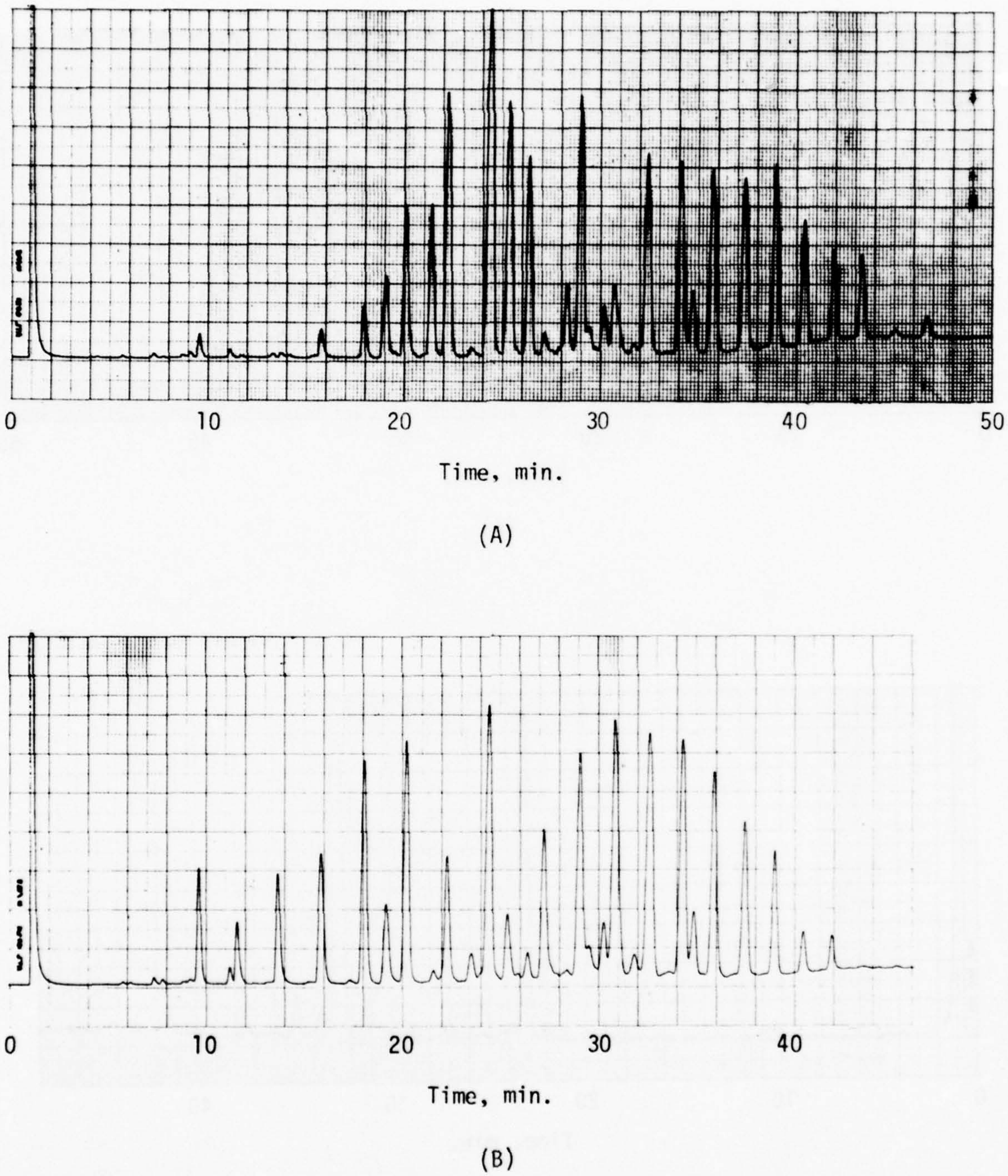
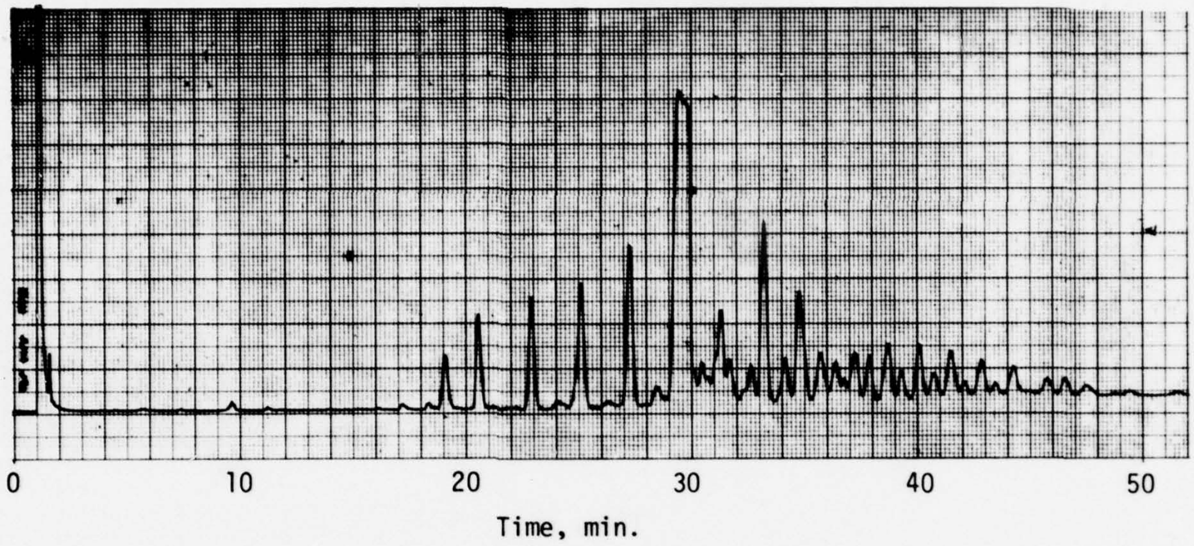
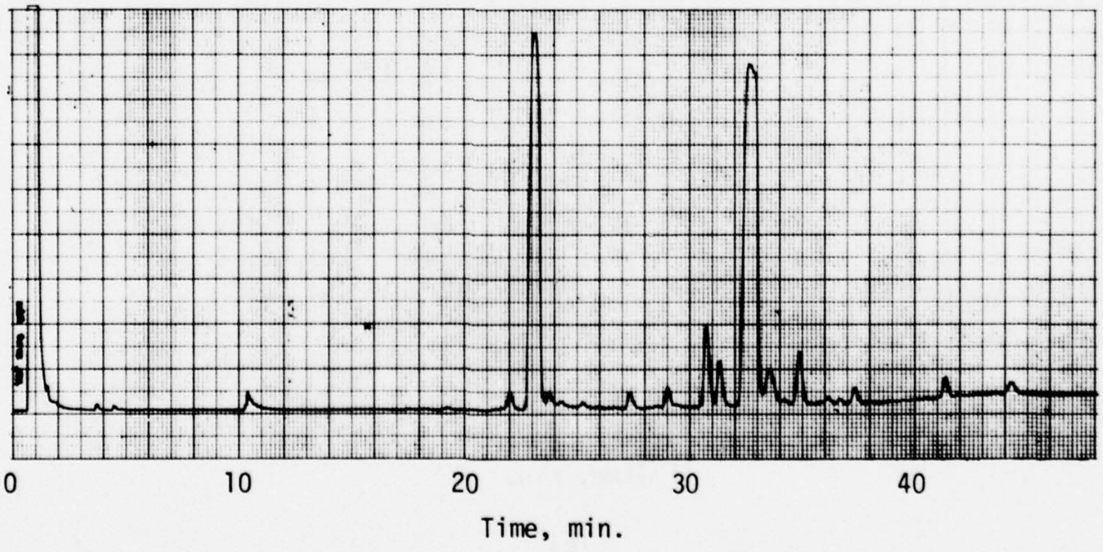


Figure 7. Gas Chromatograms of New Oils: (A) ATL-6021 and (B) ATL-6024

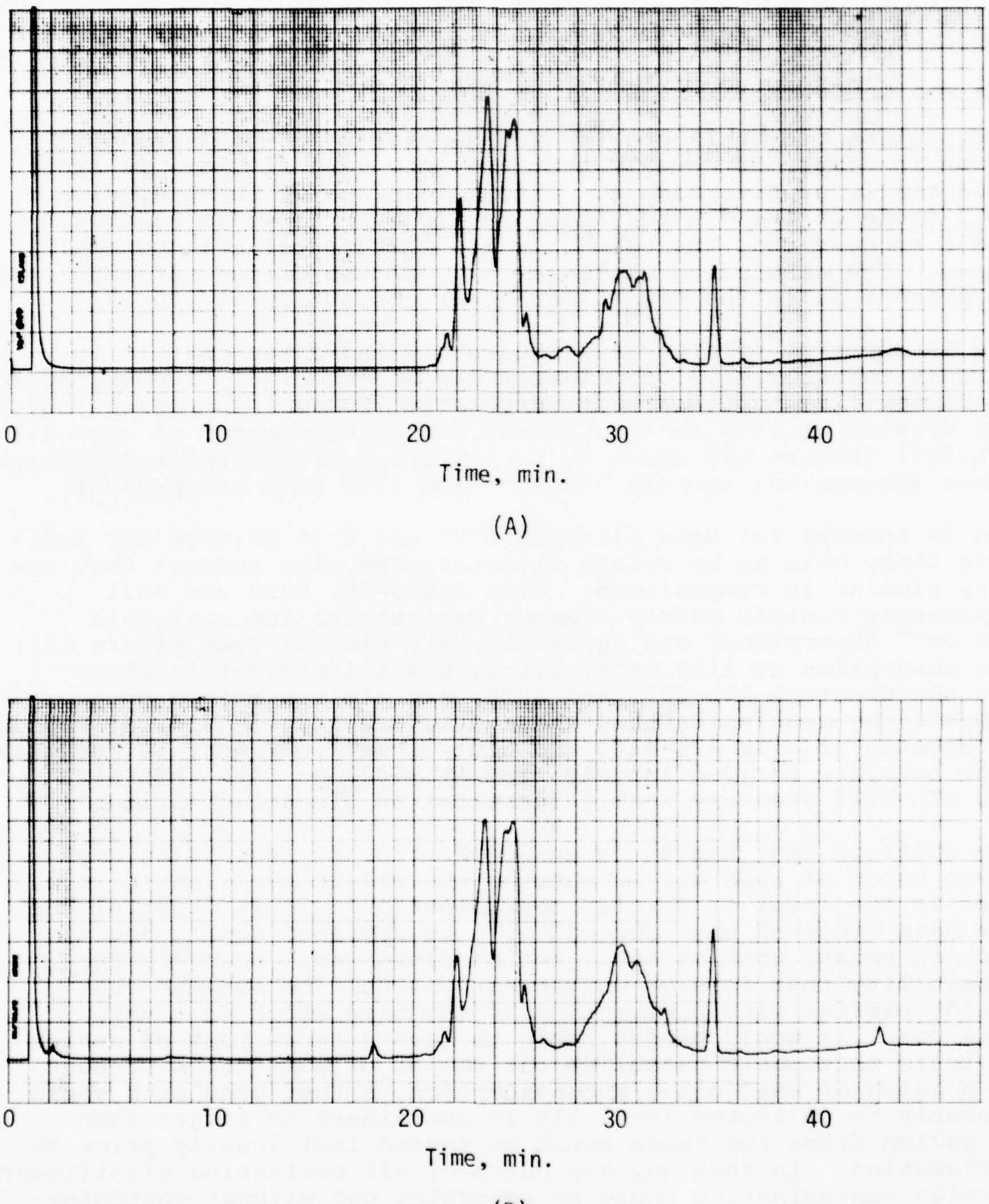


(A)



(B)

Figure 8. Gas Chromatograms of New Oils: (A) ATL-6022 and (B) ATL-6025



(A)

(B)

Figure 9. Gas Chromatograms of New Oils: (A) ATL-6023 and (B) ATL-6026

2.1.2 Used Oil Characterization

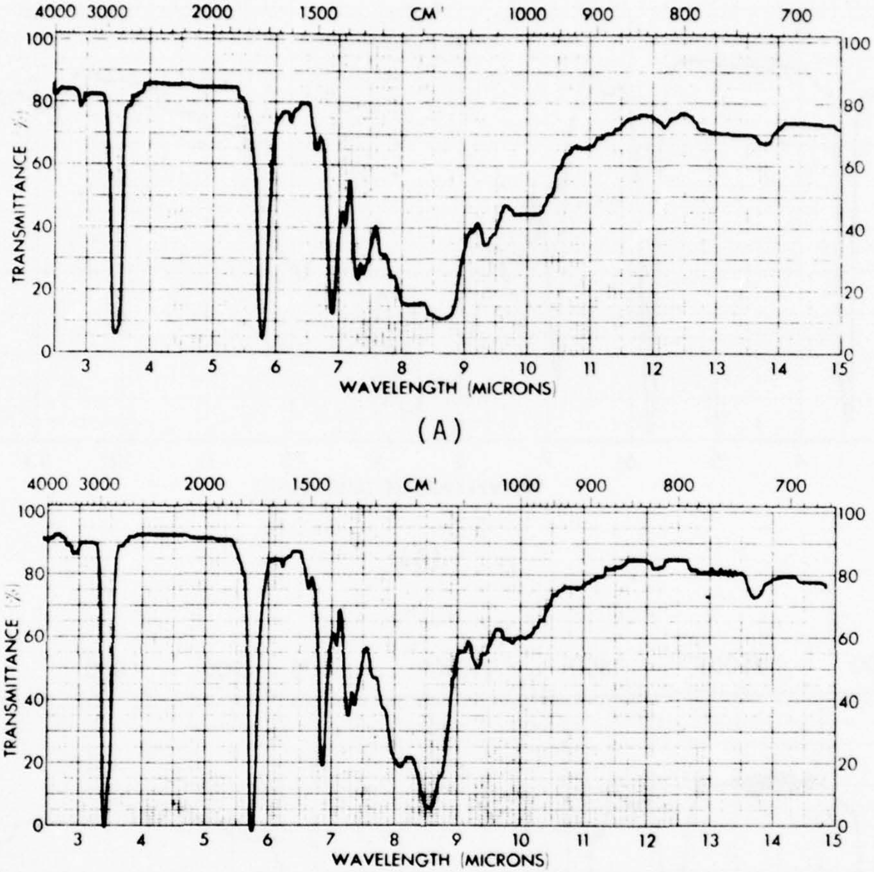
2.1.2.1 IR Spectrophotometry

Examination of the IR spectra for used oils ATL-5051 and 5052 shown in Figure 10 reveals that they are very similar, in fact, essentially superimposable. Also comparison of these spectra with those of the diester and triester type shown in Figures 5 and 6 suggest that the used oils are mixtures of both general types. The absorption characteristic of the diester at 1350 cm^{-1} is present as is the typical triester absorption at 720 cm^{-1}.

The IR spectrum of ATL-7069 (Figure 11) indicates that it is largely triester, i.e. no diester can be detected. The absorption characteristic typical for triesters at 720 cm^{-1} is present but that for diester at 1350 cm^{-1} is absent. The IR spectrum of used oil ATL-7071 (Figure 11) shows it is a mixture of diester and triester since absorptions at both 720 cm^{-1} and 1350 cm^{-1} are present.

The IR spectra for used oils ATL-6027 and 6028 (Figure 12) indicate these oils to be mainly triesters and also suggest they are very similar in composition. Oils ATL-6029, 6030 and 6031 apparently contain mainly diester base stocks (no noticable 720 cm^{-1} absorption) and again are very similar (see Figure 13). The absorption at 1100 cm^{-1}, although not identical to those for the diesters ATL-6023 and 6026, are similar enough to support the conclusion that these oils are largely diester based. IR spectra of oils ATL-6100 and 6101, shown in Figure 14, suggest that both are derived largely from ATL-6023 or 6026 (ATL-6023 and ATL-6026 are very nearly identical as discussed earlier).

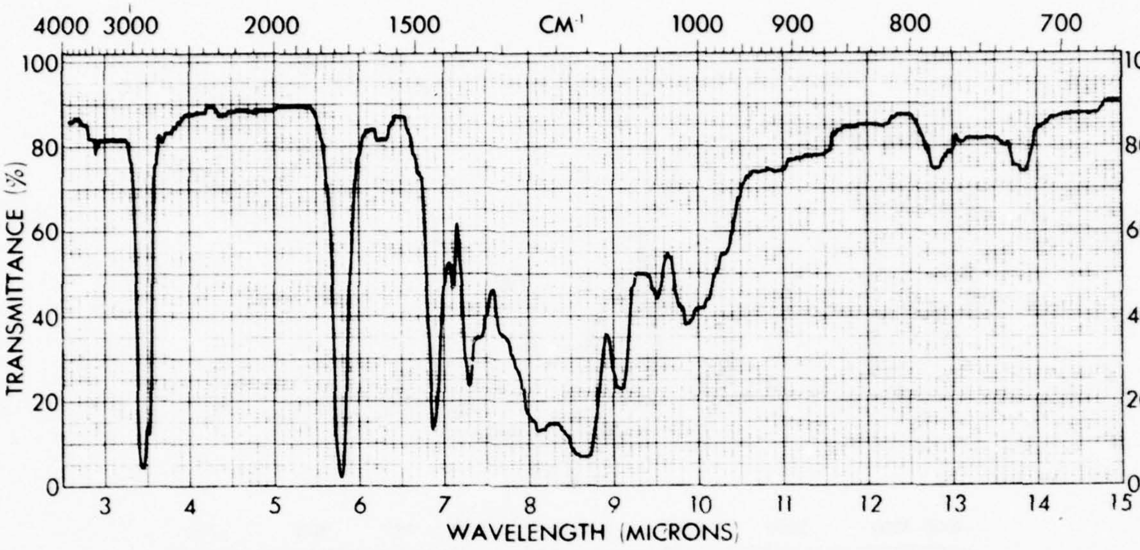
One question that has to be answered prior to reclaiming any given batch of used oil is whether the oil is reclaimable, i.e. what is the level of foreign contamination? It is doubtful that the base stock of any used oil will be degraded during use to such an extent that it could not be reclaimed. However, the possibility that foreign contamination could be present that would interfer with reclamation of the base stock is a very real one. It would be desirable to have a rapid test or series of tests that would establish the amount of base stock present in a batch of used oil. The assumption is that used oils would probably be collected initially in containers no larger than 55 gallon drums and these could be tested individually prior to reclamation. In this way any batch of oil containing significant foreign contamination could be separated out without contamination of a very large batch. In all likelihood only a very few batches of oil would contain significant amounts of foreign contamination but this would have to be definitely established. The types of foreign contamination present would also have to be established to insure that they would not interfer with the reclamation process and result in a non-qualifiable oil after reclamation.



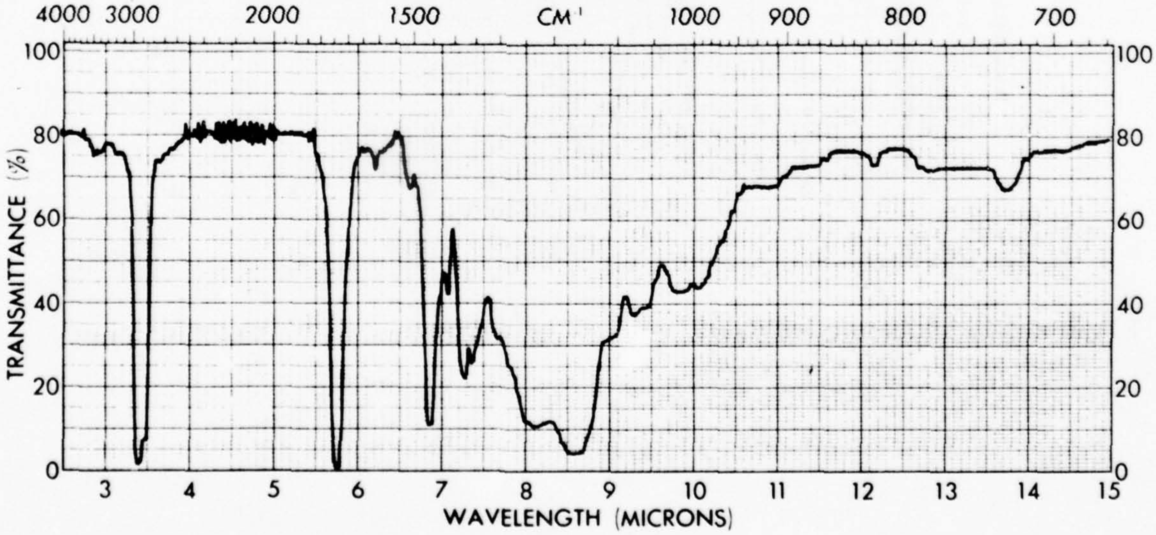
(A)

(B)

Figure 10. Infrared Spectra of Used Oils: (A) ATL-5051 and (B) ATL-5052

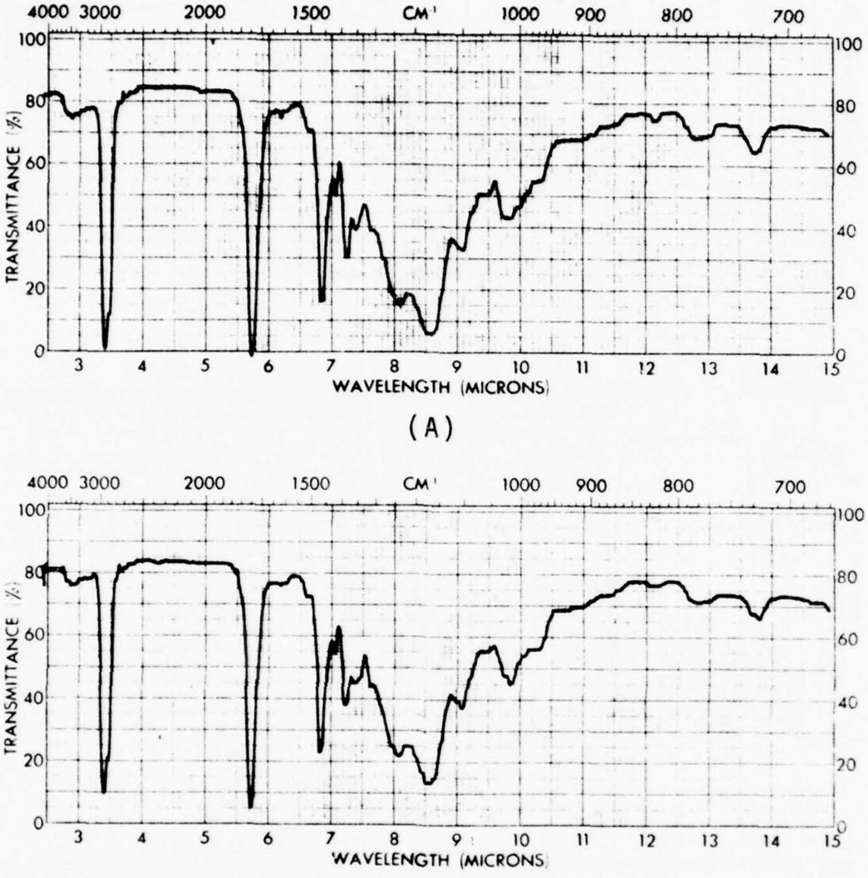


(A)



(B)

Figure 11. Infrared Spectra of Used Oils: (A) ATL-7069 and (B) ATL-7071



(A)

(B)

Figure 12. Infrared Spectra of Used Oils: (A) ATL-6027 and (B) ATL-6028

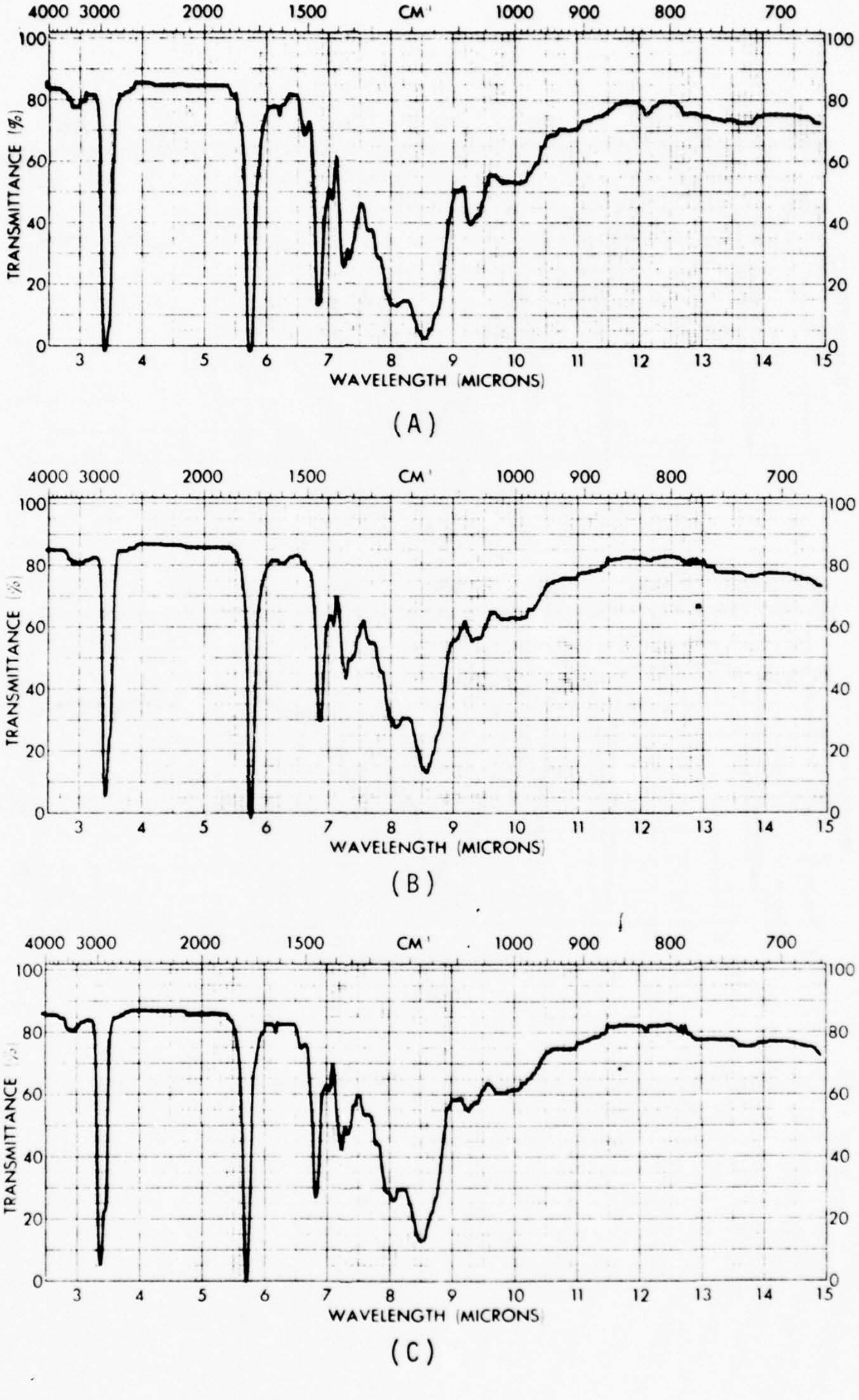
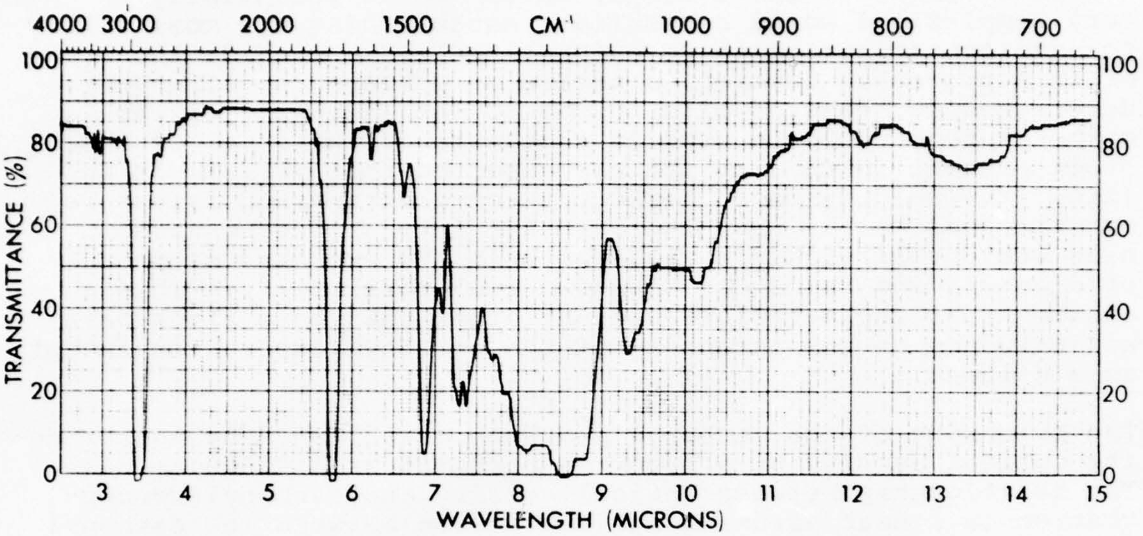
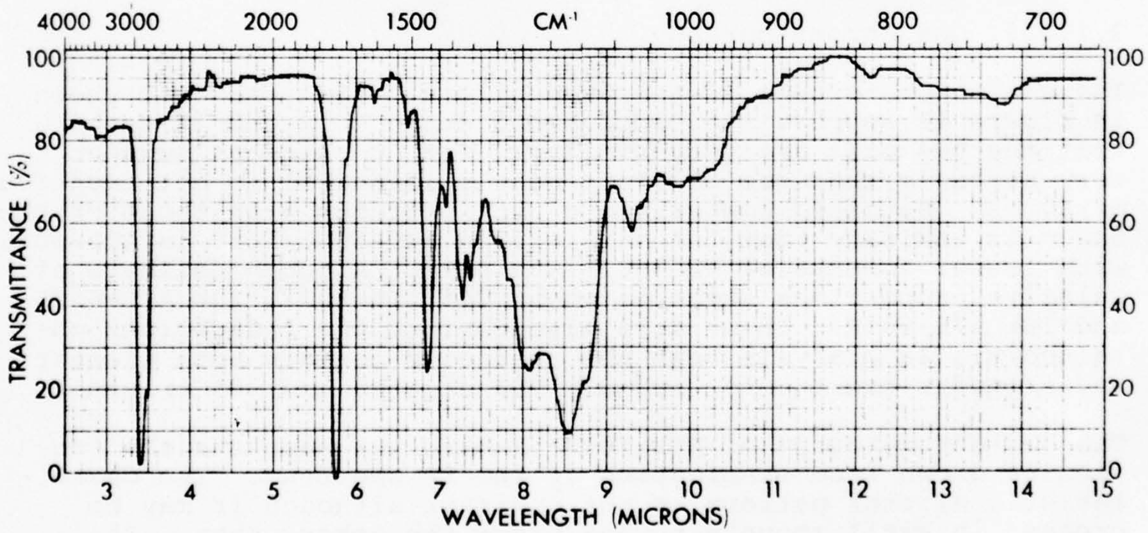


Figure 13. Infrared Spectra of Used Oils: (A) ATL-6029, (B) ATL-6030 and (C) ATL-6031



(A) ATL-6101



(B) ATL-6100

Figure 14. Infrared Spectra of Oils: (A) ATL-6101 and (B) ATL-6100

The development of these tests, which could potentially be very complex and would necessitate establishing the most likely foreign contamination to be encountered, were outside the scope of this project. However, a series of infrared spectra were determined on selected oils to see if the intensity of the carbonyl peak could be used as a measure of the level of base stock present in an oil. It was expected that variations in intensity would be encountered between diesters and triesters but the possibility that the carbonyl intensities of unknown oils would fall within a range between the extremes of those of diesters and triesters seemed a real possibility. This assumes that the materials present other than base stock have no influence on the intensity of the carbonyl adsorption except as a diluent.

The intensity of the carbonyl peak was established by measuring its optical density on a spectrum obtained in a 0.010 mm cell. The relationship between optical density and carbonyl concentration is linear assuming no interaction between the carbonyl and diluent. The data obtained are given in Table 7. The variations in optical density seen in these data established that the additives influence the intensity of the carbonyl adsorption sufficiently to negate its use as a measure of ester concentration. This is readily seen by the data for ATL-7071 reclaimed base stock (1.59) and reclaimed oil (1.28). The optical density for the carbonyl adsorption of ATL-7071, reclaimed oil, should be 1.52 (i.e., 95.65% of 1.59) if the additives did not influence the intensity.

2.1.2.2 Gas Chromatography

The gas chromatograms of the used oils ATL-5051 and 5052 shown in Figure 15 support the conclusions drawn from the IR spectra that the two oils are very similar. The GC patterns suggest very strongly that the oils are nearly identical if not identical mixtures. Detailed comparison of the patterns with those of the new oils indicate that the main oil in ATL-5051/5052 is ATL-6026 with lesser amounts of ATL-6025 and 6022. A rough estimate of relative proportions suggests about 70% ATL-6026, 20% ATL-6025 and 10% ATL-6022. These data also confirm the indications obtained via IR analysis that the used oils contain both diester and triester components, roughly 70% diester and 30% triester.

The gas chromatogram of ATL-7069 (Figure 16) supports the conclusion drawn from examination of the IR spectrum. The characteristic diester pattern is not dominant although it may be present in small amounts buried under the other peaks. The major used oils that comprise ATL-7069 cannot readily be identified indicating this used oil is a complex mixture.

Table 7

CARBONYL OPTICAL DENSITIES OF SELECTED OILS

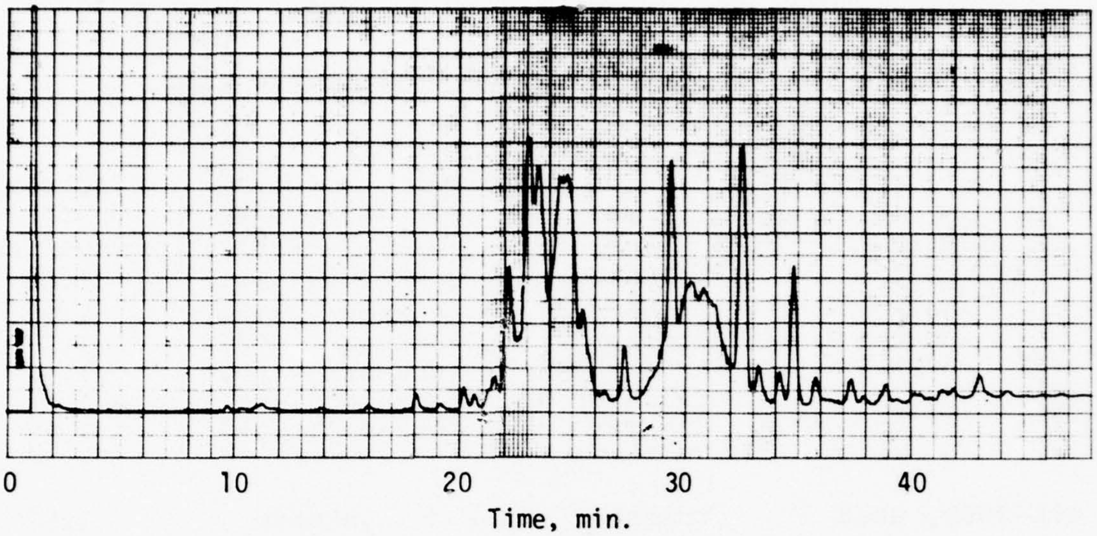
Oil	Base Stock Type	Base Stock Level[1], %	Carbonyl Optical Density[2]
ATL-6021	triester	unknown, <97.2	1.46
-6022	triester	unknown, <96.9	1.29
-6023	diester	unknown, <98.2	1.37
-6024	triester	unknown, <96.4	1.42
-6025	triester	unknown, <96.7	1.57
-6026	diester	unknown, <96.6	1.12
ATL-7069, used	triester	unknown	1.52
ATL-7069, reclaimed base stock	triester	100	1.49
ATL-7069, reclaimed oil	triester	95.65	1.36
ATL-7071, used	diester/triester	unknown	1.28
ATL-7071, reclaimed base stock	diester/triester	100	1.59
ATL-7071, reclaimed oil	diester/triester	95.65	1.28
Emery 2958[3]	diester	100	1.43
Emery 2932[4]	triester	100	1.63

[1] Values given as less than were determined from knowledge of levels of additives determined during analysis of oils. All additives not identified.

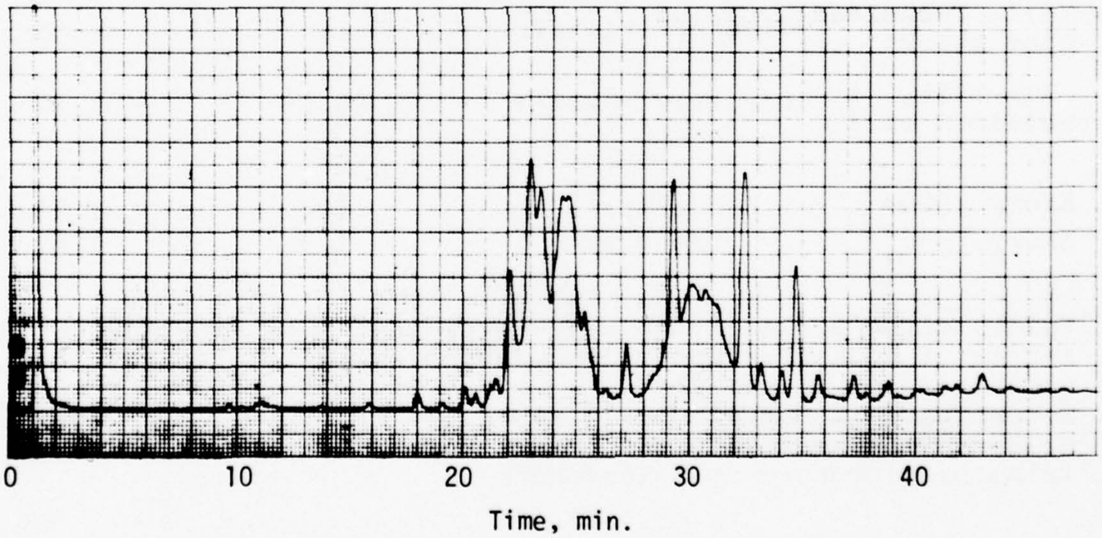
[2] Determinations made in 0.010 mm cell.

[3] Di-2-ethylhexyl azelate

[4] Trimethylolpropane tripelargonate



(A)



(B)

Figure 15. Gas Chromatograms of Used Oils: (A) ATL-5051 and (B) ATL-5052

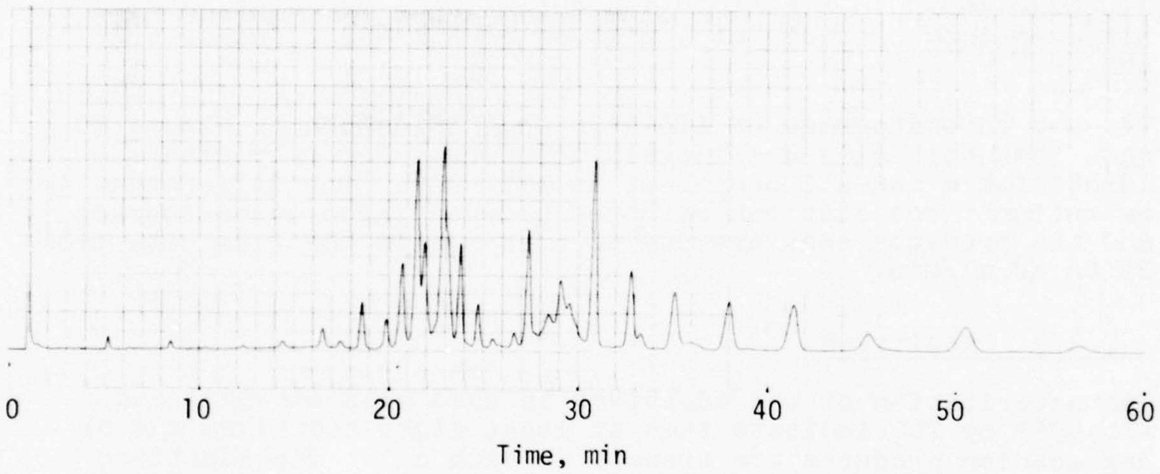


Figure 16. Gas Chromatogram of Used Oil ATL-7069

The gas chromatograms of the used oils ATL-6027 thru ATL-6031 are shown in Figures 17, 18, and 19. The patterns for ATL-6027 and 6028 (Figure 17) are identical and suggest that they contain mainly triesters. Comparison with the patterns for new oils suggests that ATL-6027 and 6028 are comprised of mixtures of mainly ATL-6022 and 6025 with some 6021. The IR spectra of these two oils were also identical.

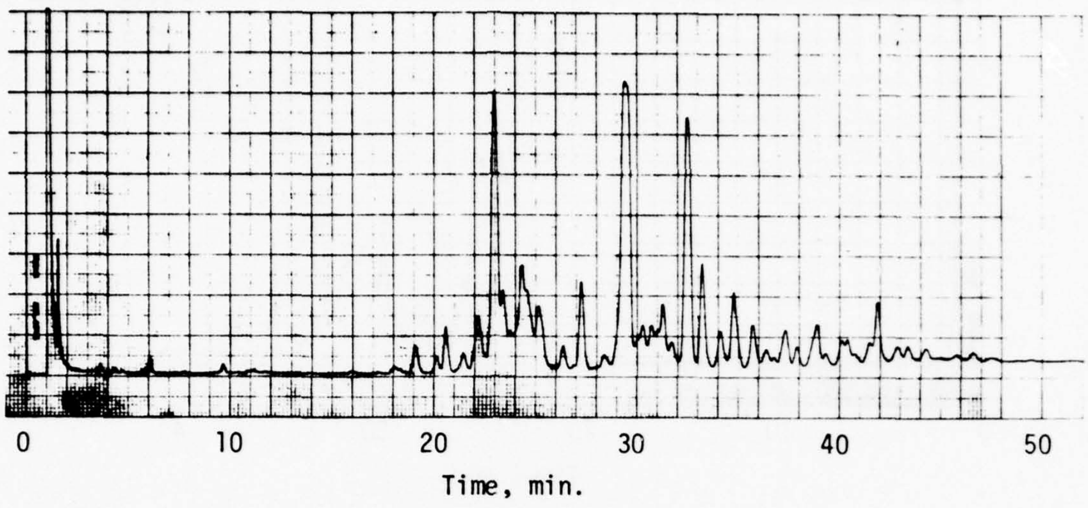
The patterns for ATL-6029 and ATL-6031 shown in Figure 18 are similar also. Comparison with new oil patterns indicate these oils to be mainly diesters made of mixtures of ATL-6023 (and/or 6026) with lesser amounts of 6022 and 6025, probably present in different ratios in the two used oils. The pattern for used oil ATL-6030 shown in Figure 19 indicates it to be mainly a diester oil comprised probably of a mixture of ATL-6023 (and/or 6026) and 6025.

The gas chromatograms of ATL-6100 and 6101 shown in Figure 20 show that both oils are largely diesters. The only other identifiable new oil component is ATL-6022. The differences in retention times that can be noted between these chromatograms and the previous ones are due to a change in the flow rate from 25 to 30 ml/min.

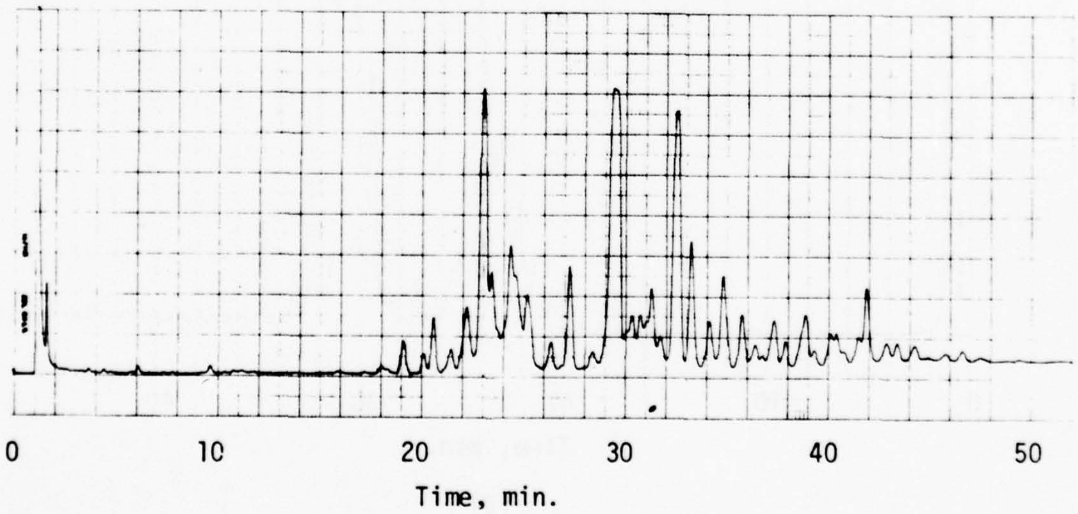
2.1.2.3 Additives

Characterization of the additives in used oils ATL-5051 and ATL-5052 by TLC indicate that at least eight additives and/or degradation products are present in each oil. The additives identified are: DODPA, TCP, PANA and quinizarin. In addition four unknown materials were detected in each oil. The unknown additives are identical again indicating that the two oils may be identical as was suggested by the IR and GC data. The HPLC patterns, shown in Figure 21, differ in that the retention times are very similar but the peak heights of several peaks are significantly different possibly indicating different additive levels. However, it is also possible that a slight change in the wavelength used for detection of these materials would cause the change in peak intensity observed. No definite conclusion can be drawn from this data. It is interesting to note that the DODPA peak (∿3.6 min) is still present in the used oil indicating that this additive had not significantly degraded during use of this oil.

The HPLC pattern of ATL-7069 shown in Figure 22 indicates few aromatic materials present in the oil. The peak at about 10 min represents DODPA (0.56%) and the peak at about 13 min represents PANA (0.18%). This is the lowest level of DODPA found in any of the used oil samples available in this project.

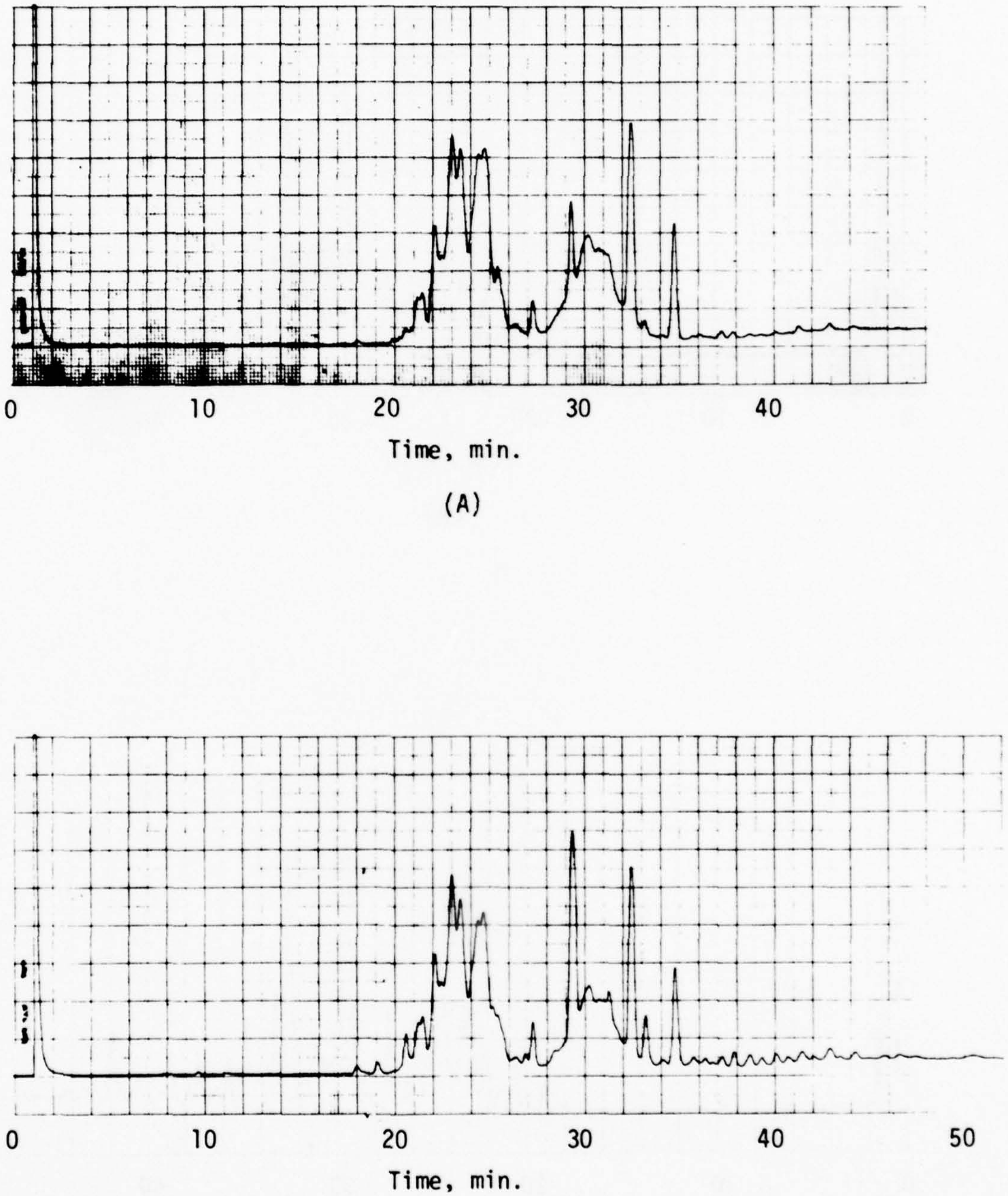


(A)



(B)

Figure 17. Gas Chromatograms of Used Oils: (A) ATL-6027 and (B) ATL-6028



(A)

(B)

Figure 18. Gas Chromatograms of Used Oils: (A) ATL-6029 and (B) ATL-6031

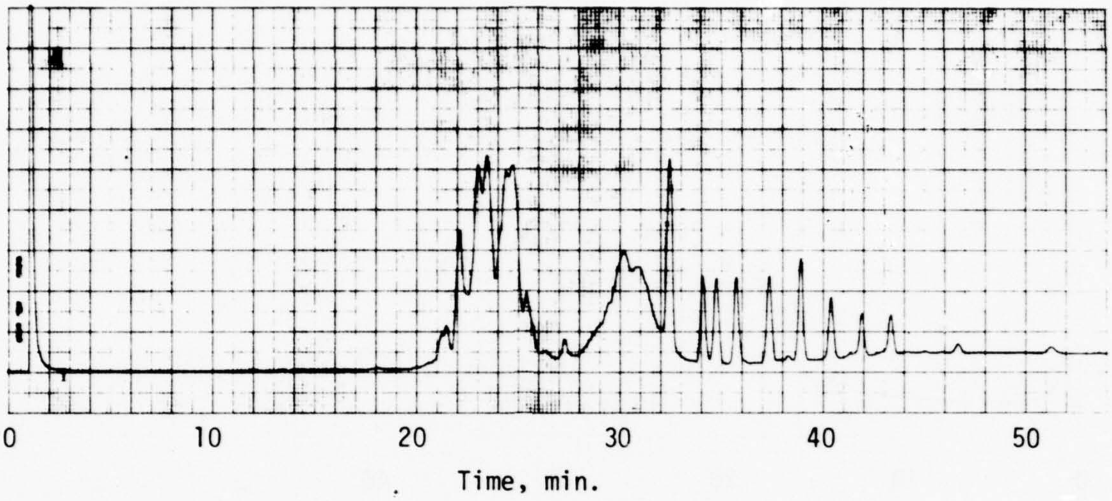


Figure 19. Gas Chromatogram of Used Oil ATL-6030

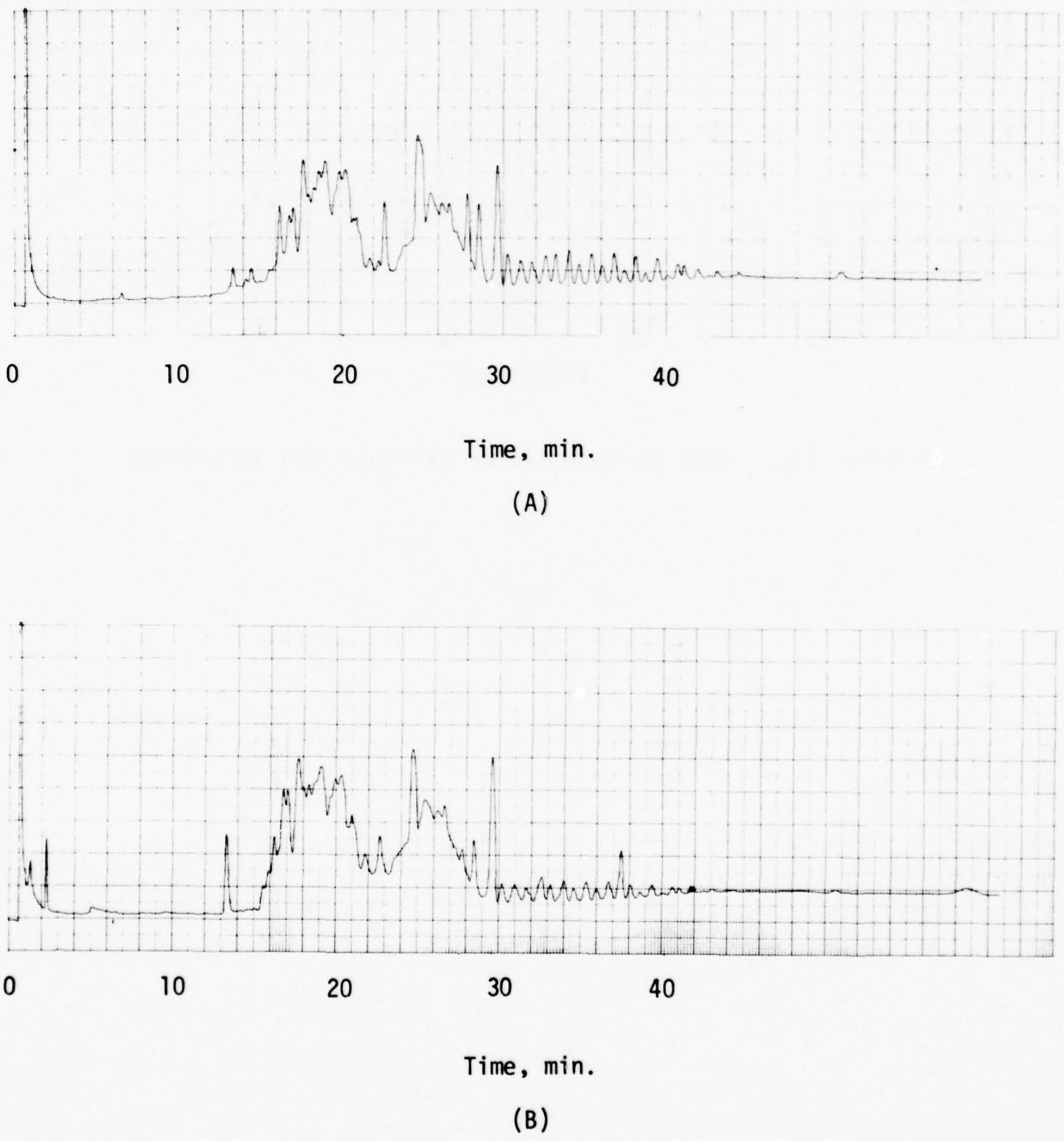
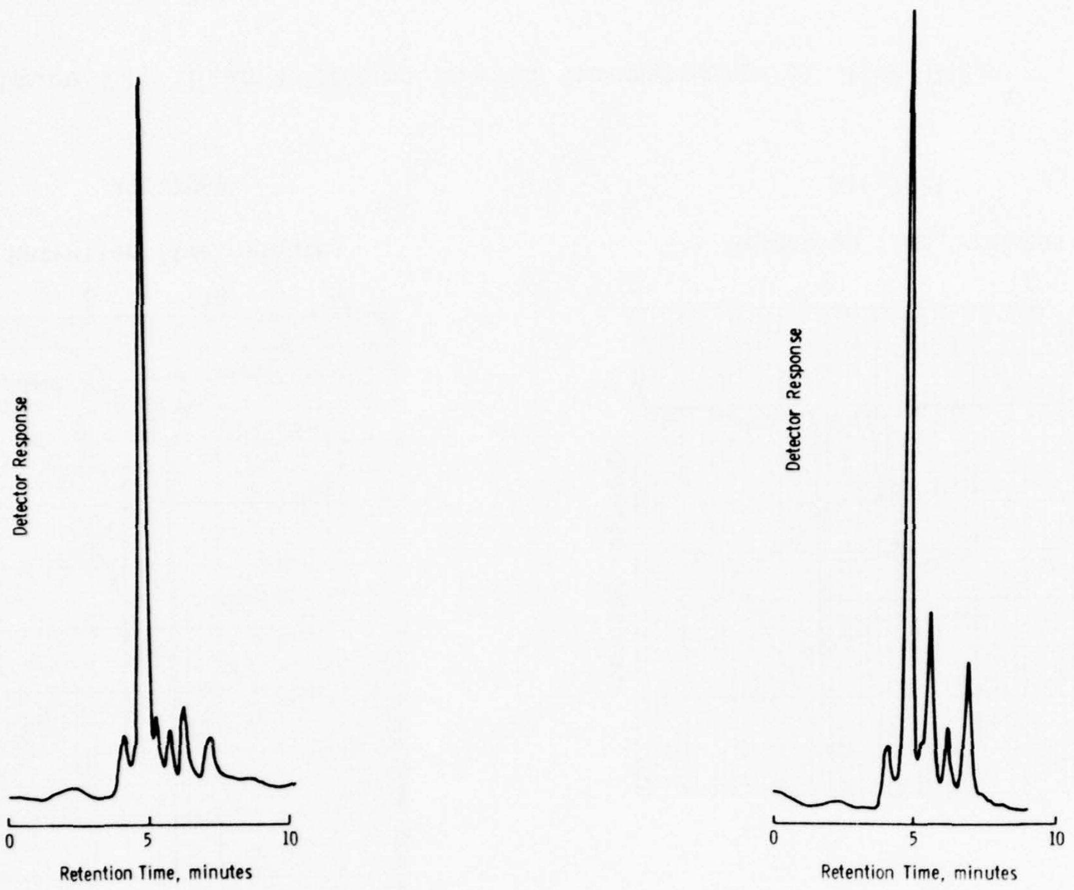


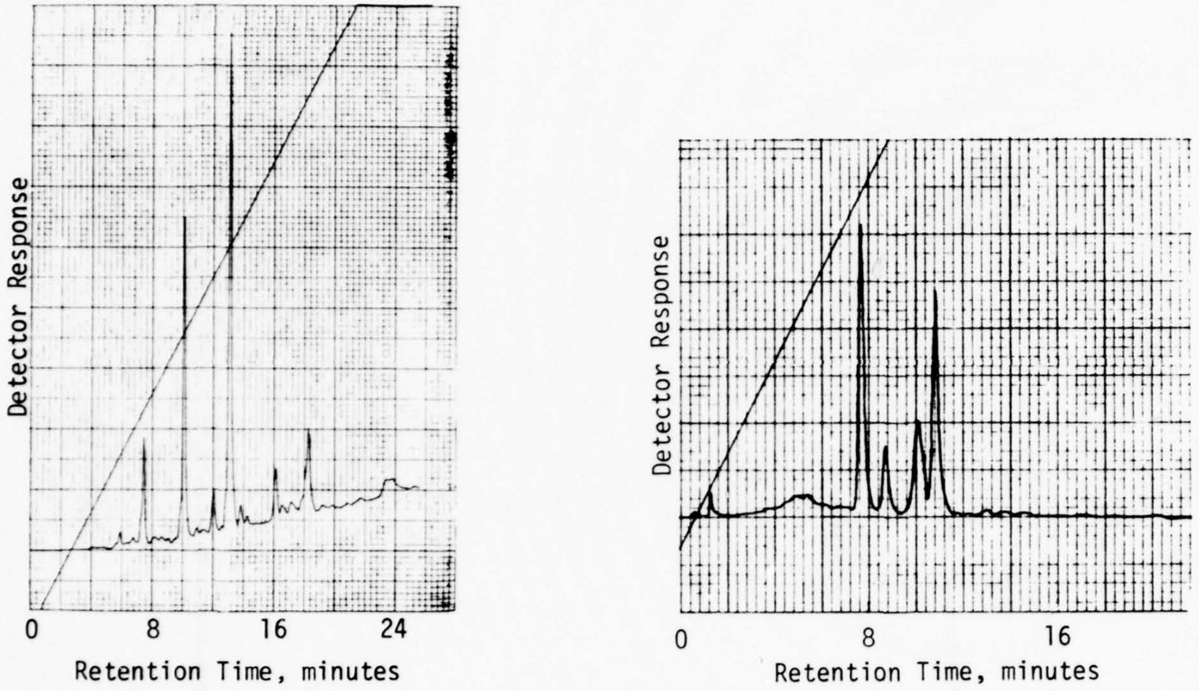
Figure 20. Gas Chromatograms of Used Oils: (A) ATL-6100 and (B) ATL-6101



ATL-5051

ATL-5052

Figure 21. High Pressure Liquid Chromatogram of Used Oils



ATL-7069

ATL-7071

Figure 22. High Pressure Liquid Chromatogram of Used Oils

The level of identifiable aromatic materials found in ATL-7071 was DODPA (1.55%), PANA (0.13%) and 3,7-dioctylphenothiazine (DOPTA) (0.24%). The HPLC pattern is shown in Figure 22. The difference in retention time and peak intensity for common materials in the chromatograms for ATL-7069 and 7071 is the result of slight changes in instrumental operating conditions and attenuation respectively.

The HPLC patterns of used oils ATL-6027 and 6028 shown in Figure 23 shows the same phenomenon observed in the patterns for ATL-5051 and 5052, i.e. same peaks but different intensities. Since these two analyses were done on different days slight changes in both retention time and peak intensity would not be considered uncommon. The fact that the GC and IR patterns for these two oils were also identical strongly suggests the same source for both samples.

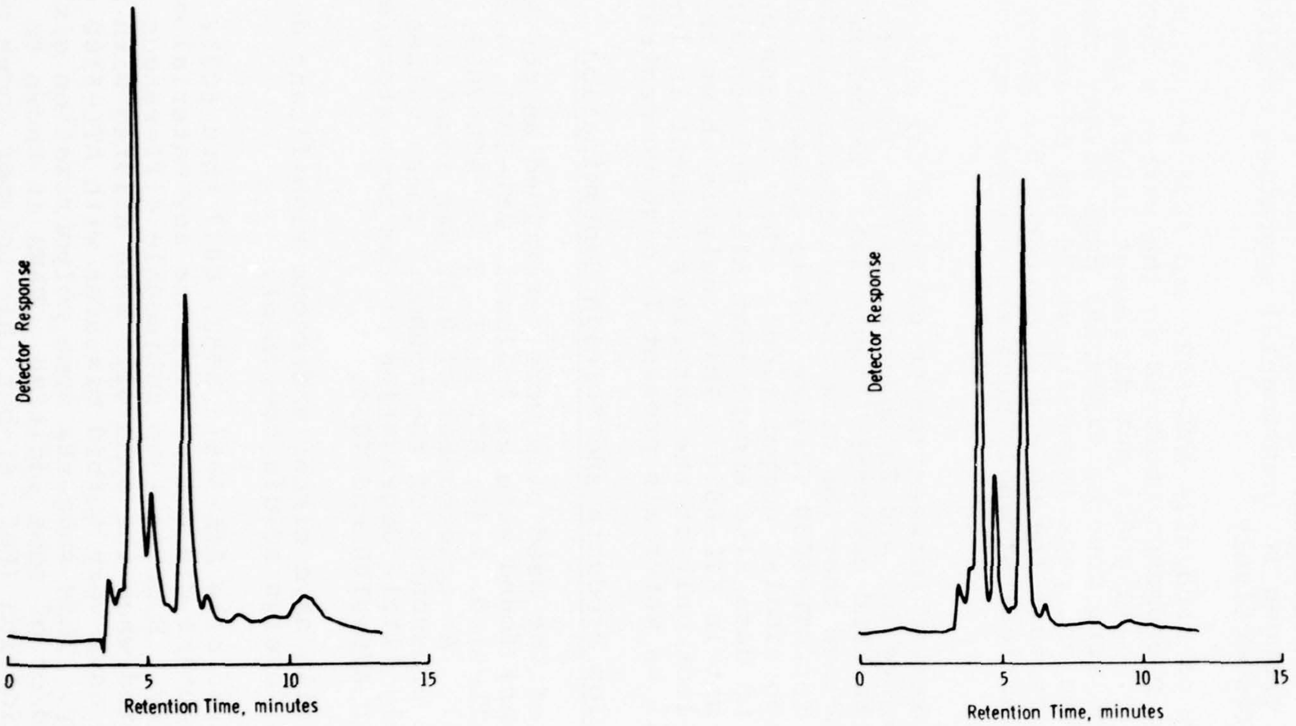
The similarity observed between the GC patterns for oils ATL-6029 and 6031 (Figure 18) and IR spectra (Figure 13) does not carry over into the HPLC patterns (Figure 24). Therefore one would have to conclude that the oils are not identical mixtures. The HPLC pattern for ATL-6030 (Figure 25) is somewhat similar to ATL-5051 suggesting similar compositions. This conclusion is supported by the GC data also except that ATL-5051 contains some ATL-6022 that is not in ATL-6030. This analysis shows the value of being able to look only at the materials present in low concentration as well as materials present in high concentrations.

2.1.2.4 Degradation Products and Foreign Contamination

The acid numbers of the used oils were determined as per ASTM D-664. Acid numbers found were as follows: ATL-5051, 0.35; ATL-5052, 0.45; ATL-6100, 1.41; ATL-6101, 0.32; ATL-7069, 4.09; and ATL-7071, 0.87. An acid number of 0.30 was found for ATL-6026 run as a crosscheck of the method. These values indicate relatively little degradation of the base stock/additive mixture except for ATL-6100 and 7069.

These latter two oils have either undergone significant degradation or contain a foreign acidic component.

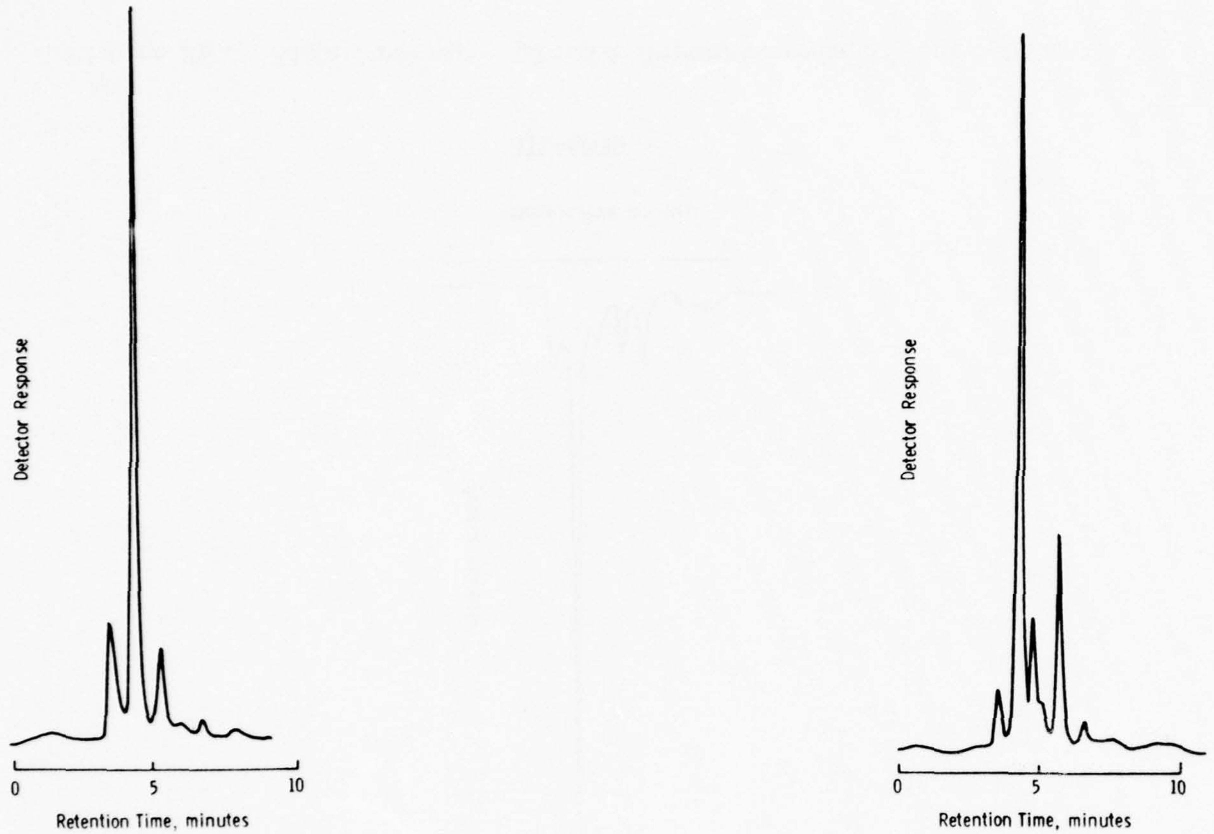
Dilution of the used oils ATL-5051, 5052, 6027 thru 6031, 6100 and 6101 with *n*-pentane did not precipitate any material or cause any turbidity. However some noticeable differences in turbidity were noted when the same oils were diluted with methanol. ATL-6100 and 6101 gave very turbid mixtures with ATL-6100 giving the most turbidity. This suggests some polymerization either of the base stock and/or of some additive. PANA is known to form a low polymer on oxidation (Ref. 6) but this polymer comes out of the oil as a sludge and would probably have been removed during filtration if present. The other used oils did not give any more turibidty than can be observed by dilution of new oils with methanol.



ATL-6027

ATL-6028

Figure 23. High Pressure Liquid Chromatograms of Used Oils



ATL-6029

ATL-6031

Figure 24. High Pressure Liquid Chromatograms of Used Oils

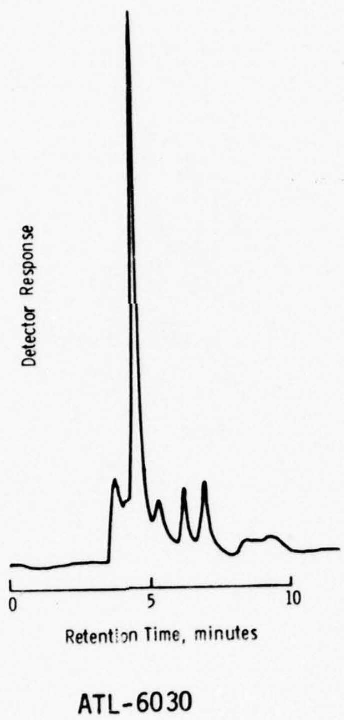


Figure 25. High Pressure Liquid Chromatogram of Used Oil

Oil soluble organosilicones are known to cause severe foaming problems when present even at low levels in turbine oils. Since organosilicones can be introduced into the oil during use a limited amount of analytical work was done to determine if low levels of organosilicone could be detected. It was found that the silicone antifoam agent could be detected at the one ppm level by Fourier transform nmr in solution. However, when the nmr spectrum of an oil containing about 10 ppm silicone antifoam was obtained it was found that there were peaks from the remaining constituents of the oil in the same region as the silicone-methyl peaks. We were not able to make a measurement in the one to fifty ppm range with the required accuracy because of this interference. There are other approaches utilizing nmr that could potentially remove the interference from these peaks. Also Fourier transform IR could feasibly be used for this analysis. No further work was done since later reclamation studies did not reveal any problem with soluble silicone.

The detection and characterization of ester degradation products and volatile foreign contamination was approached by trapping all volatiles coming from the oil at 150-160°C/1 mm and analyzing the products by gas chromatography-mass spectroscopy. The expected ester decomposition products from MIL-L-7808 oils are olefins, alcohols and acids. The volatilities of the expected olefins and alcohols are such that they would distill during this topping operation. A water layer and an organic layer were obtained from ATL-5051 and 5052 and the organic layers analyzed by gas chromatography-mass spectroscopy. ATL-5051 oil gave about 0.5% and ATL-5052 about 0.3% organic volatiles. The organic fraction from ATL-5051 oil showed the following compounds: toluene, chloroform, cyclohexane, C_2-C_4-benzenes, C_9-C_{11} alkanes, 2-ethylhexanol and possibly a trace of $\sim C_{10}$ alkenes with toluene being by far the major component. The patterns were too complex to readily afford further identification of components.

The spectral pattern for the volatiles from ATL-5052 was much simpler. Table 8 lists the components found along with the relative intensities of their strongest ion peaks. These relative intensities are a very rough indication of the relative amounts of each material. Further quantification was not considered necessary for this project.

The presence of 2-ethylhexanol in both used oils indicates that either some ester degradation has occurred or possibly there was residual 2-ethylhexanol in the oil left there from the original synthesis. Assuming that the relative intensities of the strongest ion peaks in the mass spectrogram are directly proportional to concentration the amount of 2-ethylhexanol in ATL-5051 was calculated to be roughly 0.03%. This would be a reasonable level for residual alcohol left from synthesis.

Table 8

VOLATILE PRODUCTS IN ATL-5052 OIL

Compound	Relative Intensity of Strongest Ion[1]
toluene	100
C_{10}-C_{11} alkanes	21
2-ethylhexanol	14
xylenes/ethylbenzenes	8
cyclohexane	4
chloroform	3
methylnonadiene	2
C_7-C_8 adipates	2
C_4-cyclohexanes	2
C_4-benzenes	1
diisopropylbenzenes	0.5

[1] Relative to toluene

The known diester oils were analyzed for the presence of 2-ethylhexanol along with ATL-5051 and ATL-5052. The gas chromatographic analysis technique was modified to permit detection of 2-ethylhexanol. Absolute concentrations of 2-ethylhexanol in these oils were not obtainable due to the presence of other compounds eluting at approximately the same place in the analysis. We were able to establish lower limits for 2-ethylhexanol and found these to be less than 0.03% in all four oils. The data suggest that the 2-ethylhexanol detected in ATL-5051 and ATL-5052 most likely came from the original base stocks and did not occur as a result of base stock degradation. In any event if base stock degradation has occurred, it has been to a very limited extent in these oils.

The presence of aromatics, aliphatics and chloroform indicates external contamination of the oils. The alkenes could possibly be due to ester degradation. Their low levels would suggest very small amounts of degradation if that is the source. The C_7-C_8 adipates are probably components of the base stock.

The other used oil samples were topped at 150°C/15 mm Hg to determine volatile levels. The results are given below.

Used Oil ATL-	6027	6028	6029	6030	6031	6100	6101
Wt % Volatiles	0.2	0.06	0.12	0.05	0.05	0.02	0.02

The volatiles in all oils were mostly water as determined by refractive index measurements. The lack of organic volatiles suggests that these oils were handled or stored differently than ATL-5051 and ATL-5052.

2.1.2.5 Metals Analysis

Three new oils and the four major used oil samples were analyzed for metals content via emission spectrography to obtain a benchmark with respect to the potential problem of removal of metals. (The new oils were analyzed to serve as a cross check of the technique). These samples had been filtered to remove suspended particles that could potentially have also contained metals. The results of the analysis are given in Table 9 along with the maximum values permitted under MIL-L-7808G specification.

Several metals are present in amounts in excess of the specifications but only Fe is present at excessively high levels in one sample. Other metals found but not listed in MIL-L-7808G were Si, Mn, Mo, Na and Pb. Si, Mn, Mo and Na were found in the new oils at less than 2 ppm and at less than 8 ppm in the used oils. Pb was not found in the new oils but was found in the used oils at an estimated 20, 50, 21 and 82 ppm for ATL-5051, 5052, 7069 and 7071 respectively.

Table 9

METALS CONTENT OF OIL SAMPLES[1]

	Metal Content ppm								
Oil Code	Al	Fe	Cr	Ag	Cu	Sn	Mg	Ni	Ti
MIL-L-7808G[2]	3	4	3	1	1	4	3	4	1
ATL-6021	<0.1	0.2	<0.1	<0.1	<0.1	0.8	<0.1	<0.2	<0.2
ATL-6023	0.1	0.2	<0.1	<0.1	<0.1	1	<0.1	<0.2	<0.2
ATL-6026	0.2	0.2	<0.1	<0.1	<0.1	0.8	0.2	<0.2	<0.2
ATL-5051	0.7	8	3	0.4	0.8	2	0.7	0.2	2
ATL-5052	0.8	8	4	0.4	1	3	2	0.2	3
ATL-7069[3]	0	3.5	0	0.7	0.8	5.3	0	0.3	0.5
ATL-7071[3]	0	2.6	7.7	0.1	1.5	6.8	4.3	0.1	6.5

[1] Values obtained by emission spectrographic analysis using a Bausch & Lomb Emission Spectrograph (dual grating)

[2] Values given are maximum values permitted by specification

[3] Values obtained as per MIL-L-7808G specification procedure.

2.2 STUDY OF POTENTIAL RECLAMATION PROCESSES

The approach taken to development of a reclamation process for the synthetic ester oils was to take advantage of the vast amount of technology available as a result of the development of the natural oil and fat refining industry. Considerable information is available on many processes for removal of a variety of impurities in the natural oils and some of this appeared to be adaptable to removal of the additives and impurities found in the synthetic oils. The methods evaluated that appeared to be applicable to the types of additives and impurities expected were: use of alkaline materials (aqueous or adsorbent) for removal of acids, use of acidic materials (aqueous or adsorbent) for removal of bases, distillation (low pressure and/or steam), use of bleaching earths and/or activated charcoals, chemical bleaching procedures, and solvent partitioning. Inasmuch as possible the study of these techniques will be discussed separately. However, much of the effort has involved combinations of two or more of the above techniques and consequently a sharp separation of the effect of each is not always possible.

There are two general characteristics of used oils that prevent their continued use in an engine. They can contain degradation products of many types but specifically the degradations of additives renders these oils less effective than is required for continued optimum engine performance. Also the stressed oil forms higher molecular weight base stock materials resulting in increased viscosity, particularly at low temperatures. Ideally a reclamation process should remove all degradation products (as well as foreign materials) to obtain a base stock that can be reformulated to an oil meeting specifications. The following six sections discuss four general techniques that were studied to remove mainly additive degradation products and foreign contaminants (adsorbents, oxidation, treatment with sulfuric acid and solvent partitioning) and two approaches (distillation and precipitation) to remove polymerized base stock. Distillation and precipitation can potentially work for both general areas depending on the degradation product involved.

Separation of polymerized base stock can only be approached by taking advantage of the differences in volatility, solubility or molecular size of the normal and polymerized base stock. Distillation and precipitation take advantage of the differences in volatility and solubility respectively. Separation by size differences can be readily accomplished by exclusion chromatography but this is much too costly a process for large scale use.

2.2.1 Adsorbents

The initial efforts in development of a reclamation process involved study of the effect of various adsorbents on removal of non-base stock materials from a used oil. At the same time samples of used oil were treated with aqueous acid and base in an attempt to extract out basic and acidic components respectively. In each case when treated with acid or base the used oil mixtures turned purple. It was also noted that some of the oils fluoresced at 366 mμ. Since the occurrence of color formation with acids and bases and fluorescence are undoubtedly characteristic of some of the additives present in these oils, an attempt was made to use these qualitative tools to follow changes in additive levels upon treatment with adsorbents.

The effect of concentrated sulfuric acid and 1*N* NaOH on color formation and the fluorescence characteristics of several of the supplied oils are given in Table 10. Note that the new oils ATL-6023 and 6026 have the same combination of responses to all three qualitative tests. The IR and GC analyses of these oils also suggested that they were very similar. ATL-6021 and 6022 also have the same combination of responses. Previous analyses have shown these oils to be different so the similarity of responses here suggests a particular additive(s) present in both is responsible for the responses. Also note that the used oils all give positive results with all three tests. This could only happen if the used oils were comprised of mixtures of at least two other oils or one or more of the qualitative tests was caused by the degradation product of an additive.

Used oil ATL-5051 was treated with seven different adsorbents and the products characterized with the qualitative tests and via GC analysis. The results of the qualitative tests given in Table 11 indicate that something was removed by treatment with basic Al_2O_3, activated charcoal and bentonite according to the NaOH test. Use of all seven adsorbents resulted in an improvement in color with use of attapulgus clay, basic Al_2O_3 and charcoal resulting in colors similar to new oils ATL-6024 and 6025.

GC analyses of ATL-5051 after treatment with adsorbents showed only a very minor change in one small peak in a few cases. The only exception was the complete removal of one small peak on treatment with charcoal. Since the changes were so minor the GC patterns were not included here.

Table 10

MISCELLANEOUS CHARACTERISTICS OF OIL SAMPLES

Oil Code	Color Formed With Conc. H_2SO_4	Color Formed With 1N NaOH	Fluorescence at 366 mμ
NEW OILS			
ATL-6021	none	none	strong
ATL-6022	none	none	strong
ATL-6023	red	purple	none
ATL-6024	red-orange	purple	strong
ATL-6025	brown	none	strong
ATL-6026	red	purple	none
USED OILS			
ATL-5051	purple	purple	strong
ATL-5052	purple	purple	strong
ATL-6027	purple	lt. purple	strong
ATL-6028	purple	lt. purple	strong
ATL-6029	purple	lt. purple	weak
ATL-6030	dark purple	lt. purple	weak
ATL-6031	dark red	lt. purple	strong

Table 11

EFFECT OF ADSORBENTS ON ATL-5051 OIL[1]

Sample No.	Adsorbent	Color After Treatment	Color Formed With Conc. H_2SO_4	Color Formed With 1N NaOH
ATL-5051	--	dark brown	purple	purple
194002-1-Al	attapulgus clay	yellow	dark purple	purple
194002-2-Al	basic Al_2O_3	yellow	dark purple	none
194002-3-Al	activated charcoal	yellow	red-purple	none
194002-4-Al	lime	red	red-purple	lt. purple
194002-5-Al	bentonite	brown	dark-purple	none
194002-6-Al	silica gel	brown	purple	purple
194002-7-Al	Fuller's earth	brown	red-purple	purple

[1] Fluorescence at 366 mμ was strong in all cases

Three adsorbent types were selected for further study based on the above results. These are basic alumina, charcoal and two clays, attapulgus clay and Fuller's earth. The qualitative efficiency of these adsorbents was followed using TLC. Used oil ATL-5051, topped to remove all volatiles boiling below 150°C/15 mm (conditions readily attainable in larger scale operations) was used in these studies.

Treatment of the topped ATL-5051 with 10% by weight of basic alumina at about 65°C for one hour resulted in partial removal of one unknown additive. Activation of the alumina by drying at 200°C for 4 hours prior to use resulted in more extensive removal of the unknown additive. The same trend was found when the oil was heated with attapulgus clay at about 65°C for one hour. N-Phenyl-α-naphthylamine (PANA) was partially removed with as received clay, more completely removed with heat activated clay and apparently completely removed with acid activated clay. In addition 4,4'-dioctyldiphenylamine (DODPA) was partially removed with the acid activated clay. Acid activated Fuller's earth appeared to do at least as well and possibly somewhat better than attapulgus clay as determined by TLC.

A quick series of screening tests were run to check the effectiveness of basic alumina, Fuller's earth and charcoal in removing DODPA from an ester solution since it was the main additive not removed by adsorbents. This was done to see if another material in the used oils was interferring with the adsorption of DODPA. No significant adsorption of DODPA from amyl acetate was found by TLC analysis showing that the inability to adsorb DODPA is inherent in its structure.

The above acid and base treatment were repeated using aqueous systems to see if any advantage could be found. Extraction with 1*N* NaOH removed an unknown additive. Extraction with 3*N* HCl appeared to result in complete removal of PANA and partial removal of DODPA. No benefit could be found by using the aqueous systems as determined by TLC. Also the potential for formation of emulsions when using aqueous extractants and used oils of potentially widely varying compositions makes the use of aqueous extraction rather unattractive for a general reclamation process.

Treatment of the oil with activated charcoal significantly improved the color but did not appear to remove anything as determined by TLC. However, GC analysis indicated removal of one material.

Evaluation of the use of acid ion exchange resins for removal of basic materials established that these resins are not sufficiently active to be useful in this program. Treatment of an oil with an acid ion exchange resin activated by treatment with HCl and methanol (Ref. 12) did not result in significant removal of the amine antioxidants present in the oil. Similar results were obtained by treatment of a model system of a 1% solution of DODPA in amyl acetate with the ion exchange resin. Discussions with the resin manufacturers technical staff indicates that we tried the optimum conditions and the lack of success indicates that the antioxidants are not sufficiently reactive with the ion exchange resin.

Discussions with an MRC consultant, Dr. K. Kammermeyer, concerning adsorption techniques and materials resulted in the evaluation of polyacrylonitrile, polyester and nylon as adsorbents for the used 7808G oils. These materials have been found to be useful in some rather specific adsorption applications in hydrocarbon based oils. TLC analysis of ATL-5052 treated with each material indicated no benefit from their use for this program.

Late in the program after the adsorbent treatment series had been selected used oil ATL-7069 was received and a trial reclamation attempted. A sample of ATL-7069 was reclaimed using the selected process, i.e. distillation, treatment with Fuller's earth, basic alumina and charcoal. The acid number of the reclaimed base stock was 1.76, a value well in excess of any value previously obtained on reclaimed base stocks. The acid number of ATL-7069 was also high, i.e. 4.09. Since basic alumina did not lower the acid number sufficiently a brief study of the effect of calcium hydroxide on acid number was carried out using ATL-7069. Treatment of the used oil with various weight levels of $Ca(OH)_2$ for one hour at room temperature produced the results shown below. It is not known why the $Ca(OH)_2$ level vs. acid number is an inverse relationship but the effectiveness of $Ca(OH)_2$ is well documented by the data below.

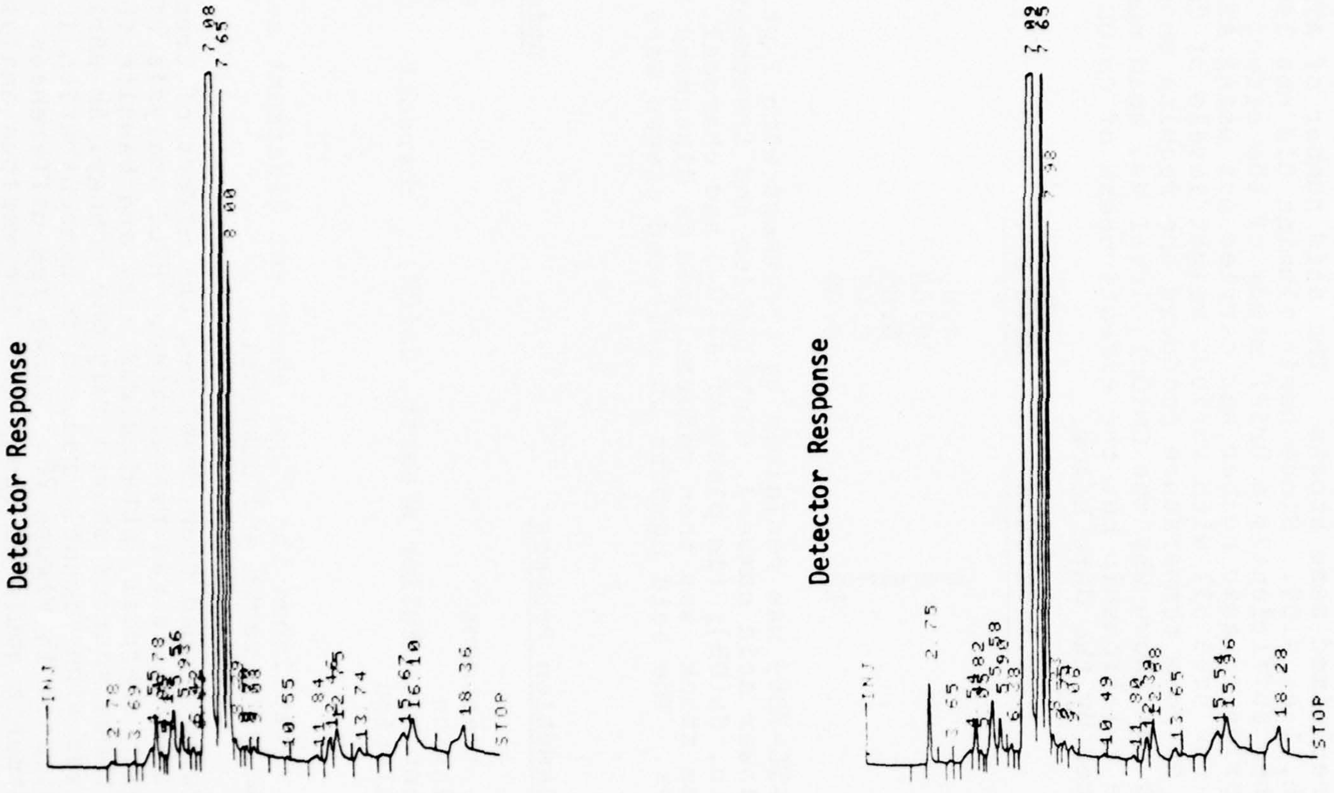
Wt.% $Ca(OH)_2$	Acid No.
0	4.09
2	0.04
5	0.05
7	0.07
10	0.09

A sample of ATL-7069 was reclaimed by treatment with 2 wt.% $Ca(OH)_2$ (to lower acid number), distillation and treatment with Fuller's earth, $Ca(OH)_2$ (in place of Al_2O_3) and charcoal. The reclaimed base stock was then reformulated as discussed later in this report. The acid numbers at selected stages were as follows:

Stage in Reclamation Process	Acid No.
Initial	4.09
After $Ca(OH)_2$ treatment	0.28
After distillation	1.14
After treatment with Fuller's earth, $Ca(OH)_2$, charcoal	0.04
After reformulation	0.13

These results established the final adsorbent treatment sequence of $Ca(OH)_2$, Fuller's earth and charcoal.

Once a HPLC procedure had been developed the effect of treating a used oil with adsorbents was reevaluated. HPLC analysis of ATL-5051 treated with charcoal, attatpulgus clay and bauxite (basic alumina) from three sources showed only one change. An early eluting component was significantly reduced in concentration in all cases as illustrated in Figure 26. Since few differences between adsorbent treatments could be shown with the various analytical techniques it appeared likely that other reclamation techniques in addition to adsorbents would be required to obtain a satisfactory reclaimed base stock.



Elution Time, minutes

197469-A: ATL-5051 treated with Attapulgus Clay

Elution Time, minutes

ATL-5051

Figure 26. High Pressure Liquid Chromatograms of Oil Samples

The above technique for treatment of used oils with adsorbents results in significant loss of oil on the adsorbent. Losses can run as high as 35% after passing through three adsorbents. We therefore examined techniques for recovery of the adsorbed oil to reduce these losses. The oil can be readily recovered by washing the adsorbents with hexane followed by vacuum stripping of the hexane. The recovered reclaimed base stock is lighter in appearance than the reclaimed base stock that passes through the filter. No significant differences can be detected by HPLC. Use of more polar solvents resulted in removal of adsorbed material from the adsorbents. This technique cut losses to 1 to 2% per adsorbent treatment.

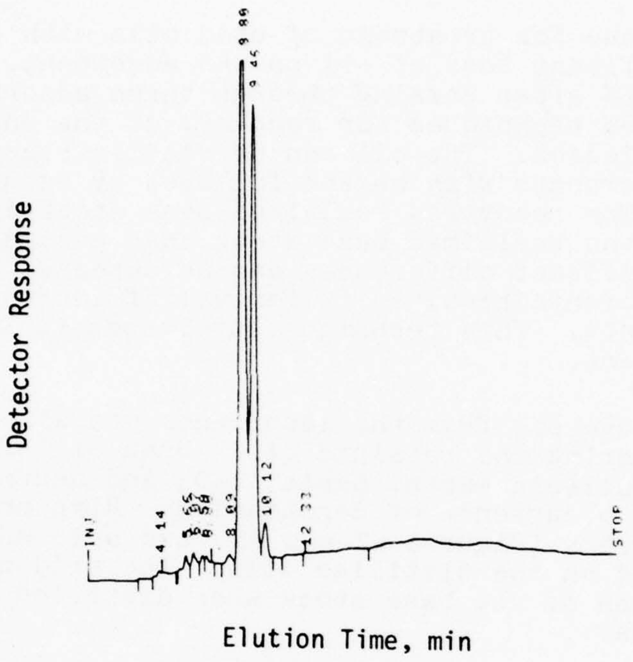
Distillation of the oil from the adsorbents was also evaluated as a means of recovering the retained oil. Used oil ATL-5052 was distilled from Fuller's earth, basic Al_2O_3 and neutral charcoal and analyzed for occurrence of degradation. High pressure liquid chromatograms (Figures 27 and 28) and acid numbers (Table 12) were obtained on the distilled oils. The acid numbers indicate decomposition of the base stock when distilled from Fuller's earth and charcoal.

Table 12

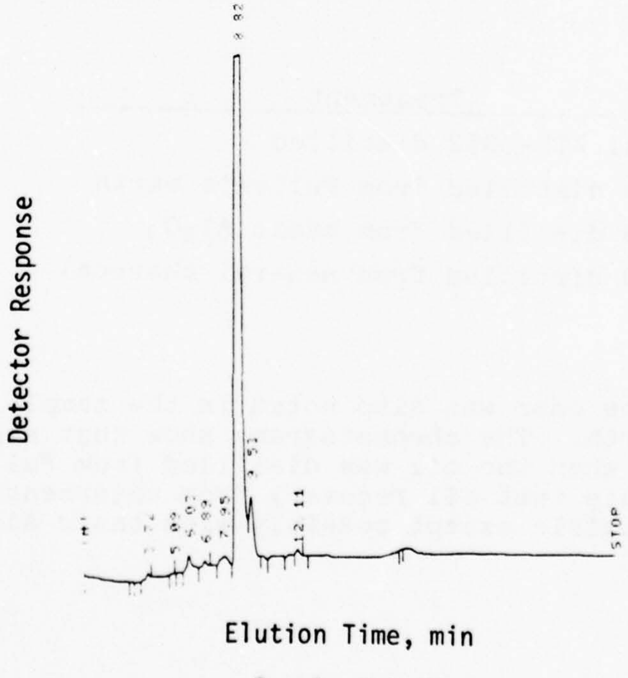
ACID NUMBERS OF OIL DISTILLED FROM ADSORBENTS

Sample Number	Treatment	Total Acid No.
200059	Initial ATL-5052 distilled	0.56
200060	200059 distilled from Fuller's earth	1.73
200061	200059 distilled from basic Al_2O_3	0.59
200062	200059 distilled from neutral charcoal	1.35

A strong acid type odor was also noted in the sample distilled from Fuller's earth. The chromatograms show that significant changes occurred when the oil was distilled from Fuller's earth. These data indicate that oil recovery from adsorbents by distillation is not feasible except possibly with basic Al_2O_3.

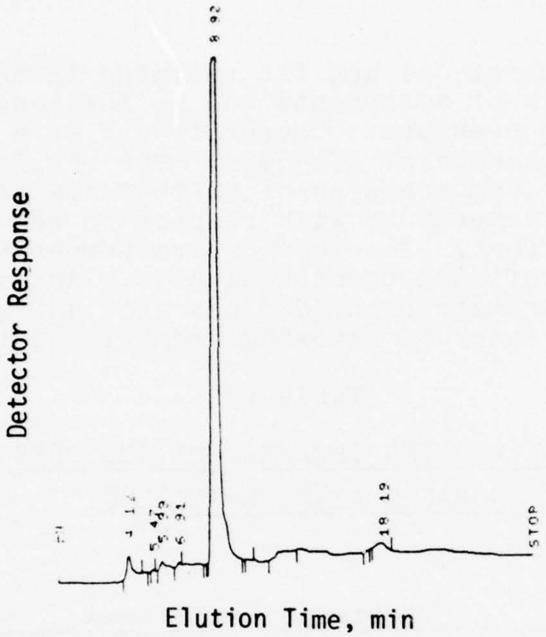


Sample 200060

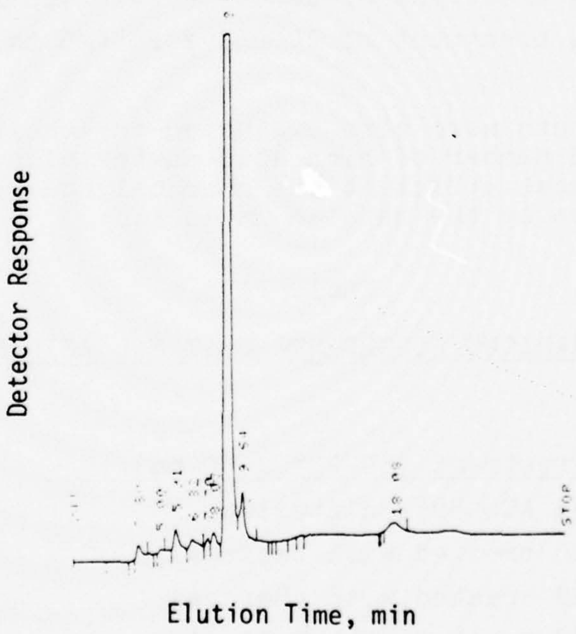


Sample 200061

Figure 27. High Pressure Liquid Chromatograms of Oil Samples



Sample 200062



Sample 200059

Figure 28. High Pressure Liquid Chromatograms of Oil Samples

Studies in the natural oil and fat refining industry have shown that the efficiency of adsorbents can be influenced by changes in temperature and pressure. These effects were studied using basic Al_2O_3 and a sample of ATL-5052. The results shown in Table 13 show that temperatures of 50-70°C are significantly better than room temperature with respect to removal of acids. Pressure has no effect. The response to temperature is similar to that found in refining of natural oils. Analysis by high pressure liquid chromatography did not show any effect of temperature on the efficiency of removing aromatic additives.

Table 13

EFFECT OF VARYING TEMPERATURE AND PRESSURE ON BASIC Al_2O_3 EFFICIENCY

Sample Number	Treatment Conditions	Total Acid No.
200059	Initial ATL-5052 distilled	0.56
200063P	Al_2O_3 treatment of 200059 @ 50-70°C/760 mm	0.04
200072C	Al_2O_3 treatment of 200059 @ 50-70°C/5 mm	0.03
200072A	Al_2O_3 treatment of 200059 @ 20°C/760 mm	0.13
200072B	Al_2O_3 treatment of 200059 @ 20°C/5 mm	0.15

All three adsorbents were also evaluated for their efficiency in reducing the acid number of high acid number oils. As expected basic Al_2O_3 was most efficient but charcoal and Fuller's earth also work as shown by the data in Table 14.

Table 14

EFFECT OF VARIOUS ADSORBENTS ON TOTAL ACID NUMBERS

Sample Number	Treatment (50-70°C/760 mm)	Total Acid No.
200059	Topped ATL-5052 distilled	0.56
200063P	200059 treated with basic Al_2O_3	0.04
200063C	200059 treated with charcoal	0.13
200063F	200059 treated with Fuller's earth	0.14

Some limited work was done on use of adsorbent columns for treatment of the oil. Since use of adsorbents in columns is a more desirable method for large scale treatments, the relative effectiveness of the batch and column methods were compared. The viscous oil passed through columns very slowly and a high percentage (15-20%) was retained on the column. Dilution of the oil with hexane allowed a sufficiently rapid flow rate in the column and only a very low percentage of oil was retained on the column (<2%). Evaluation by TLC did not show any significant differences in the two techniques. The large retention of oil on the column and low flow rate are distinct disadvantages of the column method.

The feasibility of doing adsorbent treatments in heated columns using long contact times was also evaluated. Previously we had evaluated adsorbent columns at room temperature and found batch treatment to be better overall. Used oils were passed slowly (15-20 minutes) through columns of basic Al_2O_3 and Fuller's earth held at 60-70°C. All additives came through very quickly on the basic Al_2O_3 column indicating little utility of this technique for Al_2O_3. The use of Fuller's earth was considerably better with the more polar additives/degradation products (as indicated by their location on TLC plates) being held back for a considerable length of time. This indicates the possibility that Fuller's earth could be used in a heated column method particularly after distillation.

The analysis of various oil samples by TLC indicated that some additives are less polar than the base stock and some considerably more polar. Those additives with polarities similar to the base stock appear to be effectively removed by charcoal. These polarity differences suggested that it might be possible to pretreat an oil sample with charcoal to remove selected additives and then use a second adsorbent (i.e., Al_2O_3) in a column chromatographic type process and selectively elude the less polar additives prior to elution of the base stock. This technique was given a very limited evaluation. Unfortunately the base stock and the less polar additives eluded together. A technique based on these principals could probably be developed but based on the limited data obtained it would probably be quite difficult to make it general enough to be applicable to any possible mixture of used oil mixtures that could potentially be obtained.

It is sometimes possible to mix adsorbents and thereby reduce the number of operations needed to treat a material with more than one adsorbent. This was attempted with the three types of adsorbents used in this program. Three ATL-5051 oil samples were treated with a mixture of basic Al_2O_3, Fuller's earth and charcoal and the resultant reclaimed base stocks compared with those obtained from treatment with individual adsorbents. Evaluation by TLC indicated more complete removal of materials by the multistep process. Two materials effectively removed by the multistep process were still present in the samples treated with the adsorbent mixture.

2.2.2 Oxidation

Oxidation of impurities in natural oils and fats is a useful technique for conversion of these materials to products that are readily removed. The structures of the additives in MIL-L-7808G oils suggested that many of them should be readily oxidized with strong oxidizing agents of the type used in oil and fat refining. It was suspected that their degradation products would also be easily oxidized. Also the potential degradation products from either hydrolysis or pyrolysis of the esters (i.e. alcohols and olefins) should be easily oxidized to products (acids) that could be readily removed.

Four chemical oxidizing agents were chosen for study. These were: sodium dichromate, potassium permanganate, calcium hypochlorite and hydrogen peroxide. The procedures used were those recommended by Anderson (Ref. 13). The oils were mixed with dilute aqueous, acidic solutions of the oxidizing agent and heated at about 60°C until oxidizing agent was no longer consumed. The excess oxidizing agent was destroyed and the oil separated, washed and dried. The four oxidation systems are directly compared in Table 15.

Table 15

EFFECT OF OXIDANTS ON ADDITIVES PRESENT IN ATL-5051

		Relative TLC Spot Intensity of Additives						Total Detectable
Sample No.	Oxidant	DODPA[1]	PANA[2]	TCP[3]	Quinizarin	Old Unknowns[4]	New Unknowns[5]	Materials Remaining
	none	strong	strong	medium	strong	4	0	8
194777	$KMnO_4$	light	light	light	ND[6]	1	2	6
194772	$Na_2Cr_2O_7$	light	light	light	ND	3	3	9
194775	$Ca(ClO)_2$	light	light	ND	ND	3	2	7
194770	H_2O_2	strong	strong	light	ND	4	3	10

[1] 4,4'-Dioctyldiphenylamine

[2] N-Phenyl-α-naphthylamine

[3] Tricresylphosphate

[4] Numbers indicate number of unknown materials detected that are also present in untreated ATL-5051

[5] Numbers indicate number of unknown materials detected that are not present in untreated ATL-5051

[6] ND, not detected

The potassium permanganate and calcium hypochlorite systems appeared to offer the most promise in terms of the total number of materials removed, the number of oxidation by-products developed and ease of handling. It is interesting to note that $Ca(ClO)_2$ appeared to remove TCP whereas the other three oxidants did not.

Each of the oils from the above four treatments were subsequently treated with activated basic alumina at 60°C, an activated acid clay treatment at 60°C, and a charcoal treatment in that order in an attempt to further remove additives, degradation products and oxidation by-products. The data shown in Table 16 illustrates the total number of materials removed with each absorbent as determined by TLC using UV detection.

Table 16

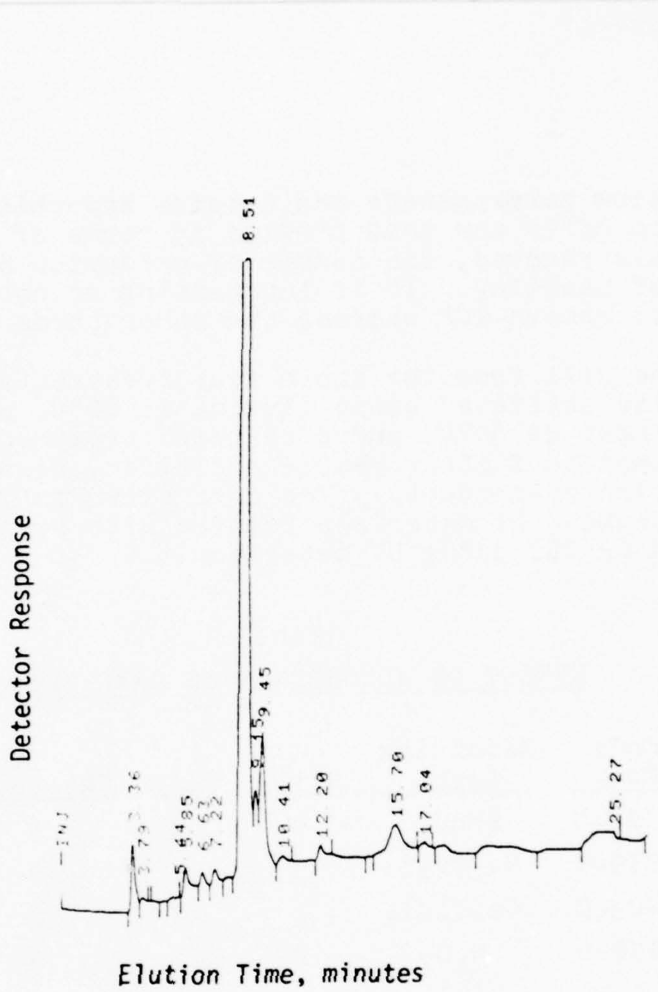
EFFECT OF ADSORBENTS ON OXIDIZED OILS[1]

Sample No.	Oxidizing Agent	Al_2O_3	Clay	Charcoal	Unknowns
197408-C	$KMnO_4$	0	1	0	5
194779-C	$Na_2Cr_2O_7$	3	1	0	6
197403-C	$Ca(ClO)_2$	1	1	0	5
194770-D	H_2O_2	2	1	0	7

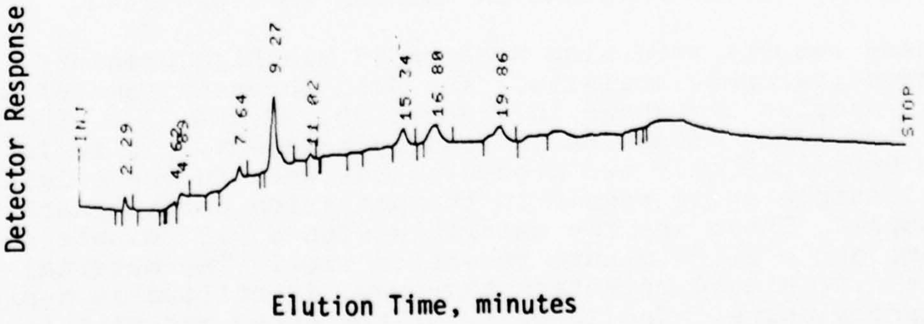
[1] Numbers refer to total number of UV detectable materials removed by the listed treatment

The $KMnO_4$ treatment followed by subsequent treatment with all three adsorbents was repeated using 2.5 times the heating time of the comparable treatment discussed above (3.75 hr vs 1.5 hr). Only a trace of PANA and an unknown were detected.

These results were also documented via high pressure liquid chromatographic analysis. The HPLC chromatograms of the various oil samples are shown in Figures 29, 30 and 31. The efficiency of the $KMnO_4$ oxidation is readily apparent. It is interesting to note that only two products that were in the original used oil sample still remain in the potassium permanganate treated sample. These are the materials with a 9.27 minute retention time and a 15.34 minute retention time. The material with the 9.27 minute retention time was identified as N-phenyl-α-naphthylamine. The identity of the other material is not known. N-phenyl-α-naphthylamine was present at 0.007% in the potassium permanganate treated sample. The remaining materials detected in this HPLC analysis must therefore be oxidation by-products of the materials that were in the original used oil sample.

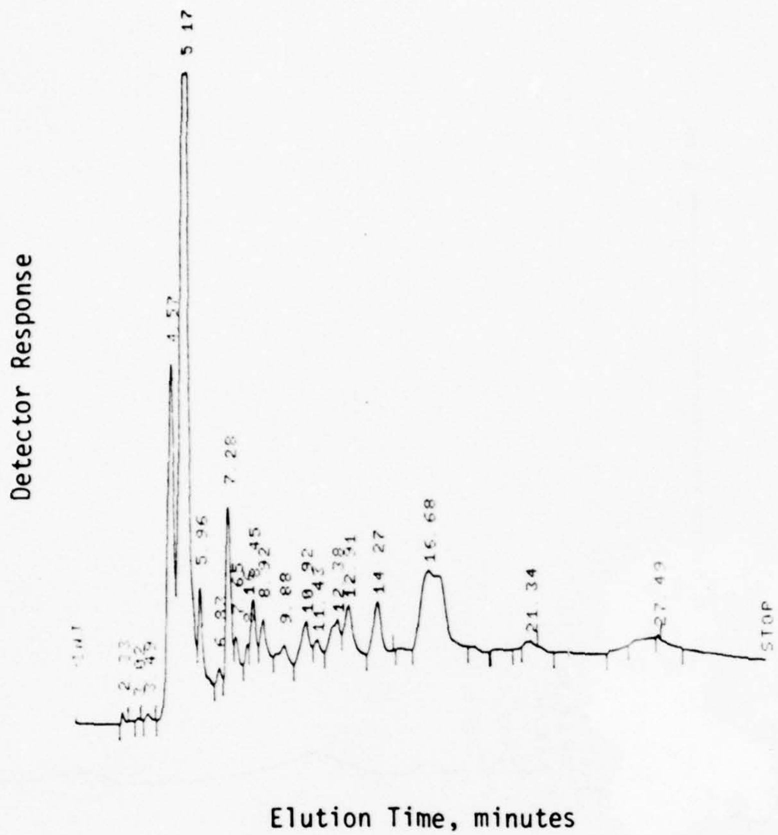


ATL-5051

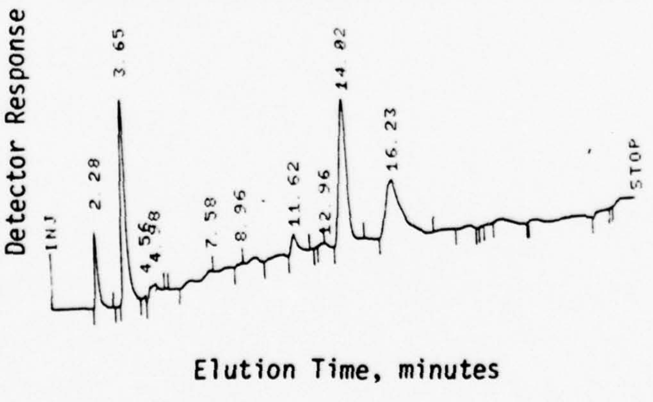


197408-C: ATL-5051 treated with $KMnO_4$, Al_2O_3, acid clay and charcoal

Figure 29. High Pressure Liquid Chromatograms of Oil Samples

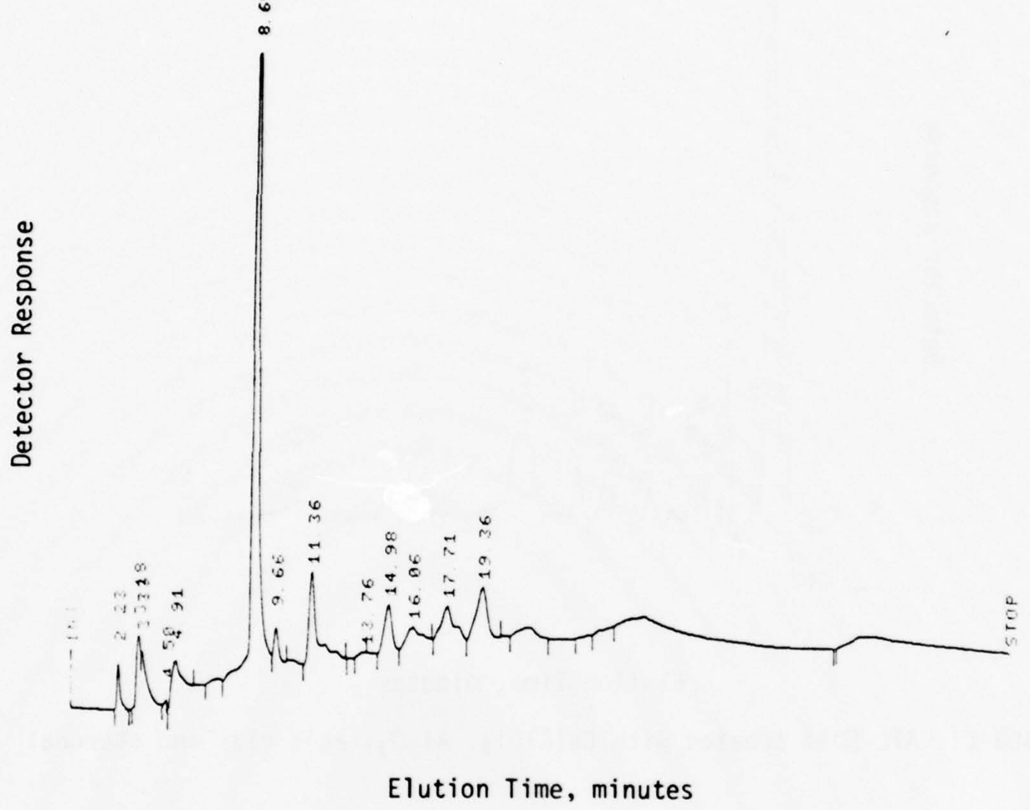


197403-C: ATL-5051 treated with $Ca(ClO)_2$, Al_2O_3, acid clay and charcoal



194779-C: ATL-5051 treated with $Na_2Cr_2O_7$, Al_2O_3, acid clay and charcoal

Figure 30. High Pressure Liquid Chromatograms of Oil Samples



194770-D: ATL-5051 treated with H_2O_2, Al_2O_3, acid clay and charcoal

Figure 31. High Pressure Liquid Chromatogram of Oil Samples

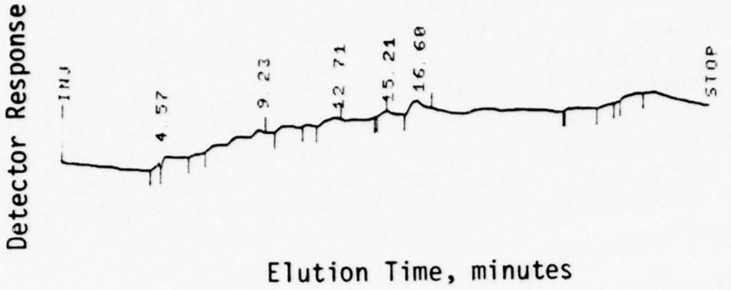
Further purification of the reclaimed ATL-5051 was accomplished by distillation through a 4-ft Vigreaux column. Most of the contaminants remained in the pot or came over in the very early fractions. The HPLC chromatograms of two of the middle fractions are shown in Figure 32. Comparison of these chromatograms with the initial reclaimed oil shown in Figure 29 as sample 197408-C shows some improvement in that fewer peaks are present and that the N-phenyl-α-naphthylamine content has dropped to between 0.001 and 0.003% whereas it was 0.007% in the oil after permanganate and adsorbent treatment. TLC analysis of these fractions showed that the major component detectable by TLC had been removed by distillation.

Potassium permanganate was the first oxidant studied prior to the studies discussed above. At that time the oxidation was done after the absorbent treatments. The samples obtained were analyzed via an HPLC method. The results tabulated in Table 17 with known materials identified at the various elution times, are normalized to reflect the amount of each material removed relative to the amount originally present in ATL-5051. The products introduced by the various treatments (as evidenced by appearance of new peaks or a significant increase in the relative value of a peak) were all present in very low amounts. HPLC chromatograms of these samples are presented in Figures 33 thru 35.

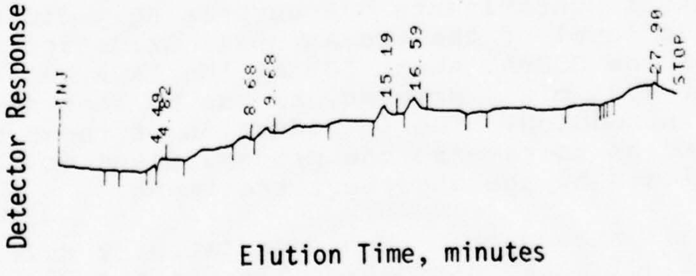
These results show the benefits of the oxidation treatment. Treatment with basic alumina removed *meta*- and *para*-TCP and the cresols but the majority of the other detectable products remained. A second treatment with Al_2O_3 (sample 194750-3) removed a considerable amount of *para*-TCP but little else. An acid clay partially removed some other contaminants but surprisingly did not significantly alter the level of the two amines. Oxidation with $KMnO_4$ removed most of the DODPA, about 50% of the PANA and all the material eluding at 4.95 min. However, as can be seen several by-products were introduced. The introduction of these by-products is what prompted us to reverse the procedure and do the oxidation first followed by the absorbent treatment.

The above studies showed that $KMnO_4$ consistently gave a more complete removal of materials detectable via the TLC technique than did $Ca(ClO)_2$. Treatment of ATL-5051 with $KMnO_4$ oxidation followed by adsorption with basic alumina, an acid clay and charcoal gave a product that exhibited only one spot on TLC analysis (UV detection). This single spot (R_f 3.9) was not present in the original ATL-5051 nor did it correspond to any known additives. It apparently was an oxidation product.

A variety of attempts were made to remove this remaining product. The exact structure of the product was not known but it appeared likely that it would contain an active hydrogen since it appeared to be an oxidation product. To check this assumption the partially refined oil was reacted with phenyl isocyanate expecting that



197410-F: Sixth fraction from distillation of 197408-C



197410-I: Ninth fraction from distillation of 197408-C

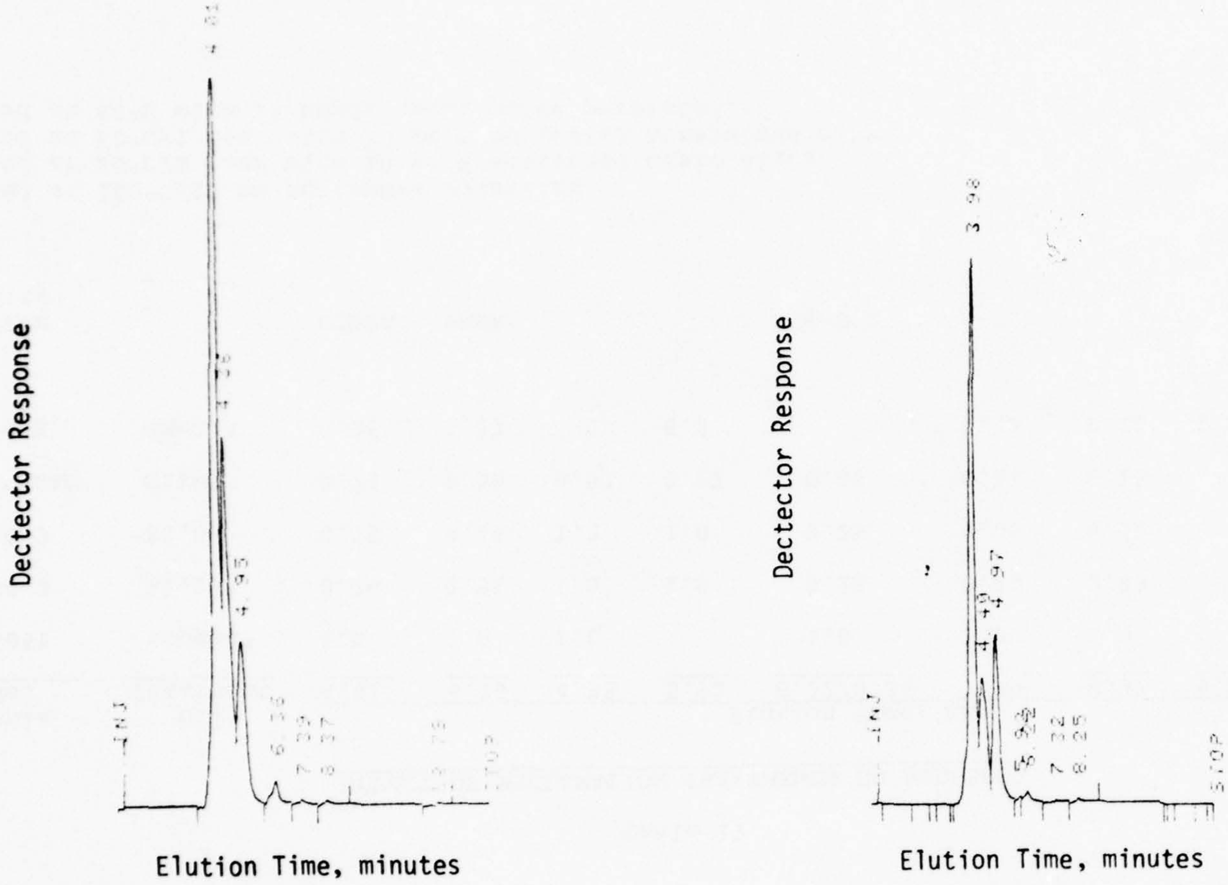
Figure 32. High Pressure Liquid Chromatograms of Oil Samples

Table 17

EFFECT OF RECLAMATION TREATMENTS ON ATL-5051

Sample No.	Oil Treatment	Elution Time, min								
		4.01	4.36	4.95	5.92	6.22/6.36	7.39	8.37	9.82	12.79
ATL-5051	topped[1]	1.0	1.0	1.0		1.0	1.0	1.0		1.0
194750-2	Al_2O_3[2]	0.76	0.51	1.0	1.0	0.25	0.44	0.83		0
194750-3	Al_2O_3	0.75	0.49	1.0	1.0	0.25	0.05	0.52		0
194750-SAC	Clay[3]	0.79	0.50	0.87	0.97	0.06	0.21	0.13		0
194750-K	$KMnO_4$[4]	0.06	0.27	0	6.2		0.32	0.10	1.0	0.02
Additive Identity		DODPA	PANA			*m*-TCP	*p*-TCP			*m,p*-cresol

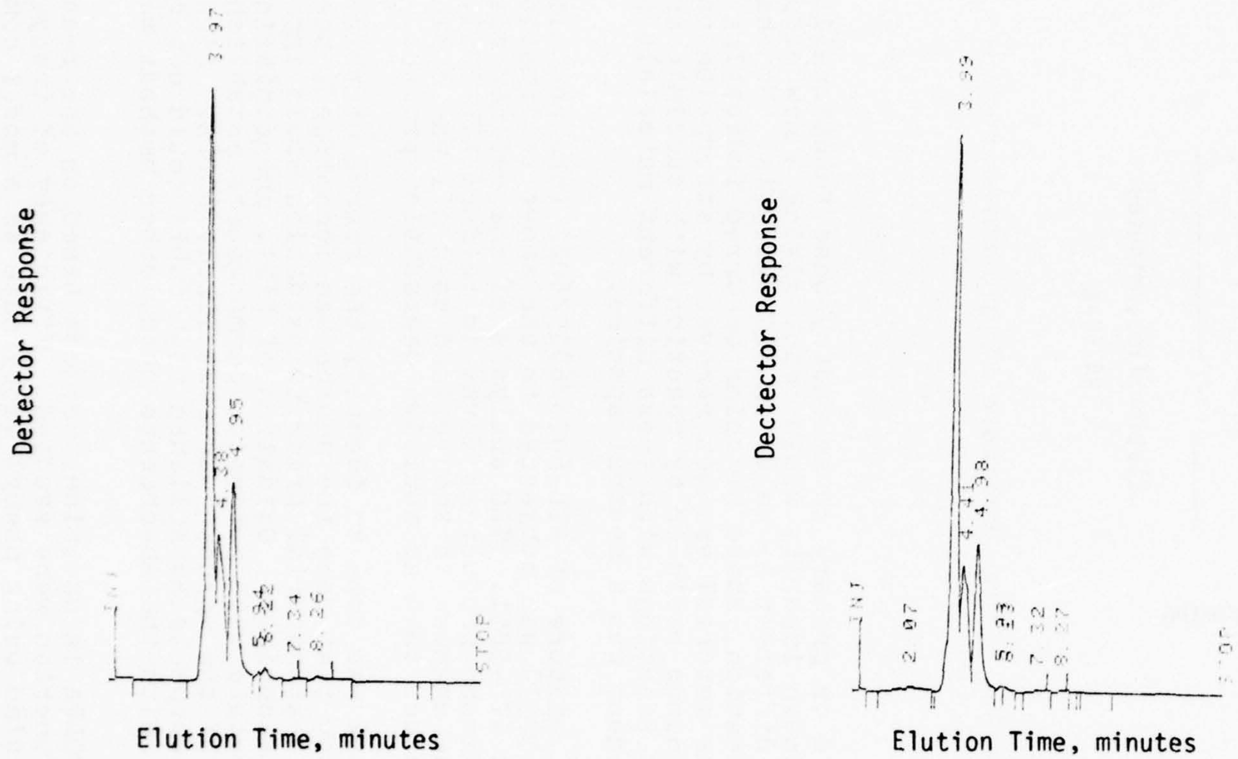
[1] Heated at 150°C/10 mm to remove volatiles
[2] Heated at 60°C/1 hour with 10 wt % activated basic Al_2O_3
[3] Heated at 60°C/1 hour with 10 wt % activated Attapulgus clay
[4] Heated at 60°C with 1% $KMnO_4$ until color persisted.



ATL-5051

194750-2

Figure 33. High Pressure Liquid Chromatogram of Oil Samples



194750-3

194750-SAC

Figure 34. High Pressure Liquid Chromatogram of Oil Samples

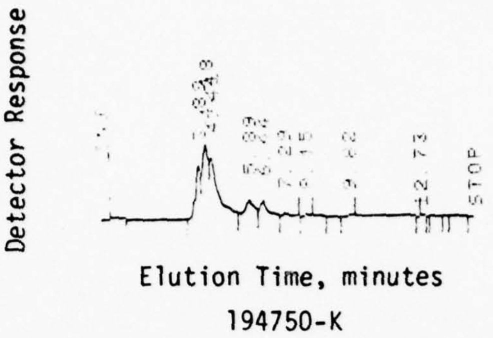


Figure 35. High Pressure Liquid Chromatogram of Oil Samples

any acid or primary or secondary base functionality present in the unknown impurity would react giving a new compound and therefore a different R_f value on TLC analysis. No change in the TLC spot location, shape or color occurred indicating no reaction. Also the material was not removed by adsorption on a strong acid ion exchange resin or by reaction with succinic anhydride. The lack of reactions with these different materials suggested that the product was a neutral species.

A 7/2/1 mixture of ATL-6026/6025/6022 (the postulated composition of ATL-5051) was subjected to the above reclamation procedure used on ATL-5051. TLC analysis of the refined mixture gave the same unknown product as found in refined ATL-5051. This indicates that the unknown in the refined used oil was coming from an additive rather than an additive degradation product.

Some work was done to identify the source of this material, reasoning that once the source was identified, then work on removing that material prior to oxidation would improve our purification technique. Oxidation of PANA, phenothiazine and DODPA in amyl acetate with potassium permanganate established that the source of the unknown was most likely DODPA. Since other work with absorbents established that DODPA could not be removed completely with the absorbents used, other methods were investigated.

Since DODPA is an amine, methods based on the reaction of the amine function were studied. Efficiency of isocyanate reaction was studied using phenyl isocyanate as a model compound. Reaction of DODPA and phenyl isocyanate in amyl acetate did not completely remove DODPA even with addition of a catalyst, use of heat, and/or long reaction times. We, therefore, decided to discontinue work on attempts to remove DODPA prior to oxidation until it had been established whether the reclaimed oil could pass qualification tests without removal of the unknown by-product from DODPA.

At the same time we were studying the reaction of DODPA with phenyl isocyanate, we also looked at reaction of phenyl isocyanate with other potential amine additives present in the oils to see what effect if any an isocyanate treatment would have on their removal. Benzotriazole and N-phenyl-α-naphthlamine and phenothiazine were reacted with phenyl isocyanate in amyl acetate. In each case, some reaction was indicated but removal was not complete.

Since $KMnO_4$ oxidation removed the aromatic additives so efficiently an attempt was made to improve its use. The oxidations discussed above using water soluble oxidizing agents required that the oxidation occur between reactants in two different phases, i.e. oil and water. Use of quaternary salts are known to solubilize inorganic anions in an organic phase (effect phase transfer) and potassium permanganate oxidations using this technique are known (Ref. 14). When this technique was applied to the used oil using potassium permanganate and tributylbenzyl ammonium chloride (phase transfer agent) the oxidation occurred as expected but significant emulsion problems occurred during work up. The emulsion problems negate any other potential benefits that could be derived from this technique.

The effect of distillation and oxidation on some of the reclaimed base stocks was studied. A comparison of the gas chromatograms of a distilled oil (sample 200033) and ATL-5052 (Figure 36 shows a decrease in amount of components eluding beyond 28 minutes indicating removal of higher boiling components. Subsequent oxidation and treatment with adsorbents results in disappearance of materials eluding at 6.7, 14.1 and 29.4 minutes as can be seen by comparing the chromatograms of samples 200033 and oxidized 200033 (sample 200038). The materials eluding at 6.7 and 29.4 minutes have been identified as phenyl α-naphthylamine and dioctyldiphenylamine respectively. The identity of the other product is not known. Distillation of 200038 again removed only the high boiling materials as shown in the chromatogram for sample 200040 (Figure 37).

High pressure liquid chromatographic analysis of samples 200040 and 200041, (oxidized and distilled ATL-5052) demonstrate the effectiveness of the reclamation process for removal of aromatic non-base stock materials. These chromatograms are shown in Figure 38.

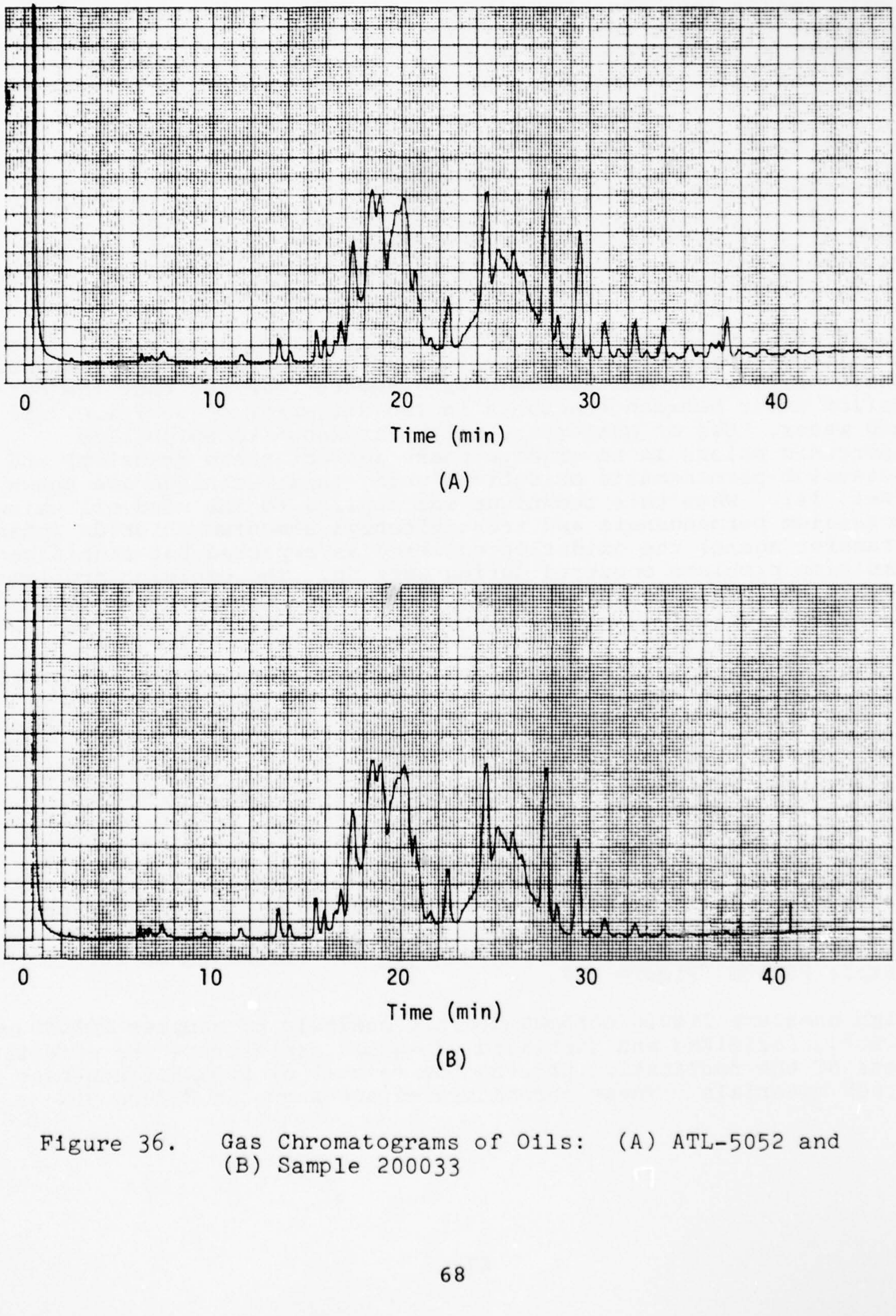


Figure 36. Gas Chromatograms of Oils: (A) ATL-5052 and (B) Sample 200033

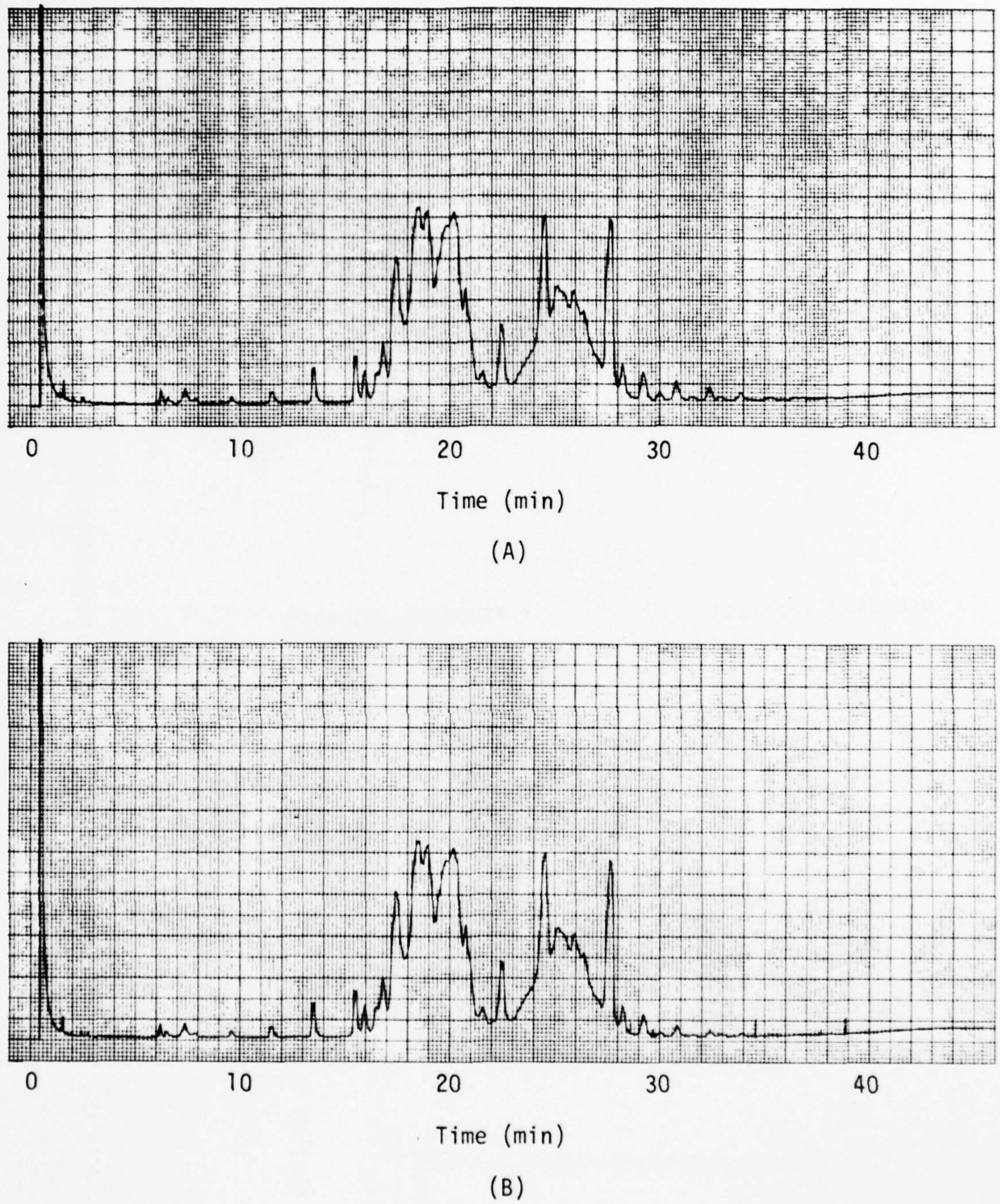
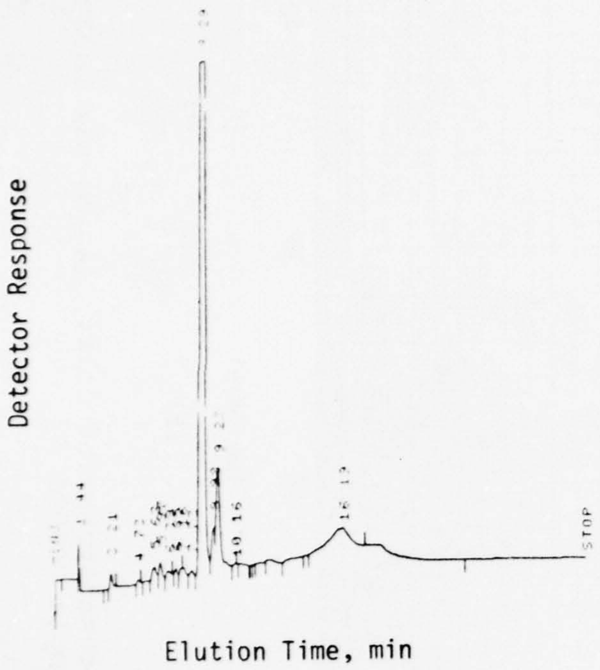
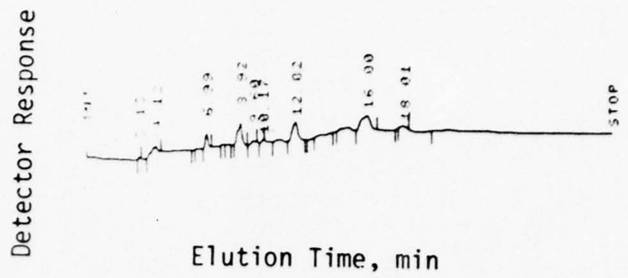


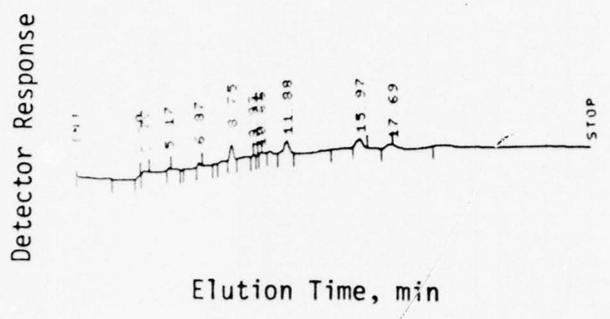
Figure 37. Gas Chromatograms of Oils: (A) Sample 200038 and (B) Sample 200040



ATL-5052



Sample 200041



Sample 200040

Figure 38. High Pressure Liquid Chromatograms of Oil Samples

It was shown earlier that some of the new oils, i.e. ATL-6023, 6025 and 6026, contain sulfur and chlorine containing additives that are not readily detectable by GC or HPLC techniques. Since these oils are components of ATL-5051 and 5052 it was of interest to determine the affect of some of the reclamation techniques on the presence of these additives. The semiquantitative data shown in Table 18 were obtained by an X-ray fluorescence analytical technique. These data are normalized with respect to the level of sulfur and chlorine in the untreated used oils to illustrate depletion. The higher sulfur levels in two of the samples reflect the semiquantitative nature of the technique.

The chlorine containing material is readily removed with adsorbents but the sulfur containing material is insensitive to adsorbent treatment. Oxidation appears to remove sulfur compounds partially from ATL-5051 (sample 197441) and not at all from ATL-5052 (sample 197472). This may indicate at least two types of sulfur compounds are present in ATL-5051.

Table 18

S AND Cl CONTENT OF RECLAIMED BASE STOCKS

		Reclamation Techniques Used				Relative Level of	
Sample No.	Initial Used Oil	$KMnO_4$	Al_2O_3	Fuller's Earth	Charcoal	S	Cl
197490	ATL-5051	--	--	--	--	1.00	1.00
197445	ATL-5051	--	yes	yes	yes	1.17	0
197441	ATL-5051	yes	yes	yes	yes	0.45	0
197492	ATL-5052	--	--	--	--	1.00	1.00
197467	ATL-5052	--	yes	yes	yes	1.22	0
197472	ATL-5052	yes	yes	yes	yes	1.00	0

2.2.3 Treatment with Sulfuric Acid

Another purification technique used in the natural oil and fat refining industry involves treatment of the oil with one to two percent concentrated sulfuric acid followed by washing and neutralization of any acid remaining in the oil with lime. The technique is referred to as degumming in natural oil and fat refining.

Preliminary evaluation of the utility of using this technique for removal of non-base stock materials was done using high pressure liquid chromatographic (HPLC) analysis to follow the course of the treatments. The following two processes were compared:

(1) ATL-5052 treated with H_2SO_4, basic Al_2O_3, Fuller's earth and then charcoal followed by distillation and retreatment with the adsorbents (Sample series 203410); (2) ATL-5052 treated with the same three adsorbents as above, distilled and retreated with the absorbents (Sample series 203406). Figures 39 and 40 show the chromatograms from each step of the above two treatments. The single large peak seen in these chromatograms is due to the presence of dioctyldiphenylamine (DODPA). It will be noted that these chromatograms differ from those reported earlier in this report. The data acquisition system for this instrument had been changed. Also these chromatograms were obtained at a lower sensitivity and consequently do not show as many materials as previously reported ones.

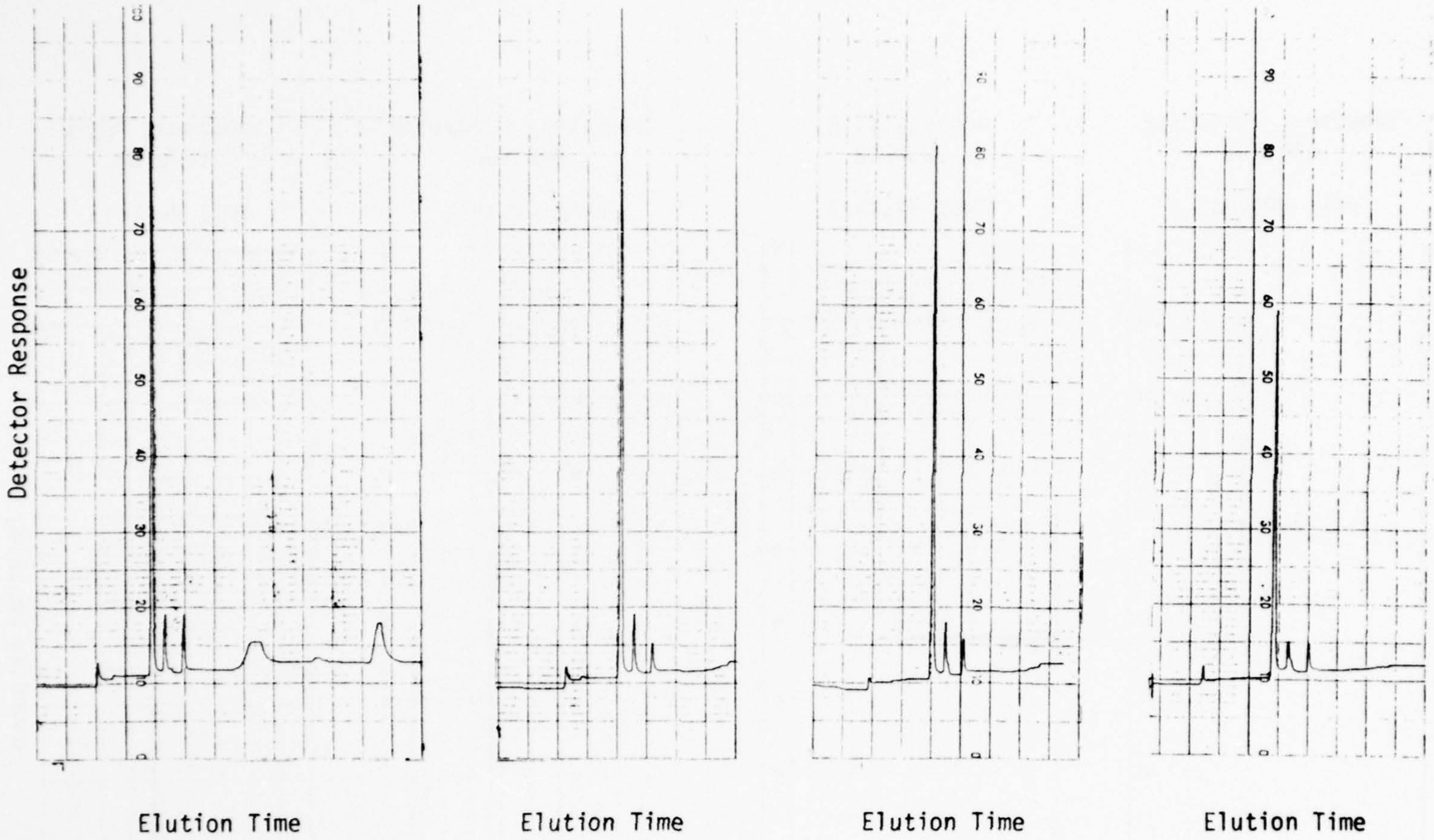
Examination of the chromatograms in Figure 39 show a continuous decrease in the levels of the three detected materials but not total removal of any. Inclusion of the H_2SO_4 treatment leads to total disappearance of the two smaller peaks after the first adosrbent treatment as can be seen in Figure 40. It appears that H_2SO_4 treatment converts these materials into products that respond to subsequent adsorbent treatment. Also note that in each series distillation lowers the DODPA content. Quantification of the DODPA content in 203410C and 203406D showed the presence of 0.06% and 0.05% DODPA respectively.

Sulfuric acid levels were varied from one to ten volume percent to evaluate the effect of acid concentration on removal of TLC detectable aromatic materials in the used oils. A level of five volume percent appeared to be the maximum amount required. All six new oils were treated with six volume percent concentrated sulfuric acid. TLC analysis indicated partial removal of DODPA and PANA in those oils containing these additives.

It is not uncommon to find that various strengths of acid have a significant influence on its behavior in a media. Concentrated H_2SO_4 was compared with fuming H_2SO_4 (20% SO_3) and dilute H_2SO_4 (75%). Treatment of oil with fuming H_2SO_4 (20% SO_3) caused noticeable degradation of the oil. The occurrence of degradation was confirmed when distillation gave an appreciable forerun relative to an oil distilled without prior treatment with H_2SO_4. The characteristic strong odor of degraded ester was also noted in the forerun.

Use of 75% H_2SO_4 resulted in stable emulsions upon addition to the oil. This emulsion was broken by filtration through filter aid but the occurrence of a colorless aqueous layer suggested that the treatment was not effective.

An evaluation of oxidation in combination with H_2SO_4 treatment as a reclamation technique to replace distillation was carried out. Used oil treated with concentrated H_2SO_4 followed by oxidation with hydrogen peroxide results in stable emulsions. The



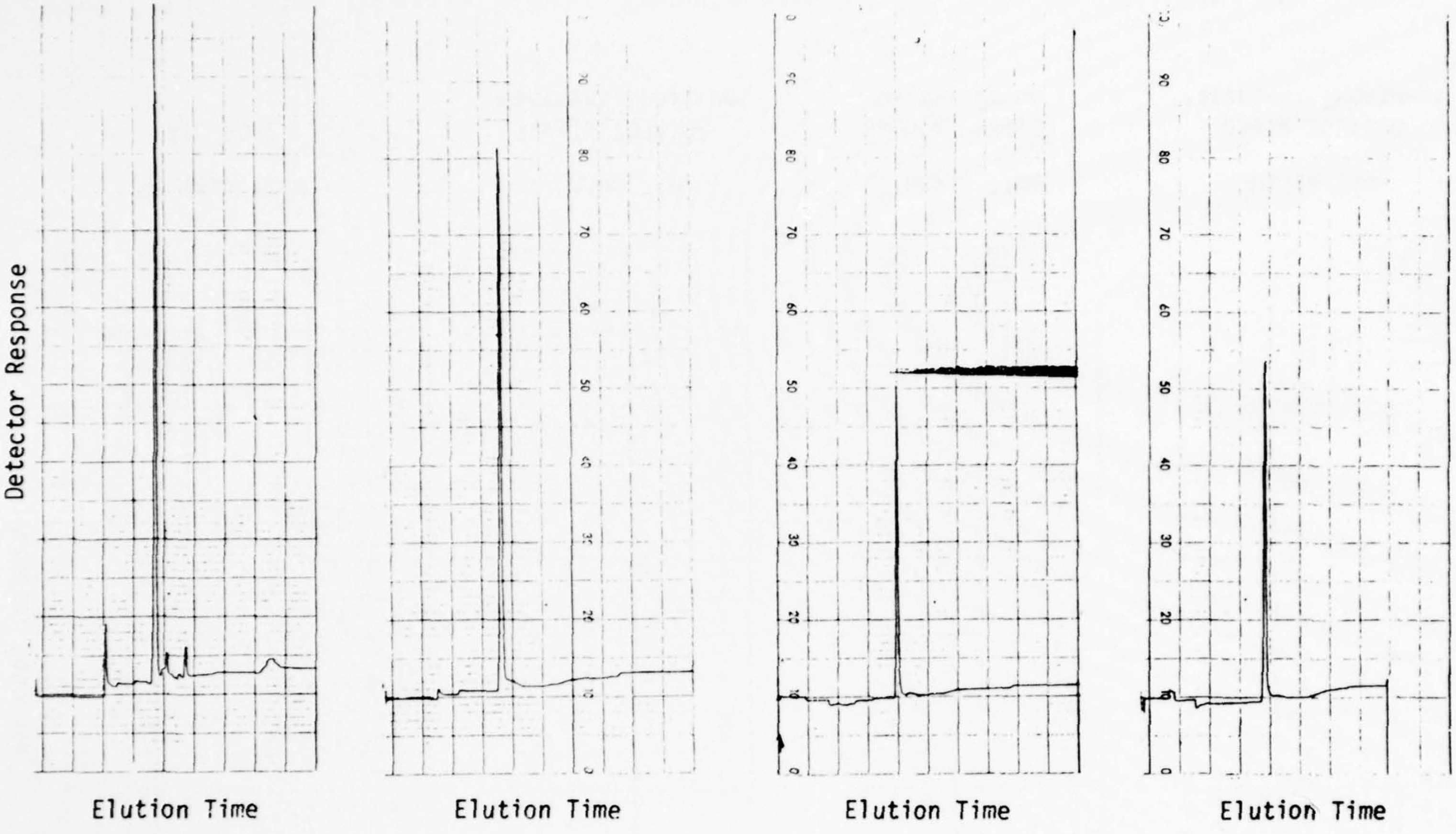
ATL-5052

Sample 203410A
Adsorbent Treatment

Sample 203410B
Distillation

Sample 203410C
Adsorbent Treatment

Figure 39. High Pressure Liquid Chromatograms of Oil Samples, ATL-5052 and 203410



203406A
H_2SO_4 Treatment

203406B
Adsorbent Treatment

203406C
Distillation

203406D
Adsorbent Treatment

Figure 40. High Pressure Liquid Chromatograms of Oil Samples, 203406

use of H_2SO_4 did not appear to effect the tendency for emulsion formation or significantly alter the stability of the emulsion. Therefore no further efforts utilizing an oxidation process appeared warrented.

2.2.4 Solvent Partitioning

Technology has been developed in the petroleum industry to separate petroleum fractions by solvent partitioning. The TLC analysis of new and used oils showed that a large number of additives and additive degradation products are less polar than the base stock. Those that are not can be removed with adsorbents. These data suggested that it may be possible to partition the mixture between a nonpolar solvent such as hexane and a more polar immiscible solvent. The base stock should have more affinity for the polar solvent and the less polar additives more affinity for the nonpolar solvent.

This technique was evaluated using hexane as the nonpolar phase and methanol/water and methyl ethyl ketone/water as the polar phase. Several experiments were carried out without any indication of significant separation of base stock and additives. Work in this area was discontinued when it became obvious that the techniques discussed elsewhere in this report had much more promise of success.

2.2.5 Distillation

The feasibility of using distillation of some type as a part of a reclamation process was evaluated by first carrying out a fractional distillation at low pressure to determine the ultimate efficiency in separation of the various components of a used oil. Distillation was carried out at 25° to 200°C at 0.04-0.06 mm. The three forerun fractions obtained were water ($\sim$0.2%), toluene ($\sim$0.6%), and a fraction that contained a mixture of ester, phenolic materials and toluene ($\sim$0.1%). The main components were obtained as ten fractions. TLC analysis showed that additives distilled over with each main fraction although the relative proportions and types changed as the distillation progressed. TCP appeared in every fraction. This was not surprising since TCP has a b.p. of 265°C at 10 mm, a value comparable to that of the base stock. These data show that some treatment of the oil along with distillation would be necessary to insure separation of additives from the base stock.

Steam distillation is known to be an effective technique for treatment of ester plasticizers to remove low levels of reactant residues. This stability of esters to steam distillation along with steam distillations known ability to remove amine and alcoholic products suggested it should be evaluated in this program as a possible method for removing additives and/or degradation products. Steam distillation at 100°C/100 mm resulted in only a trace of material being carried over in the distillate and TLC analysis did not indicate any changes in additive content of the oil. The distillate appeared to be an amine as determined by it's IR spectrum.

A sample of ATL-5051 (that had been topped to remove volatiles boiling up to 150°C/10 mm) was steam distilled at 170°C and 100 mm. Evaporation of the distillate left a thick oil whose IR spectrum suggested it contained an aliphatic ether and an aliphatic acid functionality. The odor also strongly suggested the presence of the acid. Further analysis of the distillate residue showed that an aliphatic acid, ether and alcohol were present. The total weight of distilled material was 0.2% suggesting ester degradation as the source of these materials. Some oil was also carried over during steam distillation. These data indicate that steam distillation is potentially harful to the oil and is of questionable value in a reclamation process which must be very general.

Based on the above preliminary distillation studies and the results of other attempts to remove polymerized base stock from the used oils (see section 2.2.6) it was decided that distillation would be the best approach for separation of usable base stock from polymerized base stock. Therefore, a study of the effect of distillation pressure on base stock properties was carried out to determine what pressure would be required to prevent excessive degradation during distillation. The pressures studied had to be obtainable in plant operations.

Evaluation of the effect of distillation pressure on base stock degradation was done to establish the best conditions compatible with large scale operation. Table 19 contains the data obtained at four pressures. These data suggest that distillation pressure of 10 to 15 mm should be used. Pressures above 10 mm are readily obtainable in large scale operations but the distillation temperatures at pressures above 15 mm are difficult to attain. Excessive decomposition has not occurred during these distillations as shown by the acid numbers. Treatment with $Ca(OH)_2$ will readily lower acid numbers in this range to well below specification limits.

The total acid numbers on as received and distilled ATL-5051, 5052, 6100 and 6101 were compared to establish if level of oil stress influences stability during distillation. ATL-6100 and 6101 have been used for about 1800 and 1000 operation hours respectively. The histories of ATL-5051 and 5052 are unknown. The data shown in Table 20 show that the previous history of these oils has no effect on degradation during distillation, i.e. no degradation products are present in the oil to cause differences in base stock degradation levels during distillation.

Table 19

EFFECT OF DISTILLATION CONDITIONS ON BASE STOCK PROPERTIES[1]

Sample No.	Pressure mm	Distillation Temperature, °C Pot	Distillation Temperature, °C Vapor	Acid No.	Volume % Residue	-65°F Viscosity, cs
undistilled	--	--	--	0.45	--	13,500
200087	1.3	211-243	195-239	0.45	3.2	--
203490	7	238-310	237-285	0.50	2.0	12,000
203489	15	250-300	250-300	0.68	2.6	11,900
203491	23	256-314	251-299	0.66	2.3	12,000

[1] Topped and filtered ATL-5052 was used.

Table 20

TOTAL ACID NUMBERS FOR DISTILLED USED OILS

Sample No.	Used Oil	Total Acid Number Initial	Total Acid Number After Distillation
206527A	ATL-5051	0.43	0.64
203498B	ATL-5052	0.60	0.68
206525A	ATL-6100	1.47	1.45
206525B	ATL-6101	0.36	0.29

The effect of extent of distillation (% used oil distilled) on viscosity was determined to guide selection of a distillation cut off point. The data obtained are given in Table 21. The -65°F viscosity data for distilled ATL-5052 (Table 21, samples 206533 thru 206537) suggested that a maximum of 93% of this used oil should be distilled to obtain a reclaimed base stock that has a low enough -65°F viscosity to allow it to be reformulated without exceeding the specification limit. Work by others (Ref. 15) suggests that a base stock should not have a -65°F viscosity in excess of 11000 cs. Reformulation raises this viscosity to a value approaching the specification limit of 13000 cs. However, as will be shown later in this report, the reclaimed base stock should have a -65°F viscosity below 9500 cs to allow reformulation using the additive package developed in this program and still not exceed the 13,000 cs -65°F specification limit. Addition of 2 and 4% TCP increases the -65°F viscosity as shown in Figure 41.

A correlation of -65°F viscosity and maximum distillation vapor temperature was established utilizing nine distilled samples. The data, shown in Figure 42, strongly suggest that the distillation vapor temperature can be used as a guide for determining when to end a distillation and still obtain a high yield of base stock that can be reformulated without excessive use of virgin base stock for viscosity adjustment. This correlation can only be considered as a convenient guide since the large scale distillation (∿13 liter) of ATL-7069 and ATL-7071 under these conditions gave reclaimed base stocks having -65°F viscosities ranging from 9400 to 10,300 cs.

Distillation on a large scale is more conveniently done in steel vessels rather than glass-lined equipment. The compatibility of used oils with glass, 316 and 304 stainless steels were compared to evaluate the thermal stability of these oils in the presence of the most probable materials of construction for large scale vessels. These studies were done in two ways. First, oil samples were distilled at 15 mm until 3/4 of the oil had been distilled. The remainder of the oil was refluxed at the distillation temperature and pressure (252-264°C/14-15 mm) for 24 hours and then distillation completed. Acid numbers were determined on both fractions as an indication of degradation. The distillations were carried out in an all glass apparatus and in the presence of 304 and 316 stainless steel. The data obtained are given in Table 22.

Table 21

VISCOSITIES OF RECLAIMED BASE STOCKS AND OILS FROM ATL-5052

Sample No.	Distillation Pressure, mm	Maximum Distillation Vapor Temperature, °C	Distillation Residue, %	% TCP	Viscosity, cs -65°F	Viscosity, cs 100°F	Viscosity, cs 210°F
206533	15	308	3	--	12,000	11.7	3.07
206535	15	292	5	--	11,500	11.5	3.04
206536	14	290	7	--	11,000	11.5	3.03
206537	15	285	10	--	10,800	11.3	3.00
206533-A		308	3	2	13,100	11.7	3.05
206533-B		308	3	4	15,000	11.9	3.05
206536-A		290	7	2	12,400	11.5	3.04
206536-B		290	7	4	13,800	11.6	3.03

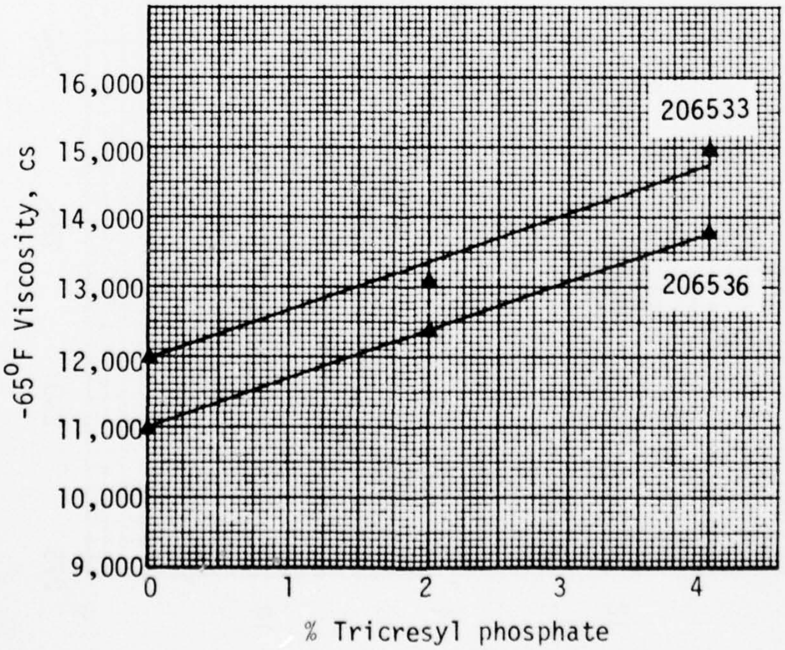


Figure 41. Effect of TCP Level on -65°F Viscosity

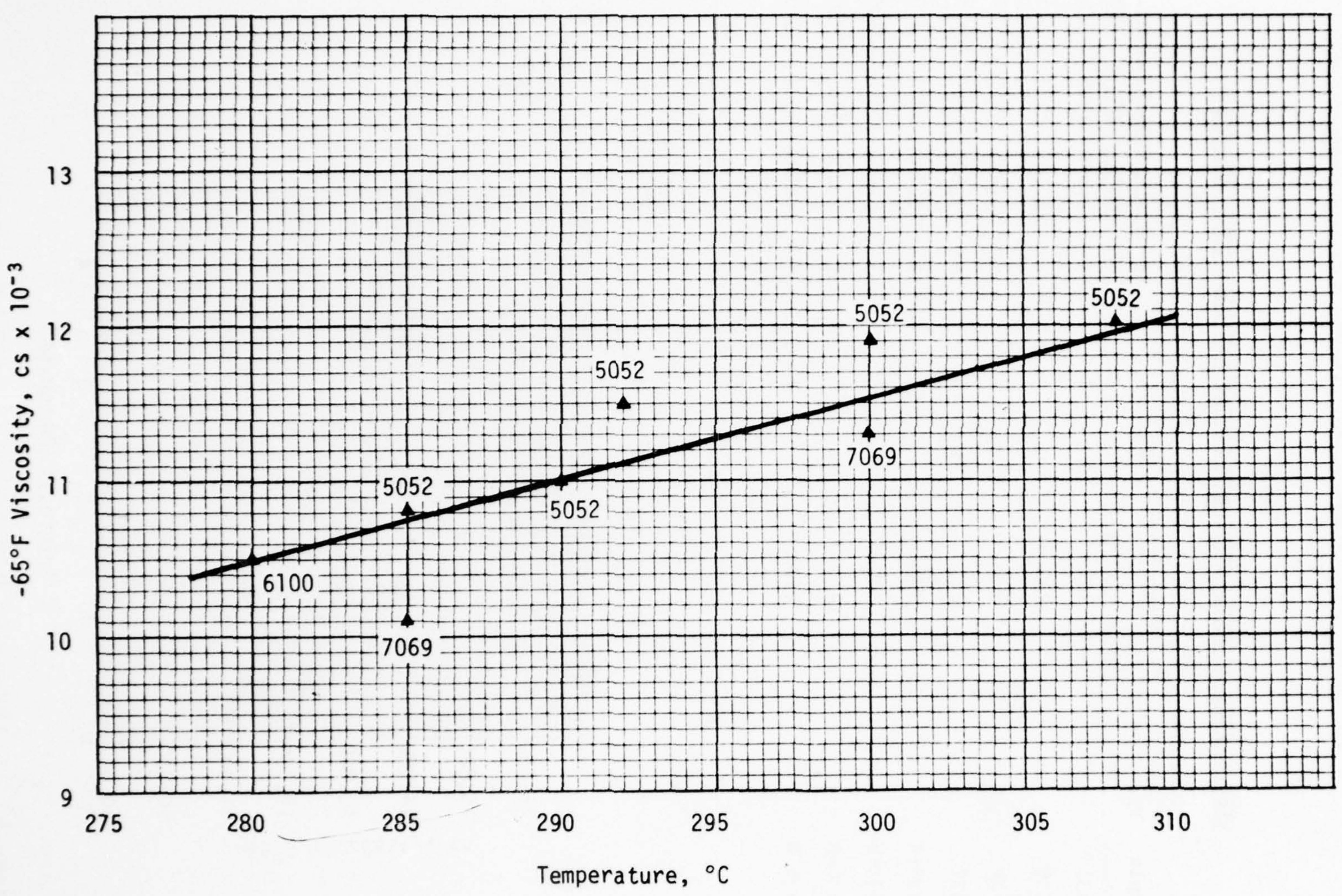


Figure 42. Effect of Maximum Distillation Vapor Temperature at 15 mm Hg on -65°F Viscosity (Numbers refer to initial used oil designation)

Table 22

STABILITY OF USED OIL TO POTENTIAL DISTILLATION CONDITIONS

Sample No.	Distillation Vessel	Reflux Temp °C	Reflux Pressure mm	Volume Distilled	Acid No.	Volatiles[1] %
ATL-5052	--	--	--	--	0.60	--
206511A	glass	--	--	initial 3/4	0.97	--
206511C		248-255	14	final 1/4	1.51	0.25
206513A	glass plus 304 stainless	--	--	initial 3/4	0.77	--
206513C		258-263	14	final 1/4	1.07	1.38
206515A	glass plus 316 stainless	--	--	initial 3/4	0.95	--
206515C		259-263	15	final 1/4	2.08	3.75

[1] Volatiles are those materials not condensed in the receiver but condensed in a dry ice trap.

These data indicate that the used oils are more thermally stable in glass than in the presence of either steel as evidenced by the amount of volatiles. The volatiles are assumed to be degradation products of the oil since their infrared spectra are very similar to the spectra of base stocks.

In a second experimental approach the entire sample of used oil was refluxed in the presence of glass, 316 and 304 stainless steel at about 250°C/14-15 mm for 24 hours and then distilled. Analysis of the volatiles generated during this period by infrared spectroscopy indicated a slight amount of decomposition. Acid numbers obtained on the distillates from these experiments are given below. No significant differences can be noted between the three materials of construction. Also the acid numbers are low enough so that treatment with $Ca(OH)_2$ will readily bring them below specification limits.

Sample No.	Reflux Vessel	Distillate Acid No.
206567	initial	0.71
206568-A	glass	2.02
206568-B	glass plus 304 stainless	1.89
206569	glass plus 316 stainless	2.10

The volatiles trapped in dry ice during refluxing in the presence of 316 stainless steel were analyzed by GC/mass spectrometry to determine their composition. The volume of the distillate represented less than 0.2% of the initial used oil. This analysis showed the volatile composition to be very roughly 62% ester, 32% of a mixture of olefins, 4.5% alcohols and less than 2% cyclopentanone. This indicates very little degradation on refluxing with the stainless steel. From these data and that obtained above it can be assumed that the used oils will be compatable with 316 and 304 stainless steels.

2.2.6 Precipitation

Differences in solubility can potentially be used for separation of base stock fractions of varying molecular weight. A brief study of this possibility was done using methanol as the solvent to precipitate the higher molecular weight fractions. Dilution of some used oils with methanol caused precipitation of a black material which was characterized by IR as an ester as shown in Figure 43 for the precipitate obtained from ATL-6100, the most highly stressed oil. ATL-6027 and 6030 also contained methanol insoluble fractions that precipitated after dilution of the oil with methanol. The other used oils and all six new oils became turbid when diluted but did not yield any precipitate. This turibity is most likely caused by some additive that is not methanol soluble.

To determine if methanol would be beneficial in the reclamation process for removal of polymerized ester, a sample of ATL-6100 was treated with adsorbents and then diluted to approximately 20% with methanol. There was a slight indication of settled material in the ATL-6100/ methanol sample. A distillation sample of ATL-6100 showed no evidence of precipitation when diluted with methanol indicating removal of the polymerized ester by distillation was more effective.

Comparison of the -65°F viscosities of ATL-6100 before and after dilution with methanol showed a decrease of about 9%, from 15,300 cs to 14,000 cs. Since distillation can be more efficiently controlled it is probably the better method for polymerized base stock removal. It may be possible to develop a process based on methanol/water mixtures to get a solvent system with the precise solubility parameter to separate base stock fractions.

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RECLAMATION OF SYNTHETIC TURBINE ENGINE OIL MIXTURES.(U)
APR 79 G GLASGOW, R J BRUNS F33615-76-C-2037
UNCLASSIFIED MRC-DA-780 AFAPL-TR-78-50 NL

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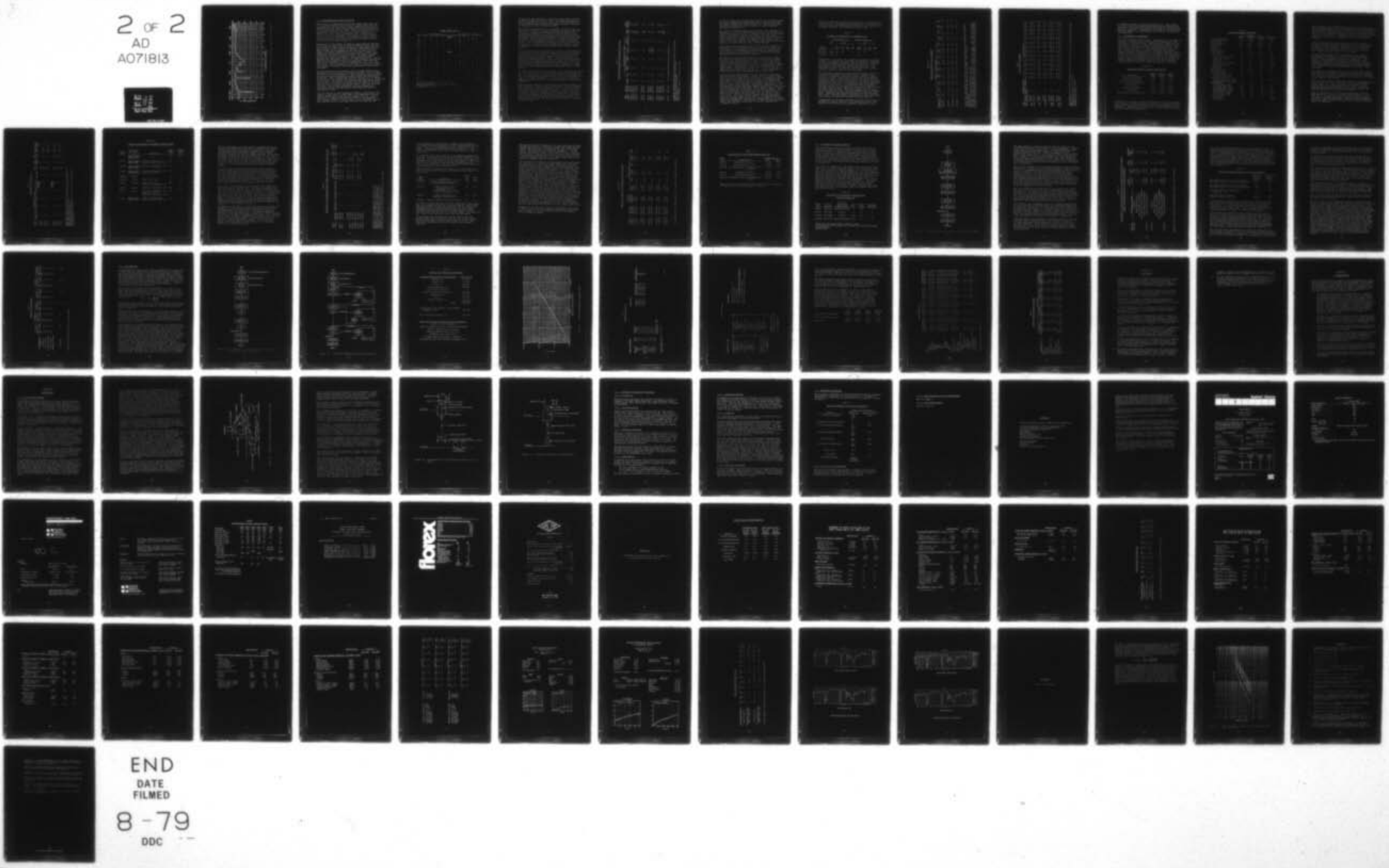

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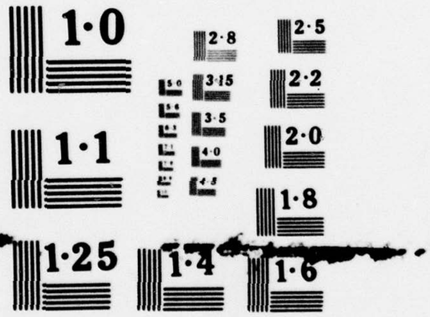
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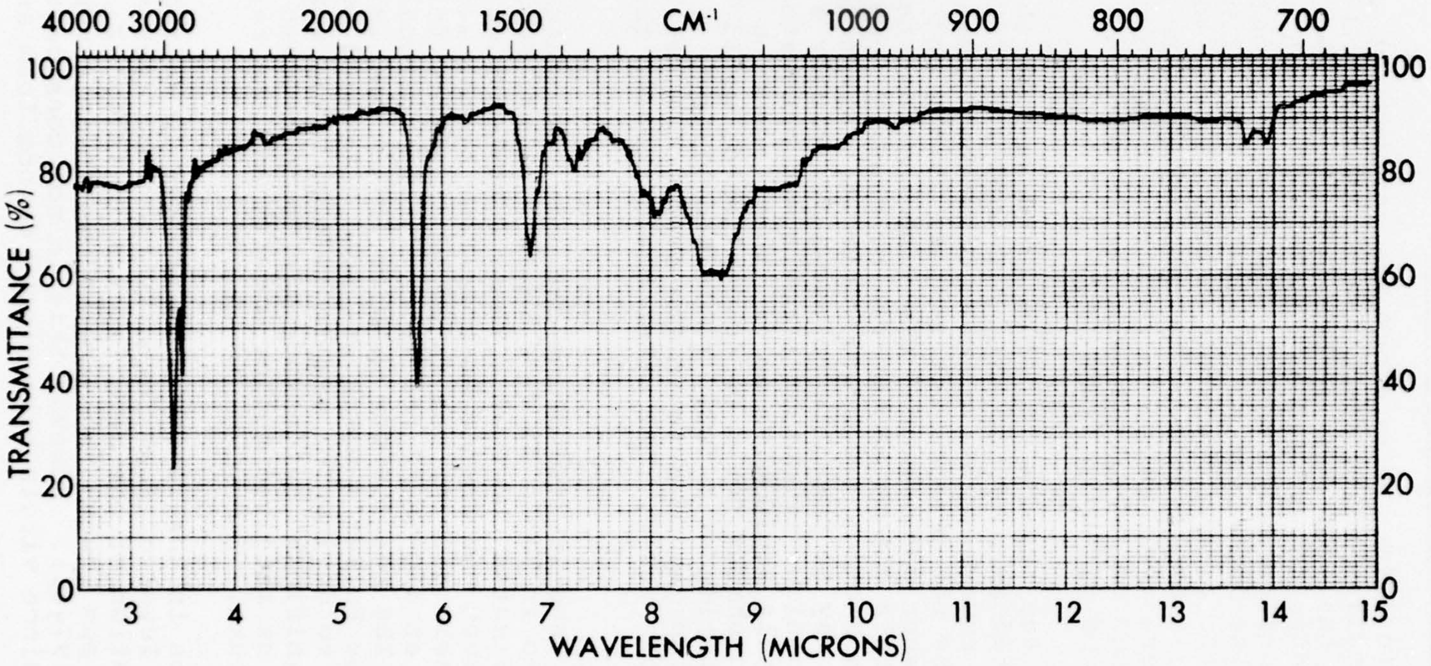

Figure 43. Infrared Spectrum of Methanol Insoluble Fraction from ATL-6100

2.3 RECLAIMED BASE STOCK EVALUATION

Evaluation of reclaimed base stock was carried out using some of the qualification tests specified by MIL-L-7808G with the exception that the foam test in MIL-L-7808G was replaced by a modified procedure identified as "Method 3213" and supplied by the contract monitor G. A. Beane. The most critical test was assumed to be the foam test so it was used extensively to follow the course of our reclamation work. A foam volume of 100 ml or less is acceptable. The results of these qualification tests were very useful in guiding the research effort. The data obtained on reclaimed base stocks derived from ATL-5051 and 5052 are given in Table 23.

Examination of the results in Table 23 shows that the addition of silicone antifoam agent to used ATL-5051 and 5052 that had been topped to remove volatiles gave oils that passed the foam test as shown by the results for samples 197490 and 197492. These results when considered along with the fact that acid numbers and metals contamination can be readily lowered with adsorbents (see Section 2.2.1 and Table 26) raises the possibility that it may be possible to use a relatively simple reclamation technique to obtain a reclaimed base stock. It is doubtful that this would give an oil that, assuming satisfactory additive replenishment could be accomplished, would have the same useful lifetime as a fully reclaimed oil but it may find utility as a stop gap measure in the event of a severe situation. This assumes, of course, that other qualification tests could be passed.

The adsorbents used in reclaiming the oils used determing the properties given in Table 23 were basic alumina, Fuller's earth and neutral activated charcoal. These adsorbents were activated by drying received adsorbents as specified by the manufactures literature. Basic alumina was dried at 450-500°C for 18 hours, Fuller's earth at 450-500°C for 18 hours and charcoal at 125°C/5 mm for 18 hours. The results for samples 197445 and 197470 differ only in that the Fuller's earth was acid activated by slurrying with HCl prior to drying for sample 197470. This was the only time that a significant difference was found between acid activiated and as received Fuller's earth and the result is considered a fluke.

Use of oxidation in the reclamation process is detrimental with respect to the level of foam found in the foam test as can be seen by examination of the data for sample 197435-2. Use of antifoam at 10 ppm lowers the foam volume to an acceptable level (sample 197441). However this is not considered a desirable approach since virgin base stocks do not foam and the

Table 23

PROPERTIES OF RECLAIMED BASE STOCKS

Sample No.	Reclamation Process						Foam Vol, ml[5]	Foam Collapse Time, sec	Total Acid No.[6]	Viscosity, cs		
	Adsorbents[1]	Distill[2]	Oxidize[3]	Adsorbents[1]	Distill	Antifoam[4]				-65°F	100°F	210°F
					ATL-5051							
197435	--	--	--	--	--	--	>350	--	0.35	12,800	--	--
197490	--	--	--	--	--	X	25	16	--	--	--	--
197445	X	--	--	--	--	X	160	20	--	--	--	--
197470	X	--	--	--	--	X	35	17	--	--	--	--
197435-2	--	--	X	X	--	--	310	--	--	--	--	--
197441	--	--	X	X	--	X	25	45	--	--	--	--
200094	X	X	--	--	--	--	5	2	0.04	--	11.7	--
					ATL-5052							
197485	--	--	--	--	--	--	>300	--	0.46	13,500	--	--
197492	--	--	--	--	--	X	25	21	--	--	--	--
197473	X	--	--	--	--	X	35	<60	--	--	--	--
200035	--	X	--	--	--	X	5	9	--	--	--	--
197448	--	--	X	X	--	--	>300	--	--	--	--	--
197472	--	--	X	X	--	X	345	<60	--	--	--	--
197477	X	--	X	X	--	X	315	15	--	--	--	--
200090	--	--	X	X	X	--	5	3	--	--	--	--
200041	--	--	X	X	X	X	5	3	0.63	--	11.1	2.96
200038	--	X	X	X	--	X	5	3	--	--	--	--
200085	--	X	X	X	X	--	5	2	--	--	--	--
200040	--	X	X	X	X	X	5	3	0.18	--	10.5	2.85
ATL-6025	--	--	--	--	--	--	--	--	--	--	14.9	3.6
ATL-6026	--	--	--	--	--	--	--	--	--	--	13.2	3.45

[1] Basic Al_2O_3, Fuller's earth and neutral charcoal used in that order

[2] Distillation done at about 1.5 mm

[3] $KMnO_4$ used as oxidizing agent

[4] 10 ppm Dow Corning 200 silicone fluid (10,000 cps) added as antifoam agent

[5] Determined as per Test Method 3213

[6] As per ASTM D-664

presence of foam indicates a potentially detrimental material in the reclaimed base stock. Use of adsorbents followed by distillation gives a reclaimed base stock from ATL-5051 with very acceptable foam volume, acid number and 100°F viscosity as shown by the data for sample 200094.

The results for ATL-5052 are very similar to those found for ATL-5051 with respect to use of antifoam, adsorbents and distillation. However, significantly different results were obtained when ATL-5052 was oxidized. An unacceptable foam volume was found when ATL-5052 was oxidized and treated with adsorbents just as found for ATL-5051. However, in this case addition of antifoam did not result in a lower foam volume as can be seen by examining the data for samples 197448 and 197472. Use of adsorbents before the oxidation was tried in an attempt to remove as many contaminates as possible prior to oxidation. Still high foam volumes were obtained (sample 197477).

Use of distillation was successful in giving a reclaimed base stock with a low foam volume as shown by the data for samples 200090 thru 200040 in Table 23. Note that the distillation can be before or after the oxidation and that antifoam is again not required (sample 200085). Reclaimed base stocks obtained by distillation can have 100°F and 210°F viscosities slightly below specification levels as shown by the data for samples 200041, 200040 and ATL-6025/6026 in Table 23. These viscosity values can be adjusted by proper addition of virgin base stocks and additives as will be discussed later in this report.

The distillation used for these samples was a rapid distillation at 1 to 2 mm resulting in distillation of about 95 percent of the oil leaving most of the additives behind as determined by TLC. The boiling point range in from 195°C to 250°C indicating that still higher pressures could be successfully utilized. Higher pressures would be more readily obtained in large scale operation.

Most work with adsorbents concentrated on Fuller's earth as an acid adsorbent to remove alkaline materials. Since attapulgus clay is used to remove contaminants from jet fuel it seemed a reasonable choice for further evaluation. When used in place of Fuller's earth in treatment of ATL-5051 a very high foam volume was obtained. Retreatment with adsorbents lowered the foam volume somewhat but the foam volume was still many times greater than that obtained when either Fuller's earth or no adsorbents were used. The data are given in Table 24, samples 197475-A, B and C.

Table 24

FOAMING CHARACTERISTICS OF RECLAIMED BASE STOCKS[1]

		Reclamation Process Used[2]							
Sample No.	Initial Used Oil	Oxidize	Al_2O_3	Fuller's Earth	Attapulgus Clay	Charcoal	Steam Distillation	Foam Volume	Foam Collapse Time, sec
197490	ATL-5051	--	--	--	--	--	--	25	16
197470	ATL-5051	--	X	X	--	X	--	35	17
197475-A	ATL-5051	--	X	--	X	X	--	240	22
197475-B	197475-A	--	X	--	X	X	--	185	18
197475-C	197475-B	--	--	--	--	X	--	110	15
197492	ATL-5052	--	--	--	--	--	--	25	21
197485	ATL-5052	--	--	--	X	--	--	255[3]	--
200013	ATL-5051	--	X	X	--	acid	--	15	12
200014	ATL-5051	--	X	X	--	neutral	--	20	22
200017	ATL-5051	--	X	X	--	basic	--	20	12
197490	ATL-5051	--	--	--	--	--	--	25	16
200018	ATL-5051	--	--	--	--	--	X	25	<50
197472	ATL-5052	X	X	X	--	X	--	345[4]	--
200011	ATL-5052	X	X	X	--	X	X	245[5]	18
200001	ATL-5051	--------extracted with dilute HCl and NaOH--------						45	21

---

[1] 10 ppm Dow Corning 200 silicone fluid (10,000 cps) added as antifoam agent
[2] Reclamation techniques were used in order listed
[3] Foam volume at end of one minute
[4] After 4 minutes
[5] Foam volume less than 25 ml for first 20 minutes

A similar result was obtained when ATL-5052 was evaluated before and after treatment with attapulgus clay as shown by the data for samples 197492 and 197485 in Table 24. Use of attapulgus clay after distillation does not result in high foaming as discussed in Section 2.5.

The effect of charcoal acidity was checked. This was done to determine if pH of the charcoal had any effect on additive, and degradation product removal. Analysis of the oils by TLC indicated no significant differences between the three samples. These samples were further evaluated with the foam test and the results are given in Table 24, samples 200013, 200014, and 200017. The data (TLC and foam volumes) indicate no significant differences result from the type of charcoal used.

Vacuum steam distillation was given only limited evaluation in development of a reclamation process as discussed earlier in this report. Determination of foam volumes of reclaimed base stocks obtained via steam distillation did not indicate any benefit would be gained through its use as shown by the data for samples 197490 thru 200011, Table 24.

ATL-5051 was extracted with dilute acid and base to evaluate the effect of replacing the Fuller's earth and basic alumina treatment with aqueous systems. This was done in the event that a decision would have to be made at a later date on the relative cost effectiveness of the use of adsorbents vs aqueous extraction. A foam volume of 45 ml was obtained (Table 24, sample 200001) compared to a value of 25 to 35 for the use of adsorbents indicating that the two methods were comparable at least as far as can be determined with the foam test.

A phenomenon has been observed in the foam test for which we have no complete explanation. Usually if an oil sample fails the foam test the foam volume will exceed the maximum allowable level within the first one or two minutes. Occasionally we have observed a situation where the foam volume remains very low for 10 to 20 minutes and then suddenly increases to a value well in excess of the maximum. Subsequent examination of the reclaimed base stocks has shown reduced levels and in some cases no detectable level of antifoam. This suggests that the antifoam is plating out on the walls of the test equipment. However, in some cases foam tests have been run for two hours without any increase in foam volume over an initial value of 25 to 35 ml. It is not readily obvious why antifoam would plate-out in some cases and not others. A situation wherein a delicate balance exists between a foaming agent and an antifoam is a possibility. The presence of antifoam was established using phase contrast microscopy, a technique suggested by H. Smith of AFAPL.

Three oils whose foam volumes were known were supplied by AFAPL to qualify our test apparatus and technique. Occasionally our foam test was requalified by repeating this test. The results obtained throughout the program are given in Table 25.

Table 25

FOAMING CHARACTERISTICS OF STANDARD OILS

	Foam Volume, ml					Collapse Time, sec			
	APL	MRC				MRC			
Oil		Sept	Oct	Feb	Aug	Sept	Oct	Feb	Aug
ATL-6060	35	30	20	40		26	25	30	
ATL-6059	100	110	115		95	50	35		21
ATL-6061	165	170				36			

Evaluation of the effect of reclamation techniques on metals content of reclaimed base stock was carried out to determine if any metal removal procedures need be developed. Analysis of four oils indicated that treatment of used oils with adsorbents did an effective job of removing metals. The data shown in Table 26 suggested that there was no need to develop a chemical method for metal removal.

The trace metal contents of some used oils before and after reclamation treatments were determined to establish the effect of reclamation techniques on metal content. Table 27 contains the data. These data indicate that treatment with adsorbents only results in increased Al, Fe and Si levels as shown by the data on ATL-6100 and 6101. The above evaluation had indicated that the use of adsorbents was beneficial for removal of trace metals. Distillation prior to adsorbent treatment results in reclaimed base stocks with metals content well below specification limits as shown by the data for ATL-5051, 5052 and 7069. These data suggest that an additive and/or degradation product leached materials from the adsorbents. Possibly some adsorbent batches are more susceptible than others. Another possible explanation is that fine particles of Fuller's earth were carried over into the oil.

Consideration of the above information along with the prior reclamation studies resulted in the decision to use a combination of distillation and adsorbent treatments as the

Table 26

METALS CONTENT OF OIL SAMPLES[1]

	Metal Content, ppm												
Sample No.	Al	Fe	Cr	Ag	Cu	Sn	Mg	Ni	Ti	Ca	Na	Pb	Si
ATL-5051[2]	0.7	8	3	0.4	0.8	2	0.7	0.2	2	<0.3	5	~20	2
197427[3]	0.1	1	<0.03	0.2	0.1	<0.03	0.5	<0.03	<0.1	<0.3	0.5	5	2
197445[4]	0.5	0.05	<0.03	<0.01	0.04	<0.03	0.4	<0.03	<0.1	<0.3	0.2	<0.1	12
197428-C[5]	0.1	0.3	<0.03	<0.01	0.05	<0.03	0.8	<0.03	<0.1	5	1	<0.1	3
197430-C[6]	0.1	0.1	<0.03	<0.01	0.05	<0.03	0.5	<0.03	<0.1	5	1	<0.1	5

[1] Values are semi-quantitative and were obtained by emission spectrographic analysis using a Bausch and Lomb Emission Spectrograph (dual grating)

[2] As-received

[3] ATL-5051 filtered through Hyflo Supercel

[4] ATL-5051 filtered through Hyflo Supercel, treated with Al_2O_3, acid clay and charcoal

[5] ATL-5051 filtered through Hyflo Supercel, treated with $KMnO_4$, acid clay and charcoal

[6] ATL-5052 filtered through Hyflo Supercel, treated with $KMnO_4$, acid clay and charcoal

Table 27

METALS CONTENT OF OIL SAMPLES[1]

Sample No.	Used Oil[2]	Reclamation Technique		Metal Content, ppm													
		Distilled	Adsorbents	Al	Fe	Cr	Ag	Cu	Sn	Mg	Ni	Ti	Mn	Pb	Cd	Na	Si
MIL-L-7808G Specification				3.0	4.0	3.0	1.0	1.0	4.0	3.0	4.0	1.0	--	--	--	--	--
	ATL-6100	-	-	0.3	2.0	0.8	0.07	0.05	0.02	3.0	0.05	0.3	0.02	5.0	30.0	1.0	2.0
203487	ATL-6100	-	X	40.0	10.0	0.7	0.05	0.02	0.1	4.0	0.1	4.0	0.1	5.0	10.0	1.0	20.0
206555	ATL-6100	X[3]	X	0.07	<0.1	<0.03	<0.01	<0.02	<0.01	<0.04	<0.03	<0.01	<0.01	<0.2	<0.2	<0.3	<0.1
	ATL-6101	-	-	0.1	2.0	0.8	0.04	0.3	0.1	0.5	0.04	0.1	<0.01	1.0	<0.3	0.8	0.8
203487	ATL-6101	-	X	20.0	38.0	0.08	<0.1	0.08	0.1	1.0	<0.03	0.3	0.02	0.2	<0.3	0.6	7.0
	ATL-5051	-	-	0.2	2.0	0.3	0.05	0.5	0.1	0.3	0.04	0.2	0.08	5.0	<0.3	3.0	2.0
203428D	ATL-5051[4]	X[5]	X	0.02	<0.1	<0.03	<0.01	0.05	<0.01	<0.04	<0.03	<0.01	<0.01	<0.2	<0.3	2.0	0.2
	ATL-5052	-	-	2.0	4.0	0.6	0.05	0.5	0.1	3.0	0.08	0.3	0.08	7.0	<0.3	2.0	4.0
200087	ATL-5052	X[5]	-	0.1	<0.1	<0.03	<0.01	<0.02	<0.01	0.02	<0.03	<0.01	<0.01	<0.2	<0.3	0.7	0.2
203488	ATL-5052	X[5]	X	1.0	0.1	<0.03	<0.01	<0.02	<0.01	0.05	<0.03	0.1	<0.01	<0.2	<0.3	<0.3	2.0
	ATL-7069	-	-	0.08	0.8	<0.03	0.1	0.1	<0.01	0.4	<0.03	<0.01	<0.01	7.0	<0.3	0.5	0.4
206560	ATL-7069	X[3]	-	<0.01	<0.1	<0.03	<0.01	<0.02	<0.01	<0.01	<0.03	<0.01	<0.01	<0.2	<0.3	0.5	<0.1
206562	ATL-7069	X[3]	X	<0.01	<0.1	<0.03	<0.01	0.05	<0.01	<0.01	<0.03	<0.01	<0.01	<0.2	<0.3	0.3	<0.1

[1] Values are semi-quantitative and where obtained by emission spectrographic analysis using a Bausch and Lomb Emission Spectrograph (dual grating).

[2] Samples all topped and filtered before treatments.

[3] Distillation done at 10 mm.

[4] Pretreated with conc H_2SO_4 and adsorbents.

[5] Distillation done at 1.5 mm.

reclamation process for used MIL-L-7808G oils. Distillation as a first step after topping and filtration was chosen since the bulk of the non-base stock material would be removed before adsorbent treatment. Consequently less quantity of adsorbents would be needed, thus decreasing oil loss due to retention in the adsorbents.

2.4 RECLAIMED OIL EVALUATION

This task consisted of two parts: qualification of an additive package for diester/triester mixtures and reformulation and evaluation of reclaimed oils. Qualification of additive packages was done using a 1/1 mixture of diester/triester virgin base stock. The three additive packages formulated for testing are given in Table 28. Not all specification tests were run. However the results obtained indicated that useful additive packages were prepared. The additive package labeled sample 203462 was evaluated prior to finding that a 2% level of TCP was more desirable than the 4% level. The -65°viscosity of these oils is not within specifications but no attempt was made to adjust this parameter since it was not of concern in additive package evaluation except for the 100°F viscosity change during corrosion and oxidation stability evaluation.

Table 28

CANDIDATE ADDITIVE PACKAGE COMPOSITIONS

Additives	Sample 203462	Sample 206506	Sample 206507
tricresyl phosphate	4.0%	2.0%	2.0%
dioctyldiphenylamine	2.0%	1.0%	2.0%
3,7-dioctylphenothiazine	--	1.0%	--
Benzotriazole	0.1%	0.1%	0.1%
triphenyl phosphite	0.1%	0.1%	0.1%
quinizarin	0.05%	0.05%	0.05%
Antioxidant 703 (Ethyl Corp.)	0.1%	0.1%	0.1%

Examination of the data in Table 29 shows that use of these additive packages in mixed diester/triester base stock results in oils whose performance properties meet or exceed the specification requirements. Therefore, potentially any of these additive packages could be used in reclaimed oils.

Table 29

ADDITIVE PACKAGE QUALIFICATION TEST RESULTS

	Sample No.			
	203462	206506	206507	Specification
Trace Sediment: ml/200 ml	--	<0.0025	<0.0025	≤0.005
Total Acid Number: mg KOH/g	0.09	0.07/0.14	0.06/0.1	≤0.3
Viscosity @ 210°F: cs	3.66	3.72	3.69	>3.0
Viscosity @ 100°F: cs	15.5	16.0/15.8	15.8/15.7	>11.0
Viscosity @ -65°F: cs	17,340	18,620	18,240	<13,000
Pour Point: °F	--	<-80	<-80	<-75
Flash Point: °F	--	445	460	>400
Evaporation: %	--	12	13	≤35
Elastomer Compatibility				
Swell (NBR-H): %	25.8	21.4/23.7	20.7/23.8	12-35
Swell (F-A): %	--	9.4	10.7	2-25
Tensile Strength (F-A): % Change	--	42	8	50 max
Elongation (F-A): % Change	--	43	25	50 max
Hardness (F-A): Change	--	10	-5	25 max
Swell (FS): %	--	3.1	2.9	2-25
Tensile Strength (FS): % Change	--	-19	-39	50 max
Elongation (FS): % Change	--	-12	-35	50 max
Hardness (FS): Change	--	-5	10	25 max
Deposition Number	--	0.1	0.9	≤2.5
Gear Load (% RR x 2900): PPI	--	2,710	2,760	>2,440
Lead Corrosion: mg/in.	-0.2	-0.3	-0.3	<6.0
Silver-Copper Corrosion				
Silver Weight Change: mg/in.^{2}	-0.5	-0.2	-0.1	±3.0
Copper Weight Change: mg/in.^{2}	-0.5	-0.8	-0.5	±3.0
Accelerated Storage Stability				
Lead Weight Change (48 hrs): mg/in.^{2}	--	1.5	1.1	≤25
Lead Weight Change (168 hrs): mg/in.^{2}	--	87.2	59.2	≤250
Corrosion and Oxidation Stability @ 347°F, 72 hr Method 5308				
Steel Weight Change: mg/cm^2	<0.1	0.0	0.0	±0.2
Silver Weight Change: mg/cm^2	<0.1	0.0	0.0	±0.2
Aluminum Weight Change: mg/cm^2	<0.1	0.0	0.0	±0.2
Magnesium Weight Change: mg/cm^2	0.1	0.0	0.0	±0.2
Copper Weight Change: mg/cm^2	--	0.0	0.0	±0.4
Viscosity @ 100°F: % Change	6.0	6.6	6.2	-5 to +15
Total Acid Number: Change	1.15	0.81	1.05	≤2.0
Foaming, Method 3213				
Foam Volume, ml	--	15	15	100 max
Collapse Time, sec	--	2	2	60 max

When reformulating reclaimed base stocks it is necessary to determine the concentration of residual additives carried through the reclamation process. This is necessary so that the final total additive concentrations do not exceed the values given in Table 28. This analysis can be done utilizing the HPLC procedure given in Section 2.1.1.1. DODPA was the only additive not completely removed by the reclamation process as determined by HPLC.

Work on reformulation of reclaimed base stocks to obtain reclaimed oils was initiated using the additive package given in Table 28, sample 203462. Selected properties obtained on these oils are presented in Table 30. In each case the foam volume of the reclaimed base stock used to formulate the reclaimed oil was in the 5 to 25 ml range.

It was readily obvious that the addition of the additive package was detrimental to foam volume for these samples. Also addition of antifoam increased the foam volume still further. This suggested that either an additive, a combination of additives or an additive-residual base stock contaminate combination was giving rise to a dispersed phase that caused foaming. This foaming was then further enhanced by the addition of more dispersed phase in the form of the antifoam.

The source of a dispersed phase in the reclaimed base stocks upon addition of additives would most likely be from interaction of an acid and base to give an insoluble salt. Based on this premise a series of experiments were carried out to identify the cause of the problem.

When the above additive package was added to virgin base stock the resultant oil had a foam volume of 170 ml (see sample 203431, Table 31). This foam volume is similar to those obtained with the reclaimed base stocks given in Table 30. This established that the base stock does not contain any residue giving rise to the high foam volume.

Next the interaction of tricresyl phosphate and tricresyl phosphate/Ethyl 703 (a strong amine) was evaluated in virgin base stock. Considerably lower foam volumes were obtained as shown by the data for sample 203438 and 203440 in Table 31. This data suggest something other than an interaction between these two additives.

Table 30

PROPERTIES OF RECLAIMED OILS[1]

Sample No.	Reclamation Process										
	Adsorbents[2]	Distill[3]	Oxidize[4]	Adsorbents	Distill	Antifoam[5]	Foam Vol, ml[6]	Foam Collapse Time, sec	Total Acid No.[7]	Viscosity, cs -65°F	Viscosity, cs 100°F
					ATL-5051						
200100	X	X	--	--	--	--	135	22	--	--	--
203404	X	X	--	--	--	X	>300	--	--	15,100	--
203414	X	X	--	X	--	--	150	12	--	--	--
203420	X	X	--	X	--	X	>300	--	--	16,600	--
					ATL-5052						
200092	--	--	X	X	X	--	>300	--	0.00	13,700	11.8
200093	--	--	X	X	X	X	>300	--	--	--	--
200086	--	X	X	X	X	--	130	30	0.00	10,600	10.8
200089	--	X	X	X	X	X	190	34	--	--	--

[1] Each sample contains the additive package given for sample 203462, Table 28
[2] Basic Al_2O_3, Fuller's earth and neutral charcoal used in that order
[3] Distillation done at about 1.5 mm
[4] $KMnO_4$ used as oxidizing agent
[5] 10 ppm Dow Corning 200 silicone fluid (10,000 cps) added as antifoam agent
[6] Determined as per Test Method 3213
[7] As per ASTM D-664

Table 31

EFFECT OF ADDITIVES ON FOAMING OF BASE STOCKS

Sample No.	Reclaimed Base Stock No.	Additives	Foam Volume, ml	Collapse Time, sec
	$\frac{\text{Emery 2958}}{\text{Emery 2932}}\ \frac{1}{1}$	--	25	10
203431	$\frac{\text{Emery 2958}}{\text{Emery 2932}}\ \frac{1}{1}$	additive package for sample 203462, Table 28	170	31
203438	$\frac{\text{Emery 2958}}{\text{Emery 2932}}\ \frac{1}{1}$	Tricresyl phosphate, 4%	60	5
203440	$\frac{\text{Emery 2958}}{\text{Emery 2932}}\ \frac{1}{1}$	Tricresyl phosphate, 4% Ethyl 703, 0.1%	50	4
203433A	203414	--	5	2
203433B	203414	Ethyl 703, 0.1%	5	2
203435	203433B	Ethyl 703, 0.1% Tricresyl phosphate, 4%	90	15
203436	203414	Tricresyl phosphate, 4%	85	11
203437	203436	Tricresyl phosphate, 4% Ethyl 703, 0.1% Triphenyl phosphite, 0.1%	95	10
203462	$\frac{\text{Emery 2958}}{\text{Emery 2932}}\ \frac{1}{1}$	additive package for sample 203462, Table 28	85	8

Similar experiments were done using a reclaimed base stock obtained by treatment of ATL-5051 with adsorbents followed by distillation and treatment with adsorbents. The data obtained from these experiments suggest that tricresyl phosphate was the cause of the foaming problem. These data are given in Table 31, samples 203433A thru 203437. This was confirmed by using TCP from another source, i.e. Kronitex from FMC. The use of this TCP in the additive package dropped the foam volume of an oil made from virgin base stock from 170 ml to 85 ml, bringing the oil into specification with respect to the foam test as shown by the data for sample 203462.

A limited amount of data on acid numbers and viscosities indicated that these specifications would not be difficult to meet in reformulated oils as shown by the data in Table 30. The viscosities at -65°F were a little high but were probably influenced by the high level of tricresyl phosphate used in these oils. New oils probably contain significantly less TCP as indicated by patent literature. Actual TCP levels were determined on new oils to help set the level used in reclaimed oils as discussed in Section 2.1.1.1.

The effect of reformulation on viscosity, acid number and foam volume was determined for reclaimed oils prepared from used oils ATL-6100 and ATL-7069. The additive package used for these oils is given in Table 28, sample 206507. Reclaimed base stock from ATL-6100 responded very well to reformulation as shown by the data for the first three samples in Table 32. The viscosities and foam volume are within specification limits. ATL-6100 was the oil with the longest known service time (1800 hours) available in the program. The ability to effectively reclaim and reformulate it further supported the viability of the reclamation process.

Reclamation of ATL-7069 to a reclaimed oil was not completely successful. The first attempted reclamation resulted in a reclaimed base stock with a -65°F viscosity of 11,300 cs, distillation was not stopped at a low enough temperature. Addition of the additive package increased the -65°F viscosity to 15,400 cs and the foam volume was in excess of the specification limit of 100ml. Addition of 10ppm antifoam increased the foam volume still further. (These data are given in Table 32, samples 206562 thru 206563-A.) The high foam volume of the reclaimed oil was unexpected. A study was initiated to find the cause(s).

Table 32

VISCOSITIES, ACID NUMBERS AND FOAM VOLUMES OF RECLAIMED BASE STOCKS AND OILS

Sample No.	Used Oil	Distillation	Absorbents[6]	Additives	Viscosity, cs			Acid No.	Foam Volume, ml	Collapse Time, sec
					-65°F	100°F	210°F			
	ATL-6100				15,300	13.3	3.36			
206555[1]	ATL-6100	X	X	-	10,500	11.2	3.00	--	--	--
206556	ATL-6100	X	X	X	11,900	11.5	3.02	--	20	4
	ATL-7069	-	-	-	19,800	15.3	3.61	--	--	--
206562[2]	ATL-7069	X	X	-	11,300	--	--	1.67	--	--
206563[2]	ATL-7069	X	X	X	15,400	12.5	3.09	1.81	155	11
206563-A[3]	ATL-7069								<300	
206576[4]	ATL-7069	X	X	-	10,100	11.2	2.89	0.04	--	--
206583[4]	ATL-7069	X	X	X	13,600	--	--	0.13	145	11
206583-A[5]	ATL-7069								<300	

[1] Distilled to a vapor temperature of 280°C at 15 mm.
[2] Distilled to a vapor temperature of 300°C at 15 mm.
[3] 206563-A is 206563 plus 10 ppm silicone antifoam.
[4] Distilled to a vapor temperature of 285°C at 15 mm.
[5] 206583-A is 206583 plus 10 ppm silicone antifoam.
[6] Fuller's earth, basic Al_2O_3 and neutral charcoal used in that order.

A second sample of ATL-7069 was reclaimed and reformulated with similar results although the $-65^{\circ}F$ viscosity was not too much in excess of specification and the acid number was a lot lower. (See samples 206576 and 206583 of Table 32.) The lower acid number was the result of using $Ca(OH)_2$ in place of basic Al_2O_3.

As a result of the above data, both the additive package and foam test procedure were examined as potential cause(s) of the problem. A foam test was run on ATL-6059, the AFAPL supplied standard, and a foam volume of 95 ml was obtained. AFAPL value was 100 ml. This showed the foam test procedure was not a cause of this problem. This was also checked using virgin base stock which gave a foam volume of 10 ml.

Additives were incorporated in groups into virgin base stock and foam values and acid numbers determined. The results are given below.

Sample No.	Additives	Foam Vol, ml	Acid No.
1206125A	dioctyldiphenylamine, 1% 3,7-dioctylphenothiazine, 1%	20	0.05
1206125B	sample 1206125A plus quinizarin, o.1% Antioxidant 703, 0.1% tricresyl phosphate, 2.0%	10	0.04
1206125C	sample 1206125B plus triphenyl phosphite, 0.1%	10	0.02
1206125D	sample 1206125C plus benzotriazole	10	0.11

The lack of foaming problems with the virgin base stock suggest that the foaming problem with reclaimed ATL-7069 results from something inherent in the reclaimed base stock. Microscopic examination of the reformulated ATL-7069 oil under phase contrast suggested that a dispersed phase might be present with particle sizes in the 5 to 10 micron range. Two approaches were taken to overcoming the high foam volume problem.

The reclaimed oil from ATL-7069 (125 ml foam volume) was blended 50/50 with a low foam volume oil (17 ml foam volume). The blend was found to have a foam volume of 92 ml. This shows that blending can be used to adjust foam volumes if necessary.

The above 50/50 blend having a 92 ml foam volume was filtered through filteraid in an attempt to remove the suspected dispersed phase material. The filtered oil had a 75 ml foam volume. The blend was also filtered through a 1 μ filter and the resulting oil had a foam volume of 80 ml. The negligible drop in foam volume (92 ml to 75 and 80 ml) obtained by filtration indicates that foam volumes can more easily be corrected through blending with low foam volume oils if the cause for foaming cannot be corrected.

The addition of an additive package significantly influences the viscosity of a base stock, particularly at -65°F and to a lesser extent at 100°F and 210°F. This effect must be taken into account when reformulating a reclaimed base stock so that viscosity specifications can be met. Data showing these effects are presented in Table 33. As can be seen by examination of the data the percent increase found is fairly consistent for four samples (∿35%) but much lower for the ATL-6100 based samples (∿13%). The only known differences in the original used oils is their base stock composition. ATL-6100 is largely diester, ATL-7069 is largely triester and ATL-7071 is a mixture of diester and triester of unknown ratio. These differences in viscosity response to additives has to be accounted for prior to reformulation. If the additives will cause the -65°F viscosity to exceed specifications then virgin base stock has to be added to adjust the viscosity. It would be desirable to have many more data points to accurately establish the effect of a given additive package on the viscosity of pure diesters, pure triesters and mixtures. If the response noted above is due to base stock structure then this would allow more accurate reformulation to be done. This would also necessitate an analysis of the reclaimed base stock to identify the relative amounts of diester and triester in each batch prior to reformulation. An analytical procedure adaptable for this type of analysis has been developed by MRC under Air Force contract (Ref. 16).

Examples of the viscosity response of reclaimed base stocks to additives and the corresponding changes when virgin base stock is added are given in Table 34 for the five gallon scale reclamation samples.

Table 33

EFFECT OF ADDITIVE PACKAGE ON OIL VISCOSITY

Sample No.	Initial Used Oil	Additive Package Identity[1]	Viscosities, cs					
			-65°F	Δ%	100°F	Δ%	210°F	Δ%
206555	ATL-6100	none	10,500		11.2		3.00	
206556	ATL-6100	206507	11,900	13.3	11.5	2.7	3.02	0.7
206562	ATL-7069	none	11,300		--		--	
206563	ATL-7069	206507	15,400	36.3	12.5		3.09	
206576	ATL-7069	none	10,100		11.2		2.89	
206583	ATL-7069	206507	13,600	34.7	--		--	
1206126	ATL-7069	none	10,300		--		2.94	
1206139	ATL-7069	206507	13,800	34.0	--		3.03	3.1
1206135	ATL-7071	none	10,300		--		2.98	
1206138	ATL-7071	206507	13,900	35.0	--		3.07	3.0

[1] See Table 28 for identification of additive package composition.

Table 34

VISCOSITIES OF RECLAIMED/REFORMULATED OILS

Sample No.	Composition	Viscosity, cs -65°F	 210°F
1206126	Reclaimed ATL-7069	10,300	2.94
1206139	Reformulated ATL-7069	13,800	3.03
1206149	Reformulated ATL-7069/Emery 2958[1] (78/22)	12,300	3.05
1206135	Reclaimed ATL-7071	10,300	2.98
1206138	Reformulated ATL-7071	13,900	3.07
1206143	Reformulated ATL-7071/Emery 2958[1] (87/13)	13,200	3.07

[1] Emery 2958 is di-2-ethylhexyl azelate with a -65°F viscosity of 7000 cs and a 210°F viscosity of 2.85 cs.

2.5 RECLAMATION PROCESS SCALE-UP

The reclamation process selected for scale-up using the oils supplied by AFAPL is shown in Figure 44. The use of filter aid for filtration of adsorbents is included here for small scale operation as a matter of convenience for batch filtrations. Large scale operations would probably use centrifuges for filtration with no need for filter aid. Otherwise the operation is the same as envisioned for large scale operations except that liquid phase separation was not needed for any oils in this program. The details of the general process are given in Section 5.1.

Four oils were subjected to the above process at the one liter scale prior to larger scale-up. These oils covered the widest base stock composition range available, i.e. from largely diesters, to mixtures, to largely triesters. The stress history was known only for used oil ATL-6100, a diester which had been used for 1800 hours. The effectiveness of the reclamation process was checked by acid number and foam volume tests. As mentioned earlier the foam test was considered to be the most difficult qualification test for reclaimed oils. The results obtained for the four oils are given in Table 35. No acid numbers are given for the first two samples as none were determined on these two specific samples. However other work with these used oils consistently gave acid numbers below the specification limit.

Table 35

EVALUATION OF RECLAMATION PROCESS WITH SELECTED USED OILS[1]

Sample No.	Initial Used Oil	Used Oil Base Stock Composition[2]	Acid No.	Volume,[3] ml	Collapse Time, sec
206552	ATL-5052	diester/triester	--	15	4
206556	ATL-6100	diester	--	20	4
1206139	ATL-7069	triester	0.03	125	9
1206138	ATL-7071	diester/triester	0.00	17	8

[1] Additives for sample 203507, Table 28 used.

[2] As determined from analysis by infrared spectrometry and gas chromatography.

[3] Method 3213.

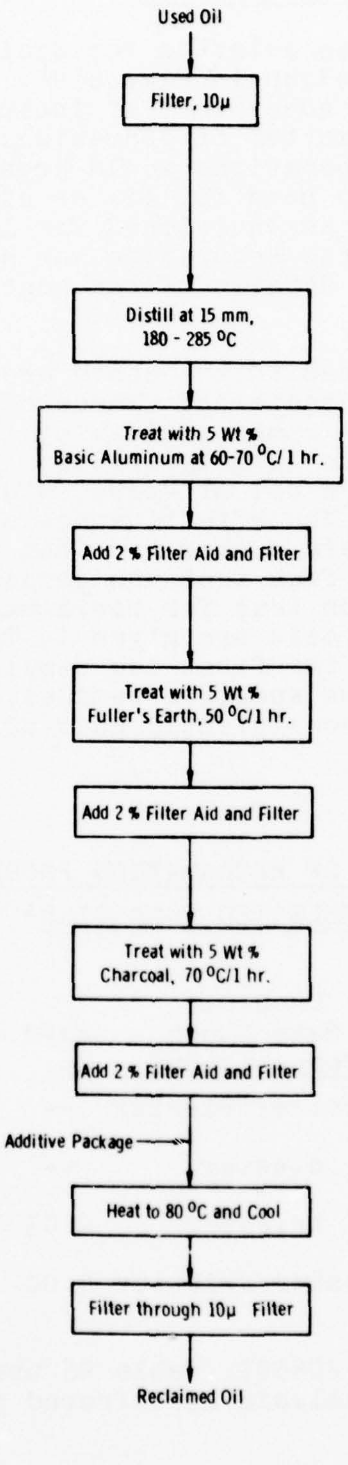

Figure 44. Reclamation Process Applied in Small Scale Studies.

The foam volumes of three of the four oils are very low. Reclaimed ATL-7069 has a foam volume of 125 ml, somewhat in excess of the 100 ml limit of Method 3213. As discussed earlier ATL-7069 consistently gave foam volumes in excess of 100 ml, ranging from 125 to 165 ml. It is interesting to note, however, that a sample which gave a foam volume of 165 ml by Method 3213 gave a value of 10 ml by the MIL-L-7808G specification method. This illustrates the severity of Method 3213. The success in reclaiming these widely different oils indicated the feasibility of the process and resulted in the decision to use it for larger scale reclamation.

The two oils available for large scale reclamation were ATL-7069 and ATL-7071. These oils were reclaimed first to obtain 5 gallons of oil for conformance tests and then approximately 30 gallons of each was reclaimed to be used for qualification testing to prove the process. The five gallon scale reclamation was carried out entirely in the laboratory. Distillation of the thirty gallon scale reclamations were done in the laboratory and the remaining adsorbent treatments and reformulations were done in a thirty gallon vessel in the pilot plant. The distillations were done in the laboratory to save the high set-up costs that would be incurred in putting together the necessary vacuum distillation equipment in the pilot plant.

Table 36 summarizes the data taken in the laboratory to follow the course of the five gallon scale reclamations of ATL-7069 and ATL-7071. All three properties used to follow the reclamation process indicated a successful technique had been developed. The foam volume for reclaimed ATL-7069 was slightly higher than the proposed specification Method 3213 test limit of 100 ml but the foam volume was not excessive when the currently required ASTM D-892 MIL-L-7808G specification test was used.

The results of the conformance tests on reclaimed ATL-7069 and reclaimed ATL-7071 established that the reclamation process was an acceptable method for reclaiming these used MIL-L-7808G oils. Reclaimed ATL-7069 (sample no. 1206148) passed all tests while reclaimed ATL-7071 (sample no. 1206176) passed all but two tests. The lead corrosion values at 325°F and copper corrosion values at 450°F were slightly higher than specification values. The complete conformance test results are presented in Appendix B.

Reclaimed ATL-7071 was studied for possible causes for the high lead and copper corrosion values. The moisture content in a retained sample was 0.015% compared to a value of 0.008% in reclaimed ATL-7069. These moisture contents would not suggest that excessive moisture caused the excessive corrosion unless the material sent to Alcor, Inc. for testing picked up moisture during shipment.

Table 36

PROPERTIES OF ATL-7069 AND ATL-7071 AT VARIOUS RECLAMATION STAGES DURING RECLAMATION OF FIVE GALLON QUANTITIES

Used Oil	Reclamation Stage	-65°F Viscosity, cs	Acid No.	Foam Volume, ml	Collapse Time, sec
ATL-7069	initial		4.09	--	--
	after distillation	--	6.80	--	--
	after $Ca(OH)_2$ treatment	--	0.10	--	--
	after Fuller's earth treatment	--	--	--	--
	after charcoal treatment	10,300	0.02	--	--
(1206148)	after reformulation[1]	12,300	0.10	165	8.5
ATL-7071	initial	12,900	0.87	--	--
	after distillation	--	1.53	--	--
	after $Ca(OH)_2$ treatment	--	0.06	--	--
	after Fuller's earth treatment	--	--	--	--
	after charcoal treatment	9,400	0.15	20	1.3
(1206176)	after reformulation	11,200	0.19	20	4.7

[1] 22% Emery 2958 virgin base stock added to adjust -65°F viscosity

The only other known differences between reclaimed ATL-7069 and reclaimed ATL-7071 are the base stock and a different level of DODPA. Reclaimed ATL-7071 contained a total of 3.2% antioxidants due to excess DODPA that had been inadvertently added. A sample of reclaimed ATL-7069 base stock was reformulated with excess DODPA equivalent to sample 1206176 and a sample of reclaimed ATL-7071 base stock was reformulated quivalent to sample 1206148. The corrosion characteristics of these new samples established that the additive package was not the cause for corrosion and that the corrosion agent was in the base stock itself as shown by the data in Table 37.

Table 37

EFFECT OF PROCESS VARIATIONS ON METAL CORROSION

	Lead Loss, 325°C mg/in.^{2}	Copper Loss, 450°F mg/in.^{2}
Reclaimed ATL-7071 excess antioxidant	-10.4	-4.4
Reclaimed ATL-7071 no excess antioxidant	-29	-3.7
Reclaimed ATL-7069 excess antioxidant	-0.4	-2
Reclaimed ATL-7069 no excess antioxidant	-0.3	-0.6
Reclaimed ATL-7071 treated with attapulgus clay	0.0	0.0
ATL-7069 initial used oil	113.6	1.4
ATL-7071 initial used oil	114.6	3.0

The antioxidant obviously helps prevent some corrosion but is not sufficient to overcome the problem even at the 3% antioxidant level. It is interesting to note that based on these limited tests it could be concluded that copper corrosion increases with antioxidant level. This could possibly be due to the known ability of amines to readily chelate copper.

With limited time remaining in the program it was possible to do only one more test in an attempt to overcome the corrosion problem. A similar corrosion problem with fuels had been overcome by filtration through attapulgus clay (ref. 17). A sample of reclaimed ATL-7071 base stock was treated with attapulgus clay, reformulated and tested. The results given in Table 38 show that this treatment is successful in removing the unknown corrosive agent. This additional treatment was therefore added into the process for the 30 gallon reclamation of ATL-7071.

The 30 gallon scale reclamation was carried out using the procedure given in Section 5.1 with one unnecessary operation omitted, i.e. no phase separation was required. In addition, the reclaimed ATL-7071 base stock after treatment with charcoal was treated with

2 weight % attapulgus clay at 20°C for 18 hours. This time was selected as a matter of convenience since no study of this adsorbent treatment had been done other than the one experiment discussed above.

The results of the qualification tests also confirm that the reclamation process developed will reclaim used 7808 oils and restore them to a useful product. The complete test results for reclaimed ATL-7069 and reclaimed 7071 are given in Appendix B. The following discussion will only review those test results which are not within specification.

The copper corrosion value for reclaimed ATL-7069 was -3.4 mg/in.^{2} (specification is 3.0 mg/in.^{2}). The same used oil gave a value of -0.6 mg/in.^{2} when the reclamation was done totally in the laboratory whereas the initial used oil gave a value of -1.4 mg/in.^{2}. This suggests that a corrosive agent was introduced or not quite completely removed during scale up. It is quite likely that continued reclamation process development in a plant operation would overcome such a minor deviation.

Reclaimed ATL-7071 had a Ag corrosion value of 3.7 mg/in.^{2} (specification limit is 3.0 mg/in.^{2}). When the same used oil was reclaimed in the laboratory a value of 0.1 mg/in.^{2} was found, whereas the initial used oil had a value of 0.1 mg/in.^{2}. This again indicates some that a corrosive agent was introduced in the scaled up process as was found for reclaimed oil ATL-7069.

All the deviations from specification limits found for the two oils are minor and should readily be overcome with experience in scale up of the process.

The efficiency of the reclamation process at three different scales is summarized in Table 38. The most pertinent information is the percent recoveries for each stage in the process. The largest loss is taken on distillation in order to get a base stock with the required low temperature viscosity. As would be expected these values are fairly consistent since all distillation were done in the laboratory. Also note that there is not much variation in % recovery between the 1 kg and 5 gallon scale. Again this is not surprising since both were done in the laboratory. Significant losses were encountered on adsorbent treatment in the pilot plant (30 gallon scale) mainly due to large scale filtration problems. These losses in no way reflect what is achievable in a plant designed for oil recovery. Very high costs would have been encountered in setting up the optimum adsorbent separation system and it was more important at this stage of the development to get the oil necessary to prove the process than to attempt to get the optimum recovery. The laboratory recovery values are more accurate reflections of potential recovery and these values are undoubtedly minimum values.

Table 38

EFFECIENCY OF RECLAMATION PROCESS

	ATL-7069						ATL-7071					
	<1 kg		5 gallon		30 gallon		<1 kg		5 gallon		30 gallon	
Reclamation Stage	Weight, g	% Recovery	Weight, g	% Recovery	Weight, lbs	% Recovery	Weight, g	% Recovery	Weight, g	% Recovery	Weight, lbs	% Recovery
initial	600	--	31062	--	276	--	935	--	24255	--	290	--
distillation[1]	412	69	22620	73	200	72	801	86	19955	82	249	86
$Ca(OH)_2$ treatment	378	92	21045	93	133	67	742	93	18630	93	214	86
Fuller's earth treatment	338	90	19362	92	120	90	674	91	17445	94	164	77
charcoal treatment	310	92	17260	89	100	83	613	91	16455	94	135	82
attapulgus clay treatment	--	--	--	--	--	--	--	--	--	--	127	94
Overall Yield		51.6		55.6		36.2		65.6		67.8		43.8

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[1] Distillation losses include both distillation foreruns and residues.

2.6 COST ANALYSIS

A cost analysis of the process used to reclaim the two large lots of used oils was carried out to estimate the cost of reclaiming used oils in batch sizes of 50, 500, 5,000 and 50,000 gallons. The operations involved in carrying the reclamation as developed in this program are shown in Figures 45 and 46. Figure 45 shows the actual process used for used oils ATL-7069 and ATL-7071 with the exception of the phase separation step. Figure 46 shows the process with recycle of waste streams that appear to be feasible for continuous operation based on laboratory studies. A cost analysis was done on both processes.

The capital cost estimates for installation of a process in an existing plant were made using a 500 gallon batch size as the basic unit and escalating the costs to other sizes using an escalation factor of 0.6, an average value used frequently in these types of calculations (ref. 17). The standard equation for such calculations,

$$\text{Cost} = \text{Cost}_o \left(\frac{S}{S_o}\right)^x$$

where Cost_o is the cost for 500 gallon scale, S is the size factor and X the escalation factor, was used. The capital cost data and assumptions are presented in Table 39 with the capital cost vs batch size data shown in Figure 47.

The installation cost assumption of 25% of capital costs was taken from Ref. 17. This cost is probably a minimum and can vary considerably depending on several factors, e.g. level of instrumentation, amount of piping required, etc. Consequently the capital cost values in Figure 47 could be increased proportionately depending on where an installation was made and how sophisticated the operation is designed.

The operating cost analysis was made based on the assumption that a plant was set up and operating continuously over a year period. This assumes an adequate used oil supply. No cost for collection of the oil is included. The assumption was also made that the plant could be operated by two men working fifty percent of the time. Base stock recovery efficiency factors found in this project ranged from 53% to 66% for the no recycle process. The projected recovery efficiency factors for the recycle process were 66% to 80%. The cost analysis given in Table 40 is based on the lowest oil recovery for the no recycle process and the highest oil recovery for the recycle process to illustrate the extremes envisioned. Other assumptions concerning material costs, process losses and cycle times are presented in Table 40. The cost assigned to utilities is considered to be a very crude estimate and was derived by calculating the cost of energy required for distillation and multiplying the answer by 5 to cover the costs of the remaining operations. This was done since it is difficult to estimate

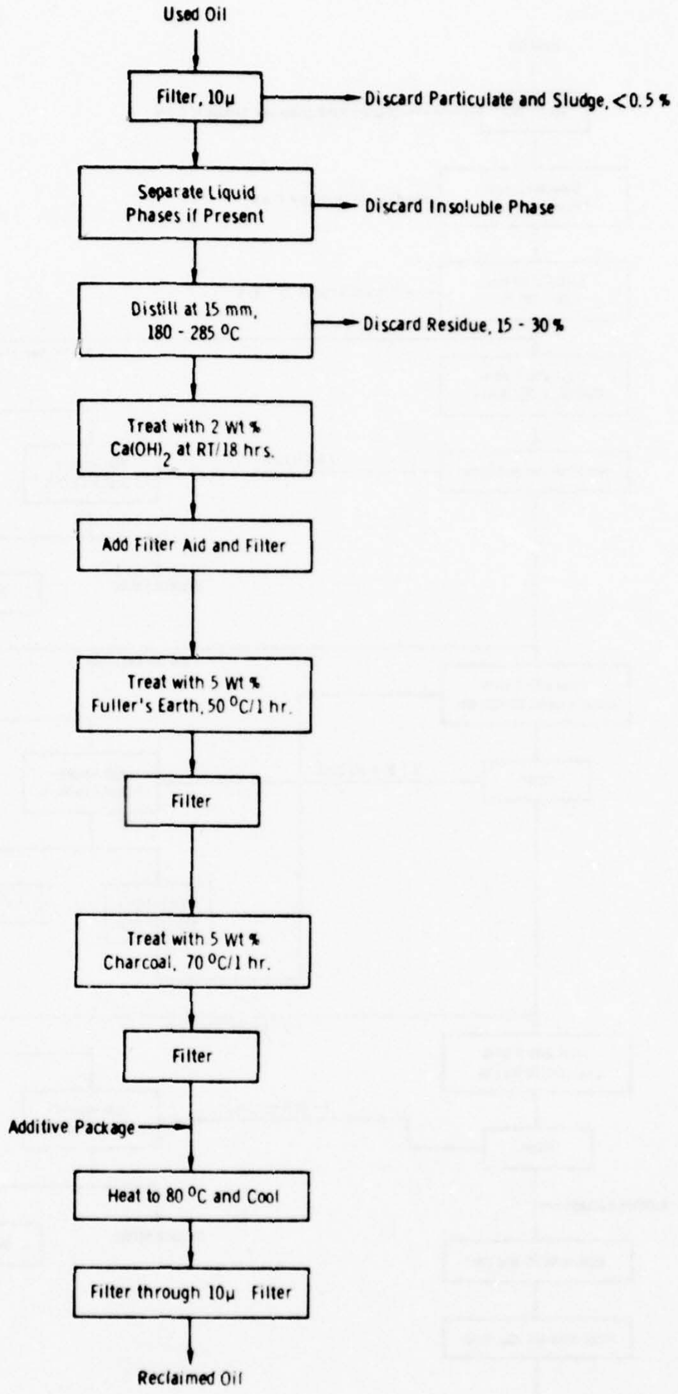

Figure 45. Reclamation Process (Without Recycle) Applied in 30 Gallon Scale Up Studies.

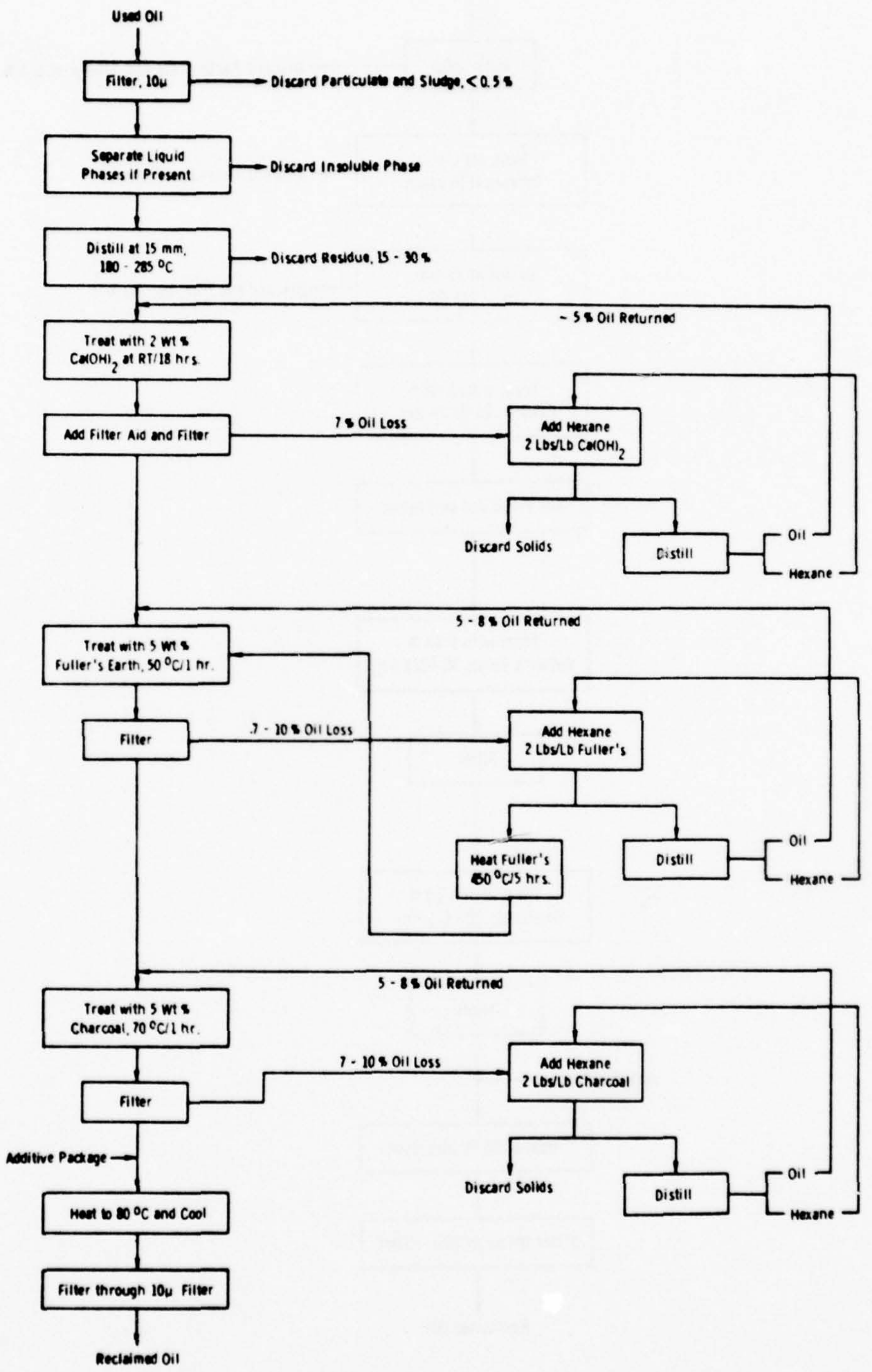

Figure 46. A Feasible Reclamation Process With Recycle.

Table 39

CAPITAL COST DATA AND ASSUMPTIONS

Equipment Requirements (500 gallons)	Cost in 1977
Filters (2)	$ 1,500
Decanter (1)	$ 2,600
Still (2)	$30,000
Vacuum equipment (1)	$19,000
Heat source available	--
Jacketed stirred vessel (1)	$15,000
Condenser (2)	$ 3,000
Kiln (1)	$ 1,200
Product Storage (1)	$ 5,500
TOTAL	$78,000
Installation cost (assume 25% purchased equipment cost)	$19,000
Total Installed Capital Cost	$97,000

Waste Oil Reclamation Capital Cost Assumptions

Source of heat available

A batch requires 5 hrs to complete distillation

Heat of vaporization 50 gcal/g.

Specific gravity waste oil 0.93

Condenser cost 10% of still

Storage capacity, product, 5 batches

Installation cost 25% purchased equipment cost

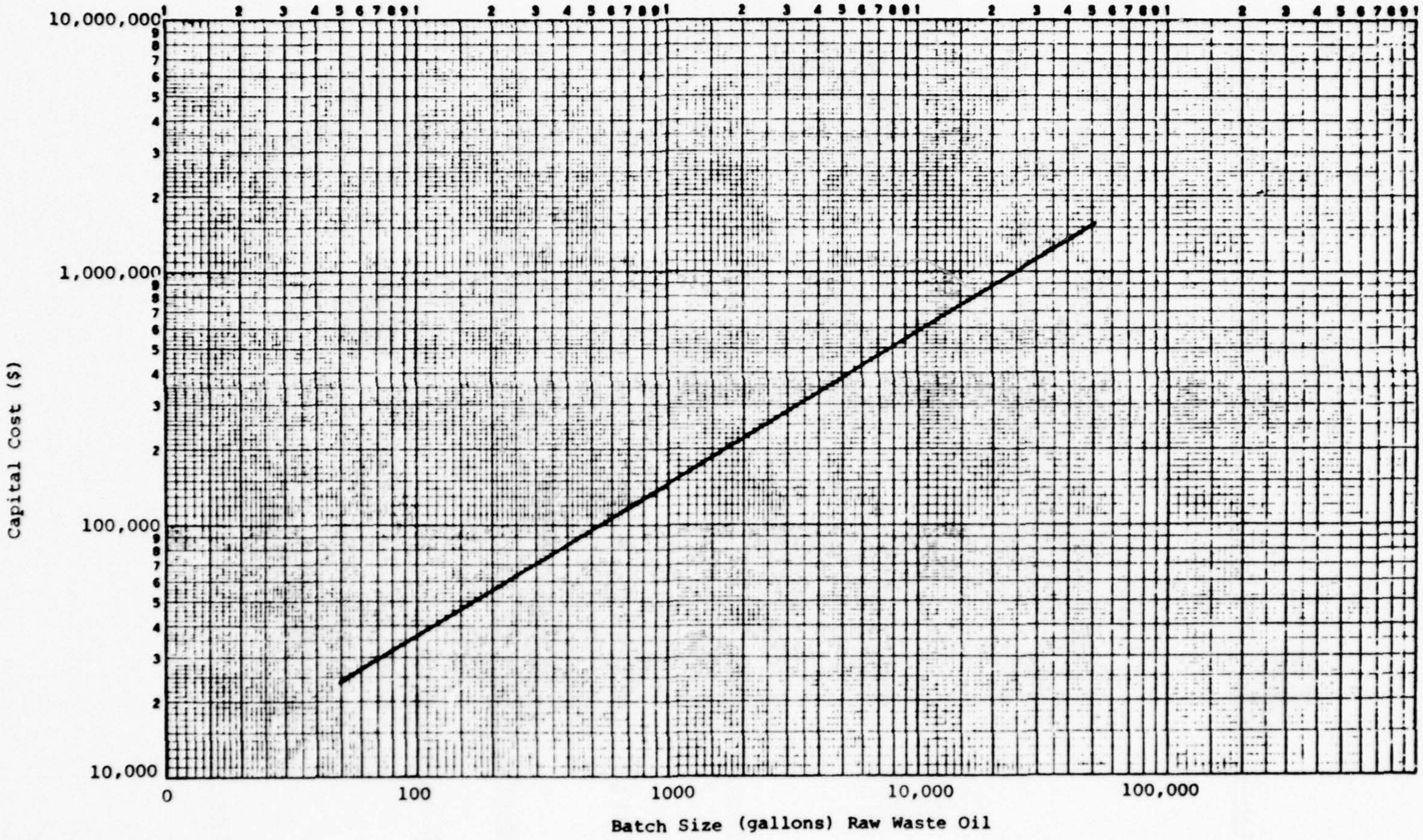

Figure 47. Used Oil Reclamation Capital Cost

Table 40

OPERATING COST ASSUMPTIONS

MATERIAL REQUIREMENTS

Materials[1]	Cost, \$/lb	Requirements lb/gal
DODPA	1.55	7.76×10^{-2}
DOPTA	3.75	7.76×10^{-2}
TCP	0.99	1.55×10^{-1}
TPP	1.60	7.76×10^{-3}
Benzotriazole	5.50	7.76×10^{-3}
Quinizarin	6.25	3.88×10^{-3}
Ethyl 703	1.43	7.76×10^{-3}
Filteraid	0.134	1.55×10^{-1}
Charcoal	0.610	3.88×10^{-1}
$Ca(OH)_2$	0.710	1.55×10^{-1}
Fullers Earth	0.03	3.88×10^{-1}
Hexane	50¢/gal	no recycle-0 recycle-2.82×10^{-1} $\frac{gal}{gal}$ assume 2% loss

[1] Materials bought in quantity to obtain lowest possible cost.

PROCESS LOSSES

Operation	No Recycle and Lowest Oil Recovery	Recycle and Highest Oil Recovery
Filter	100% of original oil	100%
Distillation	70% of original oil	85%
$Ca(OH)_2$	65% of original oil	83%
Fullers Earth	59% of original oil	82%
Charcoal	53% of original oil	80%

(continued)

Table 40 (concluded)

OPERATING CYCLE TIMES

No Recycle Operation	Time (hr)	Recycle Operation	Time (hr)
Filter	½	Filter	½
Separate insoluble liquid phase	½	Separate insoluble liquid phase	½
Distill	5	Distill	5
Treat $Ca(OH)_2$	18	Treat $Ca(OH)_2$	18
Filter	½	Filter	½
Treat Fullers earth	1	Treat Fullers earth	1
Filter	½	Filter	½
Treat charcoal	1	Treat Charcoal	1
Filter	½	Filter	½
Additives	½	Additives	½
Heat to 80°C & cool	1	Heat & Cool	1
Filter	½	Filter	½
	29½	$Ca(OH)_2$/Hexane mix	½
		Distill	4
		Fullers/Hexane mix	½
		Distill	4
		Heat Fullers	5
		Charcoal/Hexane	½
		Distill	4
			48

∴ Assume 250 cycles/yr

@ 500 gal/cycle ⟶ 250 x

500 x 0.53 = 66,250 gal product

On stream, $\frac{250 \times 29.5}{365 \times 24} = 0.84$

∴ Assume 150 cycles/yr

@ 500 gal/cycle ⟶ 500 x

150 x 0.8 = 60,000 gal product

On stream $\frac{150 \times 48}{365 \times 24} = 0.82$

MISCELLANEOUS

Waste oil specific gravity - 0.93

Hexane ΔH_{vap} - 82 g-cal/g

Oil ΔH_{vap} - 50 g-cal/g

Utilities - Total energy required for distillations (theoretical) x 5 at a cost of $2/10⁶ btu

Labor - 2 people @ 50% time @ $5/hr

Number of cycles/year - no recycle, 250; recycle, 150 cost for filtrations, pumping materials, etc. without more detailed process development data that could only be obtained by further development work. However, the cost of utilities by this estimate is 3 cents a gallon or less and so has very little impact on total costs.

The operating cost breakdown for the four batch size operations are given in Table 41 and summarized by category in Table 42 as cost per gallon of reclaimed oil. It is obvious from Table 42 that testing costs are predominate at the lower batch sizes whereas material costs predominate at large batch sizes.

Not included in the above analysis is the cost incurred if virgin base stock must be added to adjust the -65°F viscosity. This is treated here as a separate case since this addition was not always found to be necessary. The virgin base stock used in this program was Emery 2958, a di-2-ethylhexyl azelate, which costs from \$0.75 to \$0.83/lb at 1977 prices. Assuming that 10% of Emery 2958 had to be added to the reclaimed base stock the additional cost incurred would be \$0.57/gallon of reclaimed oil assuming that Emery 2958 was purchased at its lowest price. The effect of this addition on total costs are shown for the four batch sizes assuming no recycle.

	50 gallon	500 gallon	5,000 gallon	50,000 gallon
Cost without Emery 2958	159.13	17.38	3.06	1.59
Cost of added Emery 2958	0.57	0.57	0.57	0.57
Total Cost	159.70	17.95	3.63	2.16

Table 41

OPERATING COSTS SUMMARY ($)

	50 gallons/batch		500 gallons/batch		5,000 gallons/batch		50,000 gallons/batch	
	No Recycle	Recycle	No Recycle	Recycle	No Recycle	Recycle	No Recycle	Recycle
Labor	3.69×10^4	3.60×10^4	3.69×10^4	3.60×10^4	3.69×10^4	3.60×10^4	3.69×10^4	3.60×10^4
Materials								
$Ca(OH)_2$	9.68×10^2	7.03×10^2	9.68×10^3	7.03×10^3	9.68×10^4	7.03×10^4	9.68×10^5	7.03×10^5
Filteraid	1.82×10^2	1.33×10^2	1.82×10^3	1.33×10^3	1.82×10^4	1.33×10^4	1.82×10^5	1.33×10^5
Fullers earth	9.44×10^1	3.76×10^0	9.44×10^2	3.76×10^1	9.44×10^3	3.76×10^2	9.44×10^4	3.76×10^3
Charcoal	1.75×10^3	1.45×10^3	1.75×10^4	1.45×10^4	1.75×10^5	1.45×10^5	1.75×10^6	1.45×10^6
Additives								
DODPA	7.94×10^2	7.22×10^2	7.94×10^3	7.22×10^3	7.94×10^4	7.22×10^4	7.94×10^5	7.22×10^5
DOPTA	1.93×10^3	1.75×10^3	1.93×10^4	1.75×10^4	1.93×10^5	1.75×10^5	1.93×10^6	1.75×10^6
TCP	1.02×10^3	9.21×10^2	1.02×10^4	9.21×10^3	1.02×10^5	9.21×10^4	1.02×10^6	9.21×10^5
TPP	8.25×10^1	7.45×10^1	8.25×10^2	7.45×10^2	8.25×10^3	7.45×10^3	8.25×10^4	7.45×10^4
Benzotriazole	2.83×10^2	2.56×10^2	2.83×10^3	2.56×10^3	2.83×10^4	2.56×10^4	2.83×10^5	2.56×10^5
Quinizarin	1.61×10^2	1.45×10^2	1.61×10^3	1.45×10^3	1.61×10^4	1.45×10^4	1.61×10^5	1.45×10^5
Ethyl 703	7.35×10^1	6.66×10^1	7.35×10^2	6.66×10^2	7.35×10^3	6.66×10^3	7.35×10^4	6.66×10^4
Hexane	--	2.38×10^1	--	2.38×10^2	--	2.38×10^3	--	2.38×10^4
Utilities	7.50×10^1	1.80×10^2	7.50×10^2	1.80×10^3	7.50×10^3	1.80×10^4	7.50×10^4	1.80×10^5
Capital Related Costs*	4.80×10^3	4.80×10^3	1.92×10^4	1.92×10^4	7.60×10^4	7.60×10^4	3.20×10^5	3.20×10^5
Total Cost	4.91×10^4	4.72×10^4	1.30×10^5	1.19×10^5	8.54×10^5	7.55×10^5	7.77×10^6	6.78×10^6
Product (gallons)	6625	6000	66,250	60,000	662,500	600,000	6,625,000	6,000,000
Cost per gallon	$7.41	$7.87	$1.97	$1.99	$1.28	$1.26	$1.17	$1.13
Additional Costs (per gallon)								
Disposal								
Sludge & particulates	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008
Absorbents	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Organic residues	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Analytical Tests								
IR, HPLC	0.60	0.60	0.06	0.06	6×10^{-3}	6×10^{-3}	6×10^{-4}	6×10^{-4}
Viscosity @ -65°C & 210°F	0.85	0.85	0.085	0.085	8.5×10^{-3}	8.5×10^{-3}	8.5×10^{-4}	8.5×10^{-4}
Qualification Tests	150	150	15	15	1.5	1.5	0.15	0.15
Total Cost ($/gallon)	159.13	159.59	17.38	17.40	3.06	3.04	1.59	1.55

*Depreciation, taxes, insurance, maintenance, etc.

Table 42

OPERATING COSTS PER GALLON BY CATEGORY

	Batch Size							
	50 gallon		500 gallon		5,000 gallon		50,000 gallon	
Category Item	No Recycle	Recycle	No Recycle	Recycle	No Recycle	Recycle	No Recycle	Recycle
Labor	5.57	6.00	0.56	0.60	0.056	0.06	5.6×10^{-3}	6×10^{-3}
Materials	1.11	1.04	1.10	1.03	1.11	1.05	1.10	1.04
Utilities	0.01	0.03	0.01	0.03	0.01	0.03	0.01	0.03
Capital Related Costs	0.72	0.80	0.29	0.32	0.11	0.13	0.05	0.053
Disposal	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
Analytical Tests	1.45	1.45	0.145	0.145	1.45×10^{-2}	1.45×10^{-2}	1.45×10^{-3}	1.45×10^{-3}
Qualification Tests	150	150	15	15	1.5	1.5	0.15	0.15
Total Cost	159.13	159.59	17.38	17.40	3.06	3.04	1.59	1.55

SECTION III

CONCLUSIONS

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

2. The use of other operations such as oxidation of impurities and solvent treatments to carry out certain phases of the process were studied but were not successful enough to be useful for a general reclamation process.

3. Distillation at 15 mm to a maximum vapor temperature of 285°C gives a reclaimed base stock having the necessary visocosity characteristics to allow reformulation to a usable oil after removal of impurities.

4. Foaming characteristics (as determined of Method 3213) and the total acid number of reclaimed base stocks are good quality control tests for determining the success of the reclamation process.

5. A high pressure liquid chromatographic technique capable of quantifying the important residual additives in a reclaimed base stock was developed. Quantifying residual additives is necessary to allow proper adjustment of levels of additives when an additive package is introduced into reclaimed base stock.

6. It was shown that gas chromatograms were useful for estimating the ratio of base stock types in used oils, i.e., diester vs. triester. In many cases the ratio of the original new oil mixtures could be identified. Infrared spectra can also be used to qualitatively identify a used oil with respect to the presence of diester and triester base stock.

7. If necessary the viscosity of a reclaimed oil can be adjusted to meet specifications by use of a virgin base stock. An oil with a foam volume somewhat in excess of specifications can be combined with a low foaming oil to obtain a mixture that meets specifications.

8. Two additive packages were developed that are nearly satisfactory for use in reclaimed base stocks. Their utility was established in virgin base stocks. Use in four reclaimed oil formulations showed success except for minor corrosion

problems. Whether these problems can be attributed to the additive package or the reclaimed base stock is not known.

9. The cost analysis of the process established that it could be cost effective depending on the scale of operation. Continuous large batch size, e.g. in the 5000 gallon range, reclamations would be required to get reasonable cost effectiveness. The cost of qualification testing is too great at lower batch sizes.

SECTION IV

RECOMMENDATIONS

The following are areas in which it is recommended that further effort be placed for improvement and refinement of the process. The process as it now is defined has been shown to be feasible for reclamation of used 7808G oils. However, it needs to be documented by reclamation of more batches. In addition, assuming the viability of the process is further documented the following suggestions for refinement are made.

1. The amount of adsorbents to be used should be studied in more detail and the effect of changes in level followed by pertinent qualification (e.g. corrosion, flash point) and analytical tests (e.g. GC, HPLC, acid number). After a sufficient number of tests had been run it should be possible to correlate the qualification tests and analytical results to determine the degree of confidence one could have in using analytical methods to follow a reclamation process. The amount of adsorbents used in the present process are undoubtedly maximum levels and were deliberately kept high to insure, as much as possible, the generality of the process.

2. In view of the results obtained by using an attapulgus clay treatment for ATL-7071 its use in place of Fuller's earth should be studied. Early results in the program suggested the use of attapulgus clay contributed to foaming but this was not substantiated by its use late in the program.

3. The use of distillation vapor temperature as a distillation end point should be detailed further particularly using a wide variety of used oil mixtures.

4. The amount of virgin base stock required to adjust the -65°F viscosity of reclaimed base stocks should be studied to get a more accurate measure of the amount needed for a variety of reclaimed base stock mixtures. This could probably be done largely using virgin oil mixtures to simulate reclaimed base stocks.

5. The effect of $Ca(OH)_2$ on properties other than acid number should be studied to insure that ester hydrolysis does not occur during its use to such an extent as to be detrimental to long term storage stability, flash point, etc.

6. Tests for establishing whether a used oil contains foreign contamination that would prevent its reclamation should be established.

SECTION V

EXPERIMENTAL

5.1 THE OPTIMIZED PROCESS

The following discussion details the process as developed and optimized in the laboratory and pilot plant phases of this program. The operations discussed follow those outlined in Figure 45, section 2.6. The materials used are those specified in Appendix A. Not all the operations discussed were necessary for the oils reclaimed in this program, i.e. phase separation, but they are included to keep the process as general as can be envisioned being required.

Filtration: Solid insoluble materials present in the used oils (e.g. wear metals, sludges) are removed by filtration through a 10 micron cartridge type filter. These materials are present in very low amounts, usually less than 0.2% by weight. The potential presence of metals and unknown organics necessitates disposal by landfill techniques.

Phase Separation: Liquid phases are separated if present. These phases would most likely be water or some aqueous mixture as all organic liquids tested were compatible with the oils. Polarities ranging from those of hexane to methanol were compatible although some suggestion of incompatibility was noted with methanol. Addition of small quantities of water to solutions of oil and water soluble liquids such as methanol, acetone and tetrahydrofuran caused phase separation of the major portion of the organic solvent. Disposal would depend on flammability but burning would be the most desirable method. No insoluble liquid phases were found in the used oil samples available to this program.

Distillation: The oil phase from the above phase separation is distilled at 15 mm Hg. The forerun boiling up to a vapor temperature of 180°C is discarded. This fraction never amounted to more than 0.5% by weight and usually ran less than 0.1%. Disposal of this fraction would be by burning since it is mainly organic hydrocarbons and oxygenated hydrocarbons.

The remaining oil is then distilled at a constant 15 mm Hg until a vapor temperature of 285°C is attained. This fraction, i.e. boiling point 180-285°C/15 mm, can readily be reformulated to an oil that meets both the 210°F and -65°F viscosity specifications. The presence of material boiling above 285°C requires addition of significant quantities of virgin base stock to adjust the -65°F viscosity and thus adds significantly to the reclamation cost. This distillation is carried out in a short path distillation apparatus protected from contamination by organic materials.

In the laboratory the large scale distillation was done in a 22 liter flask set-up as shown in Figure 48. The used oil was pumped (gear pump) from a drum through a 10 micron cartridge filter into a 22 liter flask. The flask was fitted with a heating mantle, thermometer, mechanical stirrer, inlet and outlet ports, a water cooled condensor, a vacuum take-off and a 22 liter receiver. All glass joints were sealed using Teflon sleeves and stopcocks were lubricated using a high viscosity virgin base stock. The flask was charged with approximately 13 liter (∿3.5 gallon) of used oil at room temperature, the pressure reduced to 15 mm and the distillation carried out as above. The distillation rate was very close to 3.8 liter (one gallon)/hour. The distillation ranged from light yellow to a medium organe in color depending on the particular used oil distilled. The distillation residue is a viscous oil that can be disposed of by burning.

A foam test can be run after distillation to project if the reclaimed base stock after adsorbent treatment will meet specifications. A value of 20 ml or less (Method 3213) is usually obtained. A distilled used oil with high foaming characteristics can probably be redistilled to give a low foaming oil. This was shown by one example encountered in this program.

Adsorbent Treatments: The distilled oil was mixed with 2% calcium hydroxide by weight and stirred at room temperature for 18 hours. During this time the solid phase turns from white to yellow to organe to purple. This last color change occurs somewhere between 10 and 18 hours. It may be possible to shorten this contact time by increasing the temperature. This possibility was not studied however since the use of $Ca(OH)_2$ was established late in the program. Treatment of esters at higher temperatures has the possibility of hydrolyzing the esters and subsequently altering the viscosity of the oil. If this occurred it would necessitate another devolatilization to remove alcohols. After the 18 hour contact time an amount of filter aid (Hyflo Super Cel) equivalent to the $Ca(OH)_2$ by weight was added and the mixture filtered under vacuum through an open basket filter protected from the atmosphere by plastic sheeting. The filter aid is necessary to prevent plugging of the filter due to the fine particle size $Ca(OH)_2$.

The oil recovered from the $Ca(OH)_2$ treatment is then mixed with 5 weight % Fuller's earth (heat activated at 450°C/5 hr), heated to 50°C under dry N_2, held at 50°C for one hour, cooled and filtered. In the laboratory and pilot plant this filtration was aided by addition of 2 weight % filter aid. However in a continuous plant operation this separation would probably be accomplished using centrifuges and the filter aid would not be required.

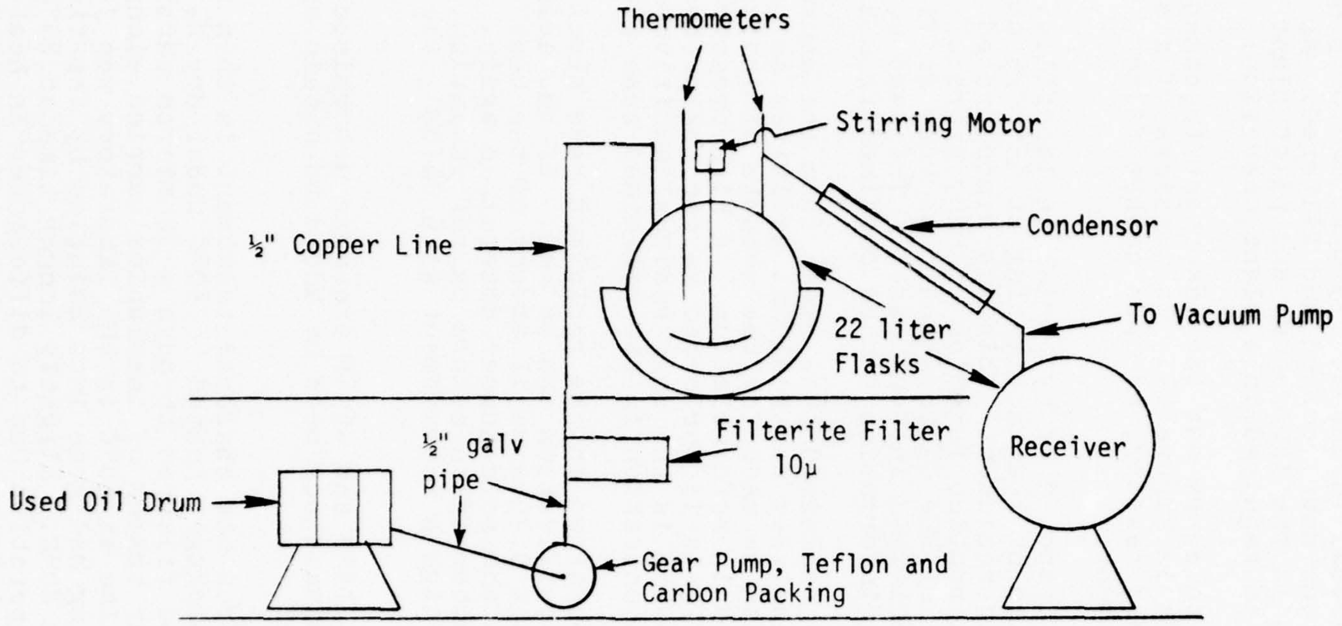

Figure 48. Apparatus for Distillation of Used Oils, 22 Liter

The oil recovered from the Fuller's earth treatment is mixed with 5 weight % charcoal (dried at 125°C/20 mm for 5 hours) under dry N_2, held one hour, cooled and filtered. As before filter aid was used in the laboratory and pilot plant but probably would not be required in a plant operation.

The equipment used to carry out the adsorbent treatments in the pilot plant is shown in Figure 49. It consists of a stirred 30 gallon glass-lined reactor, an open basket filter, receivers and auxiliary equipment.

The adsorbents are disposed of by burial in landfills. Fuller's earth can be recycled by heat activating at 450°C/5 hours to burn off the organic residues. This was demonstrated in the laboratory and is a routine function of many users of clay adsorbents. Recovery of the $Ca(OH)_2$ would be very difficult. Charcoals can be reclaimed in some cases. This was not studied in this program but information can be obtained from suppliers.

Reformulation: The reclaimed base stock from the above charcoal treatment is analyzed for residual additives so that proper adjustment can be made for the amounts of individual additives to be used in reformulation. A high pressure liquid chromatographic analysis is performed as per the procedure in Section 2.1.1.1. DODPA is the only residual additive found in any significant concentration in the reclaimed base stocks.

An acid number is obtained on the reclaimed base stock to insure that this specification can be met. If the acid number is in excess of about 0.25 a small amount of the base stock should be reformulated and the acid number determined again. A slight increase in acid number often occurs on reformulation. If the acid number is too high a retreatment with $Ca(OH)_2$ will lower it sufficiently.

The viscosities at 210°F and -65°F are also determined to find out if any virgin base stock need be added to obtain an acceptable viscosity level.

The oil recovered from the charcoal treatment is then mixed with the additive package, heated to 80°C under dry N_2 with stirring, cooled and filtered through a 10 micron cartridge filter to remove any traces of insolubles carried along through the process. The time at 80°C is the laboratory was just a few minutes as everything had gone into solution by the time the temperature reached 80°C. Slightly longer time at 80°C may be needed in a plant operation due to differences in heat transfer. The reclaimed oil was filtered through the 10 micron filter under N_2 pressure directly into epoxy coated 30 gallon drums. The drums were flushed with dry N_2 and sealed. The equipment set used for this operation is shown in Figure 50.

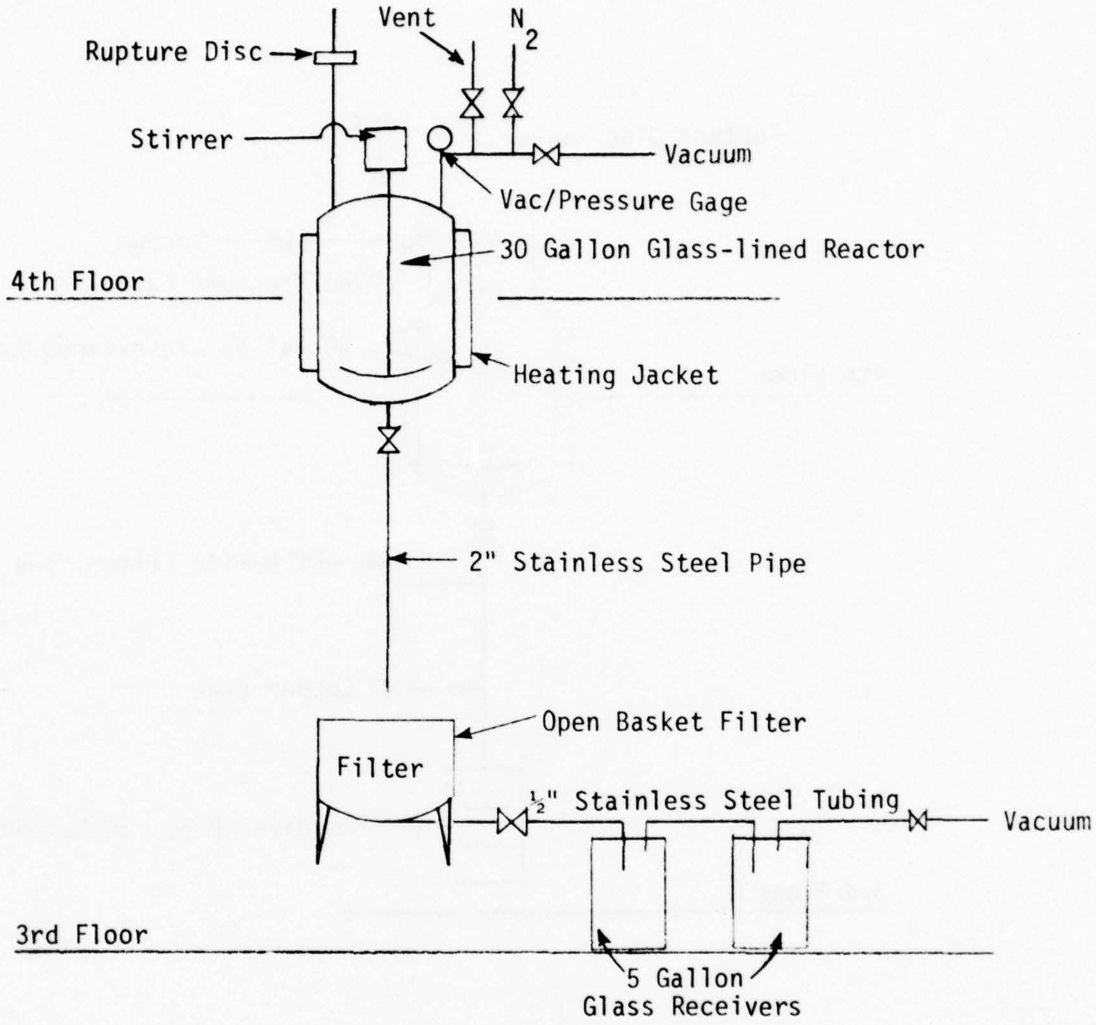

Figure 49. Equipment Design for Adsorbent Treatments in Pilot Plant

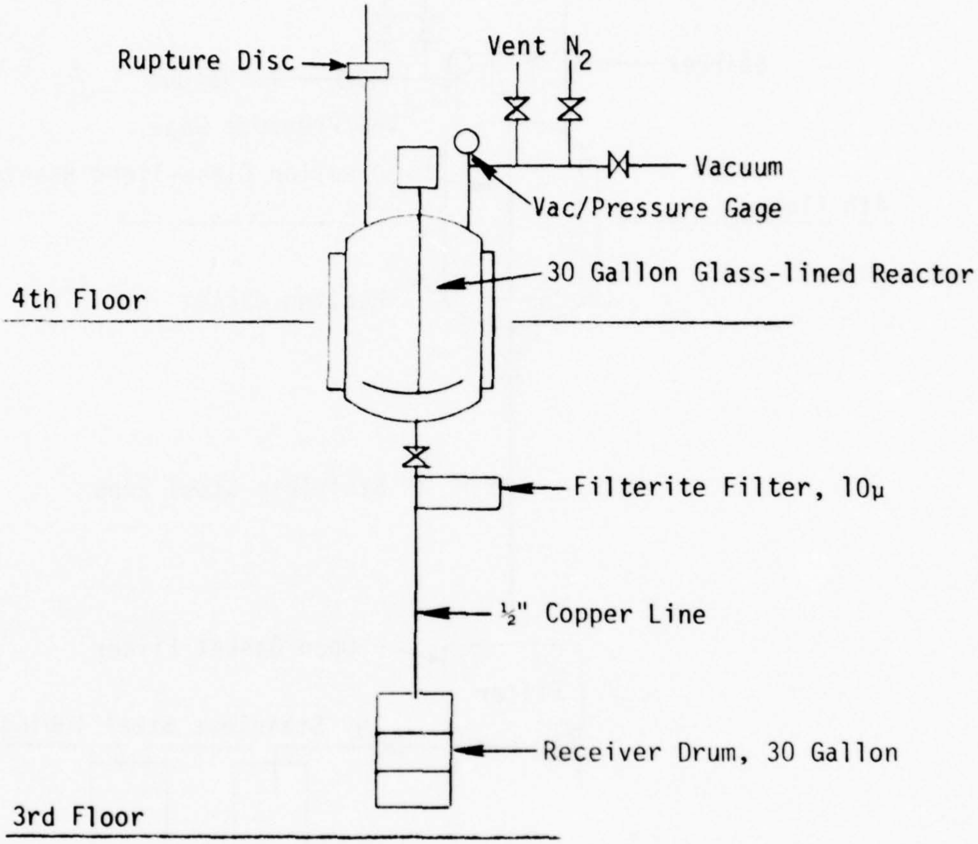

Figure 50. Equipment Design for Oil Reformulation

5.2 LABORATORY RECLAMATION TECHNIQUES

5.2.1 Filtration

Solid insoluble materials are removed by filtration of the oil through a filteraid (Hyflo Super-Cel, Johns-Manville Corp.), under vacuum. This filteraid is also used to assist in removal of adsorbents.

5.2.2 Devolatilization

Highly volatile materials are removed from the used oil by distillation under vacuum up to 165°C/5-10 mm. The receiver is cooled in a dry ice/acetone bath, thus permitting collection of the volatiles for analysis. All joints are sealed with Teflon sleeves to prevent contamination by organic grease. The oil sample is heated, with stirring to approximately 165°C and 5-10 mm pressure and devolatilization is usually complete in about 30 minutes after visible evolution of volatiles can be seen. Devolatilization time for a one liter sample is approximately 1 hour.

5.2.3 Adsorbent Treatment

Adsorbent treatment is defined as a composite treatment of 3 adsorbents; acid, basic clays and activated charcoal. Oils are treated with one adsorbent at a time. The adsorbent is added to the oil and the mixture heated to 50-70°C, for 1 hour. The adsorbents are removed by filtration through a filteraid. Adsorbents have been generally used at 10 wt % level which is undoubtedly an excessive amount.

The acid and basic clays are heated to 450-475°C for 15 hours for activation and stored in a dry atmosphere until used. Moisture content of activated charcoal is lowered by heating at 125°C at 20 mm pressure for 15 hours. The charcoal is also stored in a dry atmosphere until used.

5.2.4 Distillation

A standard short path glass distillation unit with all joints sealed with Teflon sleeves to prevent contamination by organic greases is used. The distillation is carried out at 190-250/ 1.5 mm and is terminated when:

(a) 3% of original oil volume remains in pot
(b) a sudden rise in vapor temperature occurs or
(c) distillate suddenly appears considerably darker.

The distillate is protected by a dry N_2 blanket during cool down.

5.2.5 Steam Distillation

A standard short path glass distillation unit is used. Steam, precleaned by passing through a scrubber to remove particulates, was introduced into the bottom of the oil sample through a diffusion tube. The oil was preheated to 170°C at 100 mm pressure before the steam was introduced and the steam rate was adjusted so oil was not bumped into the receiver. Distillation was terminated when the volume of condensed steam in the receiver was 1/4 volume of the oil sample.

5.2.6 Oxidation

The technique for oxidation of used oils is illustrated with the potassium permanganate oxidation procedure.

A sample of ATL-5052 (500 g) that had the insoluble phases separated and had been devolatilized was heated to 50-70°C. A 10% solution of $KMnO_4$ with pH adjusted to 2 using sulfuric acid was added to the oil in portions of 125 ml with stirring. The additions were continued until $KMnO_4$ was no longer consumed for one hour after the last addition as shown by the color of the aqueous layer. A total of 975 ml of $KMnO_4$ solution was required. Occasional additions of a few ml of concentrated sulfuric acid were required to maintain a pH of 2.

After the oxidation was complete the layers were separated and the oil layer washed six times with pH 2 water. The final wash was left in contact with the oil and sufficient sodium bisulfite was added to form sulfurous acid which destroyed any remaining manganeous salts (see page 132 of Ref. 11). The oil layer was again washed with pH 2 water twice more followed by two water washes. A considerable amount of emulsion formed as the pH of the water was lowered. (Very little emulsion formed when a similar oxidation was done on ATL-5051). As much water as possible was removed and the oil diluted with an equal volume of hexane which further broke the emulsion. The aqueous layer was separated as much as possible and $CaSO_4$ added to adsorb any remaining water. After drying the $CaSO_4$ was filtered off and the volatiles removed at 10 mm up to 100°C. At this point the oil was a pale to medium yellow color.

5.2.7 Treatment with H_2SO_4

The desired quantity of concentrated H_2SO_4 is slowly added to the oil with stirring. Reaction time is 1 hour at 20°C after which a quantity of lime in molar excess to the amount of H_2SO_4 is added and stirring at 20°C continued for 15-30 minutes. The solids are removed by filtration using filteraid.

5.3 ANALYTICAL TECHNIQUES

The following techniques were developed and utilized for detection and analysis of additives in new and used oils. A summary of techniques for detection and quantification of additives is given in Table 43.

Table 43

ANALYTICAL METHODS FOR SPECIFIC ADDITIVES

Additive	Analytical Method For Detection	Analytical Method For Quantification
tricresyl phosphate	TLC HPLC GC	HPLC
tris(β-chloroethyl)phosphate	GC	GC
4,4'-dioctyldiphenylamine	TLC HPLC GC	HPLC
N-phenyl-α-naphthylamine	TLC HPLC GC	HPLC
phenothiazine	TLC HPLC	HPLC
3,7-dioctylphenothiazine	TLC HPLC	HPLC
Primene JM-t	HPLC	--
quinizarin	TLC	--
silicone antifoam	phase contrast microscopy	--

5.3.1 Thin Layer Chromatography

The specific technique used by MRC is to apply 5 μl of a 33% solution of the oil in cyclohexane to a Silica Gel F-254 plate (EM Laboratories) activated at 100°C for one hour. A 30/70 heptane/toluene solvent was used for development.

5.3.2 High Pressure Liquid Chromatography

See text page 8.

5.3.3 Gas Chromatography

See text page 16.

APPENDIX A

Product Specifications for Additives and Adsorbents

Dioctyldiphenylamine (DODPA), Naugalube 438-R
3,7-Dioctylphenothiazine, Naugalube 459
Tricresyl phosphate, Kronitex
Quinizarin,
Benzotriazole
Ethyl antioxidant 703
Triphenyl phosphite
Di-2-ethylhexyl azelate, Emery 2958

Calcium hydroxide
Fuller's earth
Charcoal
Filter aid, Hyflo Super Cel

Product data sheets were obtained, where possible, for the additives and adsorbents used in the optimized reclamation process. The available data sheets are included here to identify the source and quality of the materials used. The following discussion identifies the source and quality of those materials for which a specification sheet was not available.

Quinizarin was obtained from GAF Corporation. It is identified only as purified 1,4-dihydroxyanthroqunone with no physical properties listed.

Tricresyl phosphate was obtained from FMC Corporation as Kronitex AA.

Ethyl antioxidant 703, a product of Ethyl Corporation, is 2,6-di-test-butyl-α-dimethylamino-p-cresol. Product literature from Ethyl Corporation states it has a minimum purity of 98%.

Triphenyl phosphite was obtained from Eastman Kodak Company. It has a boiling point of 360°C and a density at 25°C of 1.184.

Fuller's earth, grade LVM, obtained from Floridin Company, was used in a 20/40 mesh size. This is a high temperature activated material. A product analysis sheet is included in this report.

The filter aid used was Hyflo Super Cel from Johns-Manville Corporation. This material is a Celite diatomite, mainly aluminum silicates, having a specific gravity of 2.30 and the following chemical analysis: SiO_2, 89.6%; Al_2O_3, 4.0%; Fe_2O_3, 1.5%; P_2O_5, 0.2%; TiO_2, 0.2%; CaO, 0.5%; MgO, 0.6%, Na_2O and K_2O, 3.3%.

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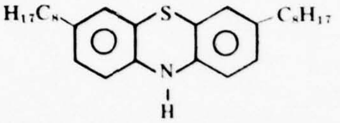
Naugatuck® Chemicals

NAUGALUBE 459



A HIGH TEMPERATURE ANTIOXIDANT FOR SYNTHETIC FLUIDS

NAUGALUBE® 459, 3,7-Dioctylphenothiazine, combines the antioxidant protection of phenothiazine while reducing the sludge formation normally associated with its use. NAUGALUBE® 459 can be used both as a primary or secondary antioxidant, and its effectiveness is greatly enhanced when used in combination with a copper deactivator.

TYPICAL PROPERTIES

Appearance	Grey, crystalline powder
Melting Point	323° F. (162° C.)
Ash, %	0.05
Benzene Insolubles, %	0.05
% Dioctylphenothiazine	99
% Monooctylphenothiazine	0.5
% Phenothiazine	0.5
Solubility	Soluble in acetone, mod. soluble in toluene, insoluble in water.

HANDLING PRECAUTIONS

Normal handling precautions should be exercised. Avoid ingestion, eye contact, prolonged contact with skin and prolonged inhalation of dust.

STORAGE STABILITY

Keep in closed container; light will slowly darken material.

TOXICOLOGY

The oral LD_{50} for rats is greater than 5 gms/kg; not considered a skin or eye irritant.

PERFORMANCE DATA

Test: Modified Allison Test
Fluid: Pentaerythritol-based ester
Conditions: 425° F. (218° C.); 72 hrs., air agitation at 5.0 l/hr.; metal catalysts

ANTIOXIDANT	CONC., %	NEUT. NO. INCREASE	% VISCOSITY CHANGE	SLUDGE RATING
None	—	27.2	Gelled	Gelled
Phenothiazine	2	4.5	44.8	Heavy
NAUGALUBE 459	2	5.2	8.0	Nil
	WEIGHT CHANGE (Mgs)			
	Mg	**Fe**	**Cu**	**Ag**
None	384	106	4.9	2.8
Phenothiazine	1.6	0.9	4.9	1.8
NAUGALUBE 459	19.0	0.5	1.5	1.1

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TYPICAL PROPERTIES

	NAUGALUBE 438-R
Chemical Composition	alkylated secondary aromatic amine
Specific Gravity	0.97
Melt Range, °C.	99-101
Flash Point, °F.	390
Ash, %	.004
Color	beige
Form	solid
Viscosity, 100°F. SUS	—
210°F. SUS	—
Solubility	Soluble in most organic liquids, insoluble in water.
Solubility in petroleum oil @ 77°F., %	5.0
Storage Stability	Excellent
Availability	Commercial

Handling Precautions:

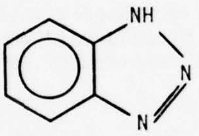
Normal handling precautions should be observed. Avoid prolonged or repeated skin contact. Avoid breathing dust or fumes.

BENZOTRIAZOLE - Photo Grade

Code: BT-PG Order Entry No.: X19 BT 5589
Synonym: 1,2,3-Benzotriazole

sherwin williams chemicals®
a division of *THE SHERWIN-WILLIAMS CO.*

technical bulletin 142



$C_6H_5N_3$

M.W. 119.12

PROPERTIES

	Specifications*	Typical Analysis
Appearance	White crystalline needles.	
Assay	98.0% min	99.5%
Appearance of 1% Solution	Essentially clear	Essentially clear
Residue After Ignition	0.5% max.	0.08%
Volatile Matter at 70°C	0.5% max.	0.08%
Identity Melting Point	98-99°C	98-99°C

*Meets requirements of American National Standard Institute specification PH4.204-1972. Methods of analysis are given in the specification.

USES

Photographic chemical--developer, anti-fogging agent and restrainer in gelatin emulsions. Also in other areas where light sensitive substances are useful. (See References).

TOXICITY	The oral LD_{50} in white rats is 560 mg per kg. Chemicals with values of this order are generally considered moderately toxic. Tests made on intact and abraded skin of rabbits showed no skin irritation.
SAFE HANDLING	Benzotriazole and its solutions are not serious industrial hazards provided that workers are properly instructed and adequately supervised in handling procedures. Where adequate ventilation is not available, approved respiratory and eye protection are required in dust laden areas.
AVAILABILITY	Readily available from stock. Package sizes, prices and other details of sale are stated in our latest Chemicals Price List.

REFERENCES

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sherwin
williams
chemicals®
P.O.Box 6520, Cleveland, O. 44101

TABLE I

SPECIFICATIONS OF EMERY LUBRICANT BASES

Specification	Emery 2910	Emery 2911	Emery 2957	Emery 2958	Emery 2960	Emery 2934	Emery 2932
Acid Value, Max.	0.2	0.2	0.2	0.2	0.02	0.08	0.10
Hydroxyl Value, Max.	3.0	2.0	2.0	2.0	3.0	3.0	3.0
Iodine Value, Max	- -	2.0	2.0	2.0	1.0	- -	- -
Flash Point, °F, Min.	400	300	400	400	430	480	460
Fire Point, °F, Min.		350	450	450	- -	- -	- -
Cloud Point, °F, Max.	-40	-40	-40	-40	-40	- -	-40
Pour Point, °F, Max.	-70	-90	-50	-75	-75	-65	-75
Viscosity, Cs.							
210°F, Min.	2.60	1.60	3.20	2.85	4.3	4.65-4.85	4.0
100°F, Max.	- -	- -	- -	- -	- -	22.0-24.0	- -
-40°F, Max.	- -	- -	1800	- -	- -	- -	5000
-65°F, Max.	6500	800	- -	7000	- -	- -	- -
*SOD Lead Corrosion, Mg/sq. in. 1 Hour, Max.	±4	- -	±4	±4	±4	No negative** values	No negative** values
*Oxidation Stability, 347°F Hours, Min.	100	- -	100	100	- -	- -	- -

---

*Contains 0.5% purified phenothiazine
0.1% Ethyl anti-oxidant 703

**Contains 0.5% purified phenothiazine

J. T. Baker Chemical Co. 4/29/77

Calcium Hydroxide, Powder
'Baker Analyzed'^{R} REAGENT
Suitable for Thin Layer Chromatography
Product No. 1372

Specifications

Assay ($Ca(OH)_2$)	95.0 % min.
Insoluble in HCl	0.03 % max.
Chloride (Cl)	0.05 % max.
Sulfur Compounds (as SO_4)	0.1 % max.
Heavy Metals (as Pb)	0.003 % max.
Iron (Fe)	0.05 % max.
Magnesium and Alkali Salts (as SO_4)	1.0 % max.
Suitability for TLC	passes test

FULLER'S EARTH FROM FLORIDIN CO.

florex®

Typical Chemical Analysis (Volatile Free Basis):

Si as SiO_2	66.21%
Al as Al_2O_3	11.71%
Fe as Fe_2O_3	4.02%
P as P_2O_5	0.99%
Ca as CaO	2.92%
Mg as MgO	9.70%
K as K_2O	1.07%
Other	3.38%

Note:

Although major constituents shown in the typical analysis are reported as oxides, they are actually combined as complex silicates in FLOREX.

Typical Physical-Properties

	RVM	LVM
Color	Gray	Tan
Free moisture (as produced), %	7	2
Combined moisture, %	9	6
pH	8	8
Surface area, m²/g	125	125
Specific gravity	2.5	2.5
Angle of repose, degrees (100/up and 200/up 30°)	31	31
Base exchange capacity (milliequivalents/100 g)	20	20
Pore volume, ml/g	0.514	0.524
Void space & porosity, %		
Grades up to 24/48	45	45
Grades 30/60 and finer	39	39
Bulk density, free fall, lbs./ft.³	34	34
Water Breakdown	Readily breaks down in water	Resists water break down

NACAR

ACTIVATED CARBON TECHNICAL DATA

TYPE G117

Specifications

Carbon tetrachloride activity, weight percent, minimum	70
Apparent density, packed, grams per cubic centimeter (ASTM D 2854)	0.27-0.32
Ash, total, weight percent, maximum (ASTM D 2866)	7
Iron content, weight percent Fe, maximum	0.10
Copper content, parts per million, maximum	20
Sulfur as sulfide	nil
Water soluble content, weight percent, maximum	4.0
HCl soluble content, weight percent, maximum	6.0
Moisture content, weight percent, maximum, as packed (ASTM D 2867)	7
Particle size, U.S. Sieve Series: (ASTM D 2862)	
On 12 mesh, weight percent, maximum	5.0
12 x 30 mesh, weight percent, minimum	90.0
Thru 30 mesh, weight percent, maximum	5.0

Properties

Surface area (BET), square meters per gram	1000-1100
Pore volume (N_2), cubic centimeters per gram	0.72-0.80
Specific heat at 15°C	0.24
pH of water extract	4.5-5.5

120172

NORTH AMERICAN CARBON
COLUMBUS, OHIO 43219

APPENDIX B

Conformance and Qualification Test Results for Reclaimed ATL-7069 and ATL-7071

ADDITIVE LEVELS FOR RECLAIMED OILS

	Conformance Tests		Qualification Tests	
Additives	ATL-7069 (Sample 1206148)	ATL-7071 (Sample 1206176)	ATL-7069 (Sample 1209025MN)	ATL-7071 (Sample 1209023AB)
tricresyl phosphate	2.0%	2.0%	2.0%	2.0%
4,4'-dioctyldiphenylamine	1.0%	2.2%	1.0%	1.0%
3,7-dioctylphenothiazine	1.0%	1.0%	1.0%	1.0%
benzotriazole	0.1%	0.1%	0.1%	0.1%
triphenyl phosphite	0.1%	0.1%	0.1%	0.1%
quinizarin	0.05%	0.05%	0.05%	0.05%
Antioxidant 703	0.1%	0.1%	0.1%	0.1%
Emery 2958	22%	0	0	13.7%

CONFORMANCE TEST RESULTS FOR RECLAIMED ATL-7069 (SAMPLE 1206148) AND ATL-7071 (SAMPLE 1206176)

	Specification	Results	
PHYSICAL AND CHEMICAL PROPERTIES		ATL-7069	ATL-7071
Total Acid Number	0.30 Max.	0.17	0.20
Viscosity, cs @ 210°F	3.0 Min.	3.1	3.1
Viscosity, cs @ 100°F	11.0 Min.	12.0	11.9
Pour Point, °F	-75.0 Max.	-95	-90
Flash Point (COC), °F	400.0 Min.	400°F	400°F
Evaporation, 6.5 hrs. @ 400°F			
Weight Loss, %	35.0 Max.	8.3	19.9
VISCOSITY STABILITY @ -65°F			
Original Oil, cs		10,589	10,855
After 3 hours, cs	13,000 Max.	10,325	10,974
Viscosity Change, %	6.0 Max.	-2.4	+1.1
TRACE SEDIMENT			
Precipitation mg/200ml	0.005 Max.	0.000	0.000
FOAMING CHARACTERISTICS			
75°F			
Volume after 5 min. aeration, ml	25 Max.	20	10
Volume after 1 min. settling period	0	0	0
200°F			
Volume after 5 min. aeration, ml	25 Max.	10	10
Volume after 1 min. settling period	0	0	0
75°F(after test at 200°F)			
Volume after 5 min. aeration, ml	25 Max.	20	10
Volume after 1 min. settling period	0	0	0
H ELASTOMER COMPATIBILITY, 168 Hrs. @ 158°F			
% Swell	12 - 35	26.5	24.1

	Specification	Results	
FA ELASTOMER COMPATIBILITY, 72 Hrs. @ 347°F		ATL-7069	ATL-7071
% Swell	2.0 - 25.0	+16.2	+17.3
Tensile Strength, % Change	50 Max.	+1.1	+6.5
Elongation, % Change	50 Max.	+19.7	+21.0
Hardness, Shore Durometer, No. Change	25 Max.	5	5
FS ELASTOMER COMPATIBILITY, 72 Hrs. @ 302°F			
% Swell	2.0 - 25.0	5.6	5.6
Tensile Strength, % Change	50 Max.	-13.8	-19.8
Elongation, % Change	50 Max.	-17.6	-17.6
Hardness, Point Change	25 Max.	-10	10
CORROSION AND OXIDATION STABILITY, 72 Hrs. @ 347°F			
Corrosion:			
Steel, mg/cm^2	±0.2	+0.014	-0.034
Silver, mg/cm^2	±0.2	-0.014	+0.014
Aluminum, mg/cm^2	±0.2	+0.007	-0.007
Magnesium, mg/cm^2	±0.2	+0.014	0.000
Copper, mg/cm^2	±0.4	-0.007	+0.041
Appearance of Metal Specimens:			
Pitting	None	None	None
Etching	None	None	None
Corrosion	None	None	None
Staining	Report	None	None
Oxidation:			
Viscosity @ 100°F, cs, Initial	Report	12.0	11.9
Viscosity @ 100°F, cs, Final	Report	13.1	12.9
Viscosity @ 100°F, cs, Change	Report	1.1	1.0
Viscosity @ 100°F, % Change	-5 to +15	9.2	8.4
Total Acid Number, Initial	Report	0.17	0.20
Total Acid Number, Final	Report	1.23	1.21
Total Acid Number, Change	2.0 Max.	1.06	1.01
Evaporation Loss, %	Report	0.2	0.2
Appearance	Report	Dark Brown	Dark Brown
LEAD CORROSION, 1 Hour @ 325°F			
Weight Change, mg/in^2	6 Max.	-0.3	-10.4

	Specification	Results	
SILVER AND COPPER CORROSION, 50 Hrs. @ 450°F		ATL-7069	ATL-7071
Silver Weight Change, mg/in^2	3.0 Max.	0.0	-0.1
Copper Weight Change, mg/in^2	3.0 Max.	-0.6	-4.4
DEPOSITION NUMBER			
Deposit Number	2.5 Max.	0.63	0.20
RYDER GEAR TEST			
Determinations, ppi	2440	2735	2780
WORKMANSHIP	Clear & Transparent	Yes	Yes
ACCELERATED STORAGE STABILITY @ 230°F			
Lead Weight Loss, mg/in^2			
48 Hours	25 Max.	3.0	12.3
168 Hours	150 Max.	61.4	94.2

TRACE ELEMENT CONTENT,[1] ppm

Oil Identification	Fe	Ag	Al	Cr	Cu	Mg	Ni	Pb	Si	Sn	Ti	Mo
Used ATL-7069	3.5	0.7	0	0	0.8	0	0.3	21	2	5.3	0.5	0.9
Reclaimed ATL-7069	0.7	0	0	0	0.5	0	0.1	0.1	0.7	6.9	0.5	1.7
Used ATL-7071	26	0.1	0	7.7	1.5	4.3	0.1	82	7.8	6.8	6.5	1.0
Reclaimed ATL-7071	0.4	0	0	0	0.4	0	0	0	2.8	3.4	0.3	0.8

---

[1] Trace element content determined as per MIL-L-7808G procedure.

QUALIFICATION TEST RESULTS FOR RECLAIMED ATL-7069 (SAMPLE 1209025 MN) AND ATL-7071 (SAMPLE 120923AB)

	Specification	Results	
PHYSICAL AND CHEMICAL PROPERTIES		ATL-7069	ATL-7071
Total Acid Number	0.30 Max.	0.22	0.20
Viscosity, cs @ 210°F	3.0 Min.	3.04	3.04
Viscosity, cs @ 100°F	11.0 Min.	12.0	11.7
Pour Point, °F	-75.0 Max.	-85°F	-80
Flash Point (COC), °F	400.0 Min.	400°F	420
Evaporation, 6.5 hours @ 400°F Weight Loss, %	35.0 Max.	19.8	10.0
VISCOSITY STABILITY @ -65°F			
Original Oil, cs		11,760	10,560
After 3 hours, cs	13,000 Max.	11,770	10,560
After 72 hours, cs	17,000 Max.	11,780	10,590
TRACE SEDIMENT			
Precipitation, mg/200 ml	0.005 Max.	0.000	0.000
FOAMING CHARACTERISTICS			
75°F			
Volume after 5 min. aeration, ml	25 Max.	20	20
Volume after 1 min. settling period	0	0	0
200°F			
Volume after 5 min. aeration, ml	25 Max.	20	20
Volume after 1 min. settling period	0	0	0
75°F			
Volume after 5 min. aeration, ml	25 Max.	20	20
Volume after 1 min. settling period	0	0	0
FOAMING CHARACTERISTICS, METHOD 3213			
Foam volume, ml	100 Max.	50	50
Collapse time, sec	60 Max.	11	50

	Specification	Results	
CORROSION AND OXIDATION STABILITY, 72 HOURS @ 347°F		ATL-7069	ATL-7071
Corrosion:			
Steel, mg/cm^2	±0.2	-0.007	0.000
Silver, mg/cm^2	±0.2	-0.069	-0.027
Aluminum, mg/cm^2	±0.2	-0.027	0.000
Magnesium, mg/cm^2	±0.2	0.000	-0.021
Copper, mg/cm^2	±0.4	-0.041	-0.034
Appearance of Metal Specimens:			
Pitting	None	None	None
Etching	None	None	None
Corrosion	None	None	None
Staining	Report	None	None
Oxidation:			
Viscosity @ 100°F, % Change	-5 to +25	+10.0	+7.7
Total Acid Number, Change	2.0 Max.	0.93	1.03
Evaporation Loss, %	Report	1.0	1.1
Appearance	Report	Dk. Br.	Dk. Br.
LEAD CORROSION, 1 HOUR @ 325°F			
Weight Change, mg/in^2	6 Max.	-0.1	0.0
SILVER AND COPPER CORROSION, 50 HOURS @ 450°F			
Silver Weight Change, mg/in^2	3.0 Max.	-0.1	-3.7
Copper Weight Change, mg/in^2	3.0 Max.	-3.4	0.0

	Specification	Results	
SWELLING OF SYNTHETIC H RUBBER, 168 Hours @ 158°F		ATL-7069	ATL-7071
Swell, %	12.0 - 35.0	34.4	31.4
SWELLING OF SYNTHETIC FA RUBBER, 72 Hours @ 347°F			
% Swell	2.0 - 25.0	22.0	18.2
Tensile Strength, % Change	50 Max.	-8.9	+1.1
Elongation, % Change	50 Max.	+41.0	+14.8
Hardness, No. Change	25 Max.	5	5
SWELLING OF SYNTHETIC FS RUBBER, 72 Hours @ 302°F			
% Swell	2.0 - 25.0	6.1	5.5
Tensile Strength, % Change	50 Max.	-39.2	-39.7
Elongation, % Change	50 Max.	-19.1	-30.9
Hardness, No. Change	25 Max.	5	-5
SWELLING OF SYNTHETIC QVI RUBBER, 72 Hours @ 302°F			
% Swell	2.0 - 30.0	18.4	17.2
Tensile Strength, % Change	50 Max.	-16.6	-32.2
Elongation, % Change	50 Max.	-2.2	-4.5
Hardness, No. Change	20 Max.	-15	-15
ACCELERATED STORAGE STABILITY @ 230°F			
Lead Wt. Loss, mg/in^2			
48 Hours	25 Max.	17.5	6.3
168 Hours	150 Max.	71.3	71.3
DEPOSITION NUMBER			
Deposit Rating	1.5 Max.	0.28	0.39
Viscosity Change, %	Report	18.3	16.2
T.A.N. Change	Report	2.98	4.56
RYDER GEAR TEST			
8 Determination, ppi	2200 Min.	2526	2384

	Specification	Results	
CORROSION AND OXIDATION STABILITY, 96 HOURS @ 347°F		ATL-7069	ATL-7071
Corrosion:			
Steel, mg/cm^2	±0.2	+0.060	-0.109
Silver, mg/cm^2	±0.2	-0.069	+0.051
Aluminum, mg/cm^2	±0.2	+0.109	+0.010
Magnesium, mg/cm^2	±0.4	-0.028	-0.008
Bronze AMS4616, mg/cm^2	±0.4	+0.050	+0.006
Titanium, mg/cm^2	±0.2	+0.069	-0.080
M-50 Steel, mg/cm^2	±0.2	+0.010	+0.012
Appearance of Metal Specimens:			
Pitting	Report	None	None
Etching	Report	None	None
Corrosion	Report	None	None
Staining	Report	None	None
Oxidation:			
Viscosity @ 100°F, % Change	-5 to +15	10.8	7.7
Viscosity @ 210°F, % Change	Report	10.0	6.7
Total Acid Number, Change	2.0 Max.	1.13	0.98
Evaporation Loss, %	Report	5.4	4.9
Sludge, Volume, %	Report	1.0	1.4

	Specification	Results	
		ATL-7069	ATL-7071
CORROSION & OXIDATION STABILITY, 48 Hours @ 392°F, MIL-7808H			
Corrosion:			
Steel, mg/cm^2	±0.2	-0.004	-0.089
Silver, mg/cm^2	±0.2	-0.040	-0.061
Aluminum, mg/cm^2	±0.2	-0.050	-0.069
Magnesium, mg/cm^2	±0.4	-0.002	-0.119
Bronze, AMS4616, mg/cm^2	±0.4	-0.040	-0.069
Titanium, mg/cm^2	±0.2	0.000	-0.065
M-50 Steel, mg/cm^2	±0.2	-0.059	-0.063
Appearance of Metal Specimens:			
Pitting	Report	None	None
Etching	Report	None	Mg.
Corrosion	Report	None	None
Staining	Report	None	None
Oxidation:			
Viscosity @ 100°F, % Change	-5 to +25	+14.1	10.3
Viscosity @ 210°F, % Change	Report	10.0	6.7
Total Acid Number, Change	4.0 Max.	2.50	2.83
Evaporation Loss, %	Report	1.3	1.5
Sludge, Volume, %	Report	1.0	2.3

	Specification	Results	
		ATL-7069	ATL-7071
CORROSION AND OXIDATION STABILITY, 96 HOURS @ 392°F			
Corrosion:			
Steel, mg/cm^2	Report	-0.010	-0.079
Silver, mg/cm^2	Report	-0.163	-0.044
Aluminum, mg/cm^2	Report	-0.026	-0.015
Magnesium, mg/cm^2	Report	0.000	-0.026
Bronze AMS4616, mg/cm^2	Report	-0.188	-0.093
Titanium, mg/cm^2	Report	-0.036	-0.010
M-50 Steel, mg/cm^2	Report	-0.004	-0.040
Appearance of Metal Specimens:			
Pitting	Report	None	None
Etching	Report	None	None
Corrosion	Report	None	None
Staining	Report	None	None
Oxidation:			
Viscosity @ 100°F, % Change	Report	34.2	40.2
Viscosity @ 210°F, % Change	Report	26.7	26.7
Total Acid Number, Change	Report	9.83	16.33
Evaporation Loss, %	Report	6.3	8.5
Sludge, Volume, %	Report	1.8	3.3

Oxidation: 96 Hours @ 347°F	Specification	ATL-7069								ATL-7071							
		16	24	40	48	64	72	88	96	16	24	40	48	64	72	88	96
Viscosity @ 100°F, % Change	-5 to +15	5.0	7.0	8.3	8.3	9.2	9.2	10.8	10.8	2.6	6.0	6.0	6.8	7.7	7.7	7.7	7.7
Viscosity @ 210°F, % Change	Report								10.0								6.7
Total Acid Number, Change	2.0 Max.	0.28	0.40	0.62	0.68	0.78	0.84	0.96	1.13	0.30	0.36	0.52	0.58	0.80	0.86	0.98	0.98
Evaporation Loss, %	Report								5.4								4.9
Sludge, Volume, %	Report								1.0								1.4

Oxidation: 96 Hours @ 392°F	Specification	ATL-7069								ATL-7071							
		16	24	40	48	64	72	88	96	16	24	40	48	64	72	88	96
Viscosity @ 100°F, % Change	Report	10.0	12.5	15.0	15.0	20.8	22.5	32.5	34.2	8.5	8.5	12.0	12.8	20.5	24.8	37.6	40.2
Viscosity @ 210°F, % Change	Report								26.7								26.7
Total Acid Number, Change	Report	1.40	1.64	2.42	2.70	4.04	5.10	7.92	9.83	1.54	1.88	3.50	4.00	8.60	10.72	14.84	16.33
Evaporation Loss, %	Report								6.3								8.5
Sludge, Volume, %	Report								1.8								3.3

BEARING DEPOSITION TEST SUMMARY
Test Number 48-272

Sample - Reclaimed ATL-7069
(Rig No. I)

DEPOSITS	
End Cover	0.0
Spacer & Nut	12.0
Heater Front	26.7
Heater Rear	52.8
Seal Plate	6.0
Bearing	40.5
OVERALL RATING	23.0

SLUDGE	
Inlet Screen	0.095
Outlet Screen	0.177
TOTAL	0.272

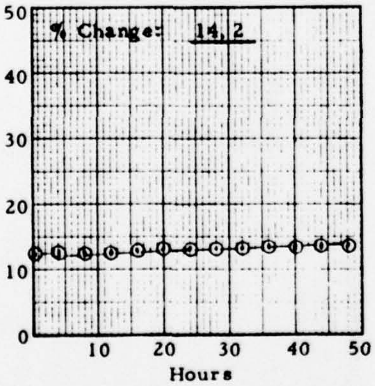
OIL CONSUMPTION, ml/hr	27.5

SUMP*	
Sides	Clean
Bottom	Clean

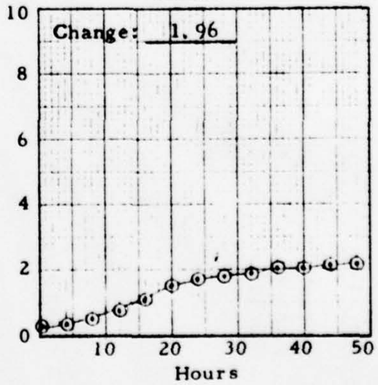
* Not included in the overall rating above.

METALS	
Aluminum	-0.040
Titanium	-0.030
Silver	-0.079
Steel	-0.059
M-50 Steel	-0.099
Bronze Alloy	-0.050
Waspoly	-0.026

VISCOSITY



T.A.N.



BEARING DEPOSITION TEST SUMMARY
Test Number 48-273

Reclaimed ATL-7071
(Rig No. 1)

DEPOSITS	
End Cover	3.0
Spacer & Nut	14.0
Heater Front	28.8
Heater Rear	48.6
Seal Plate	6.0
Bearing	45.5
OVERALL RATING	28.5

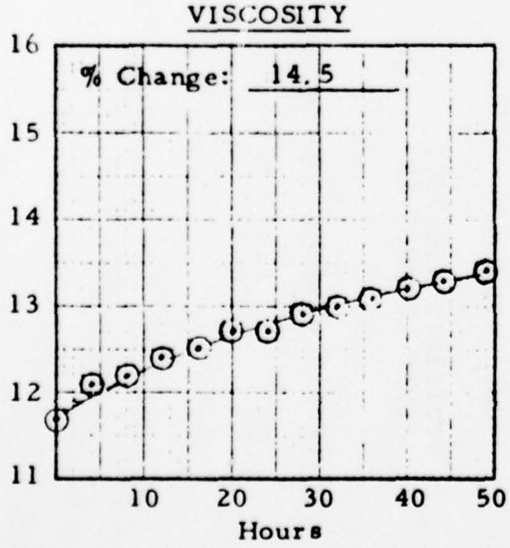
SLUDGE	
Inlet Screen	0.088
Outlet Screen	0.129
TOTAL	0.217

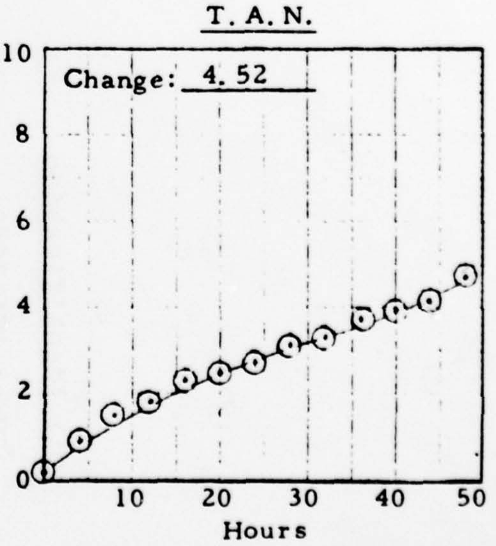
OIL CONSUMPTION, ml/hr 21.3

SUMP*	
Sides	Clean to Light Varnish
Bottom	Clean to Light Varnish

* Not included in the overall rating above.

METALS	
Aluminum	+0.065
Titanium	-0.040
Silver	+0.085
Steel	+0.020
M50 Steel	+0.050
Bronze Alloy	+0.044
Waspoly	+0.053

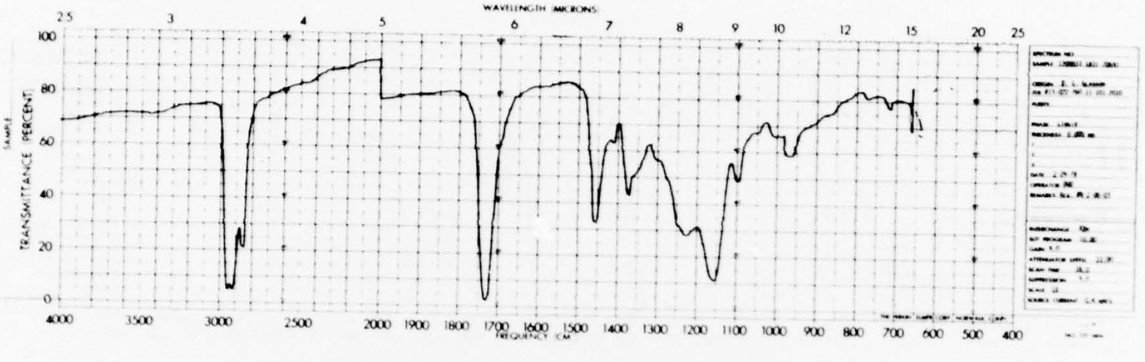




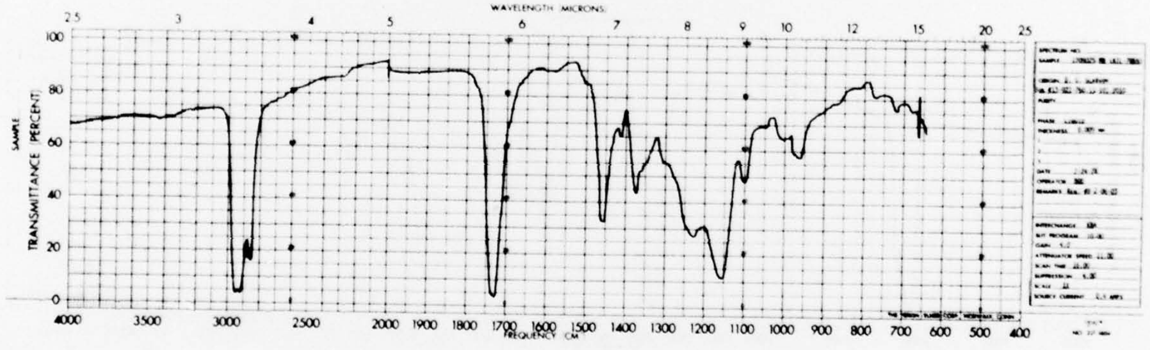
TRACE ELEMENT CONTENT[1], ppm

Oil Identification	Fe	Ag	Al	Cr	Cu	Mg	Ni	Pb	Si	Sn	Ti	Mo
Used ATL-7069	3.5	0.7	0	0	0.8	0	0.3	21	2	5.3	0.5	0.9
Reclaimed ATL-7069 (MRC 1209025MN)	0	0	0	0	0.3	0	0.4	0	0.6	6.6	0.8	0.1
Used ATL-7071	26	0.1	0	7.7	1.5	4.3	0.1	82	7.8	6.8	6.5	1.0
Reclaimed ATL-7071 (MRC 1209023 AB)	0	0	0	0	0.3	0	0.1	0	0.6	7.2	0.8	0

[1] Trace element contract determined as per MIL-L-7808G procedure.

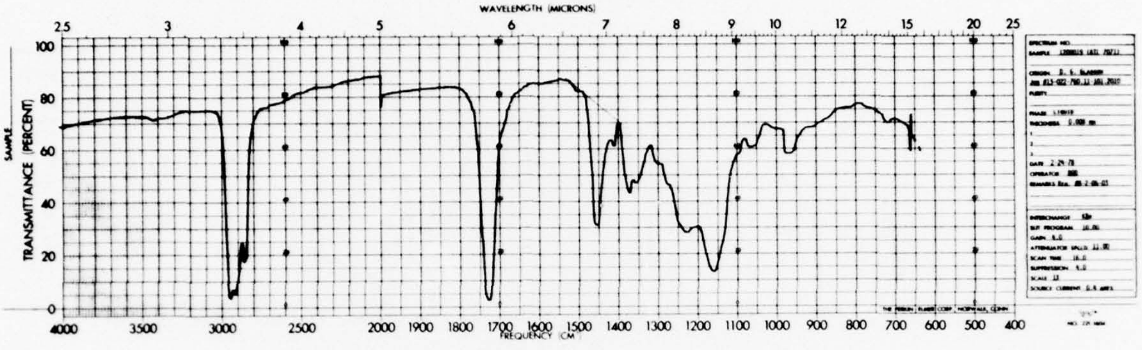


Reclaimed Base Stock

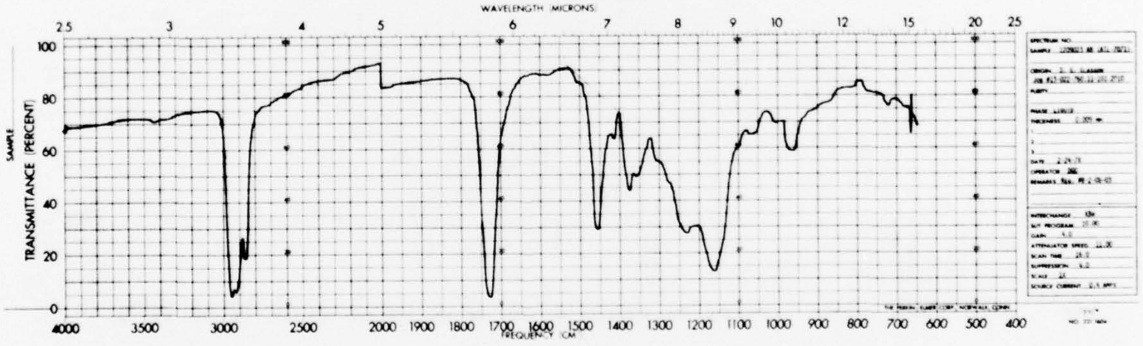


Reclaimed Oil

Infrared Spectra of ATL-7069



Reclaimed Base Stock



Reclaimed Oil

Infrared Spectra of ATL-7071

APPENDIX C

Heat of Vaporization

The heat of vaporization (ΔH_v) was required for use in estimating the cost of distillation of used synthetic ester oils. The expected accuracy of the cost estimation was not sufficient to warrant the time and cost of experimentally measuring ΔH_v. Therefore, an estimate of ΔH_v was obtained by use of the following equation where P_1 is the vapor pressure at temperature T_1 and P_2 the vapor pressure at temperature T_2. The derivation of this equation can be found in reference 20.

$$\log \frac{P_1}{P_2} = \frac{\Delta H_v}{2.303R} \left(\frac{T_2 - T_1}{T_2 T_1}\right)$$

The vapor pressure vs temperature data obtained from an AFAPL study of volatility characteristics of MIL-L-7808G oils (ref. 21) were plotted and extrapolated to the required boiling range to obtain ΔH_v for six MIL-L-7808 oils. These plots are shown in Figure C-1. The heats of vaporization calculated for each oil ranged from 25 to 50 gm-cal/gm. These data are in the same range as those reported in the literature for ethyl esters of fatty acids (ref. 22) and other lower molecular weight esters (ref. 23). The actual value of ΔH_v used in calculating the cost of distillation was 50 gm-cal/gm. This suggests that the calculated distillation cost is nearer a maximum than a minimum cost.

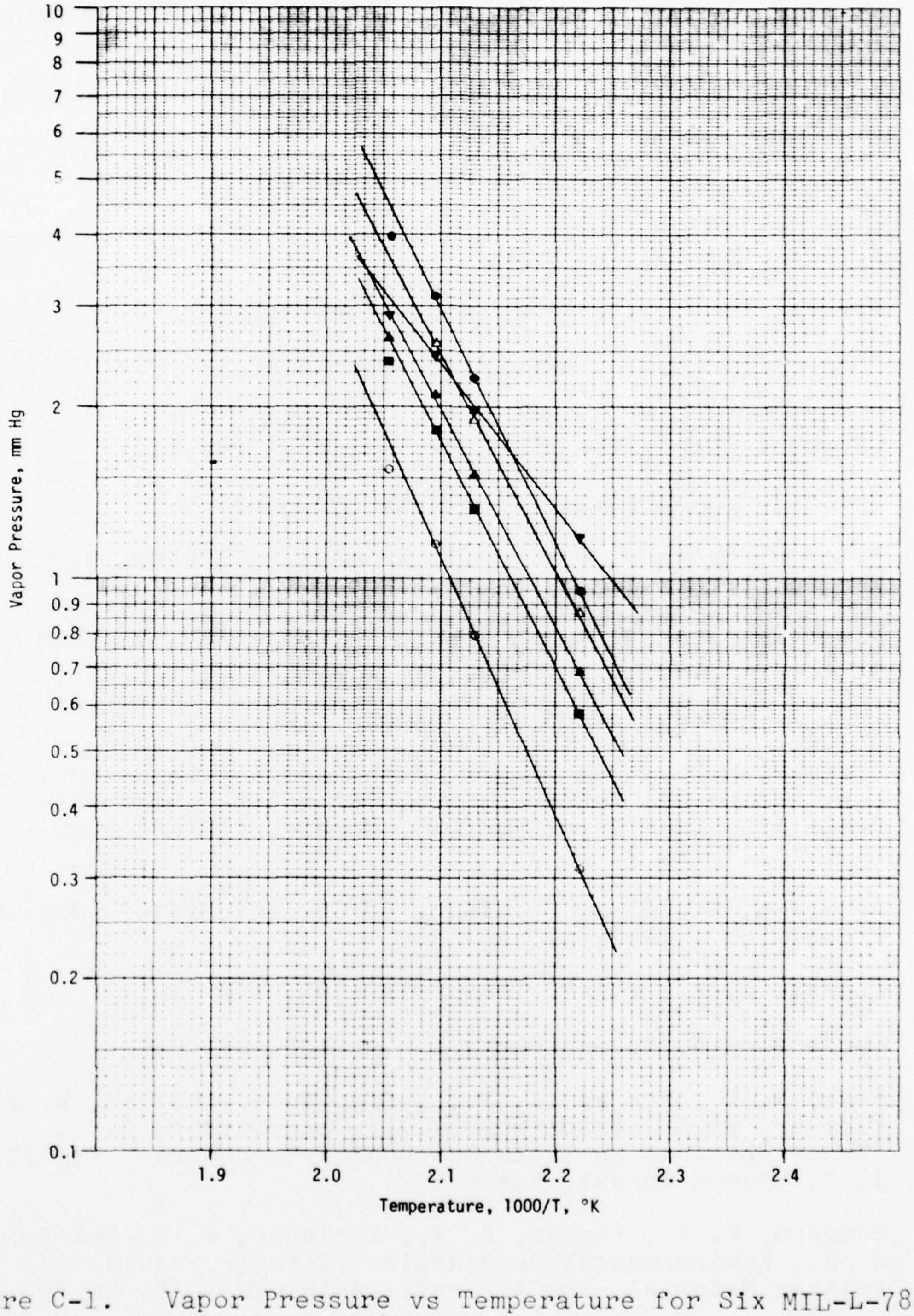


Figure C-1. Vapor Pressure vs Temperature for Six MIL-L-7808 Oils (ref. 21)

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