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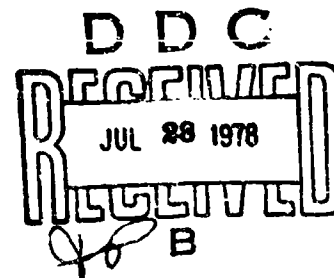
LEVEL II

**DEGRADATION STUDIES OF A
TRIMETHYLOLPROPANE TRIHEPTANOATE
LUBRICANT BASESTOCK**

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**AIR FORCE AERO PROPULSION LABORATORY
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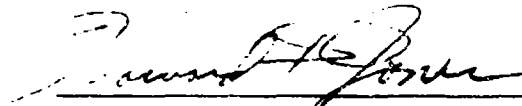
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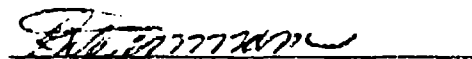
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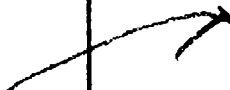
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included elucidation of the chemical processes involved in fluid deterioration, particularly as related to the formation of deposits. Reactants and products were measured by various analytical techniques, principally gas chromatography, gas chromatography/mass spectrometry, and X-ray fluorescence spectrometry. A literature search pertinent to the chemistry of synthetic, ester-base lubricants and methods of chemical analysis of such lubricants is also presented.



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PREFACE

This interim technical report was prepared by the Mobile Energy Division of Southwest Research Institute (SwRI). The effort was sponsored by the Air Force Aero Propulsion Laboratory (AFAPL), Air Force Systems Command, Wright-Patterson AFB, Ohio, under Contract No. F33615-76-C-2020 for the period 2 February 1976 to 30 September 1977. The work herein was accomplished under Project 3048, Task 304806, Work Unit No. 30480687, Mechanism of Turbine Engine Lubricant Deposition, with Messrs. L. J. DeBrohun, H. A. Smith, and P. W. Centers, AFAPL/SFL, as Project Engineers. Mr. J. P. Cuellar, Jr. of Southwest Research Institute was technically responsible for the work. The technical contributions of Dr. G. E. Fodor and Messrs. F. M. Newman, C. F. Rodriguez, and L. L. Stavinoha of Southwest Research Institute are acknowledged.

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INTRODUCTION

Commercially synthesized organic esters serve as the basestock for formulated lubricants currently used for main engine lubrication in virtually all gas turbine powered aircraft, both military and commercial. Two ester classes are predominant in such lubricant formulations: (1) dibasic acid esters formed via esterification of dibasic fatty acids and monohydric alcohols, and (2) neopentyl polyol esters of monobasic fatty acids and polyhydric alcohols. Frequently, to enhance rheological properties, blends of various ester types are employed. In the case of the polyol esters particularly, mixtures of esterification acids of varying chain length may also be used for the same purpose. Both ester classes utilize selected additives to achieve improved performance in properties such as oxidation stability, sludge dispersancy, foaming, and load-carrying capacity.

After some 30 years of use, study, and continuing improvement, it is understandable that turbine engine aircraft lubricants in present service generally provide satisfactory and reliable performance. Upgrading of lubricant formulations, lubricant specifications, and engine designs has been responsible for achievement of this performance level. Opposing this improvement trend has been the rise in engine operating temperatures due to increased aircraft speeds or, in recent years, increased inlet air temperatures to boost engine efficiency. Thus, research to define and evaluate lubricant performance properties continues. Investigation concerns the suitability of present fluids for current or future engine designs, as well as the promise of newly introduced lubricant formulations.

Of the numerous performance requirements which must be met by a lubricant formulation, deposition tendency is perhaps the most critical. The deleterious effect of lubricant deposits formed in the aircraft engine is manifested by plugging of lubricant jets and filters; malfunctioning of pumps, seals, and bearings; and accompanying increases in maintenance costs. Deposits result from thermal and/or oxidative breakdown of the lubricant formulation and are formed, primarily, in high-temperature engine zones which receive only indirect lubricant wetting, i.e., areas subjected to thin lubricant films.

The overall objective of this investigation is to examine and define the mechanisms involved in the process of deposition by ester-base lubricants. Experimental work utilized a rotating cylinder device, subsequently described in detail, for the formation of thin (0.004 in.) lubricant films under conditions of controlled temperature and atmosphere. The program schedule calls for studies of a selected polyol ester basestock and a diester basestock, both with and without additives. This interim report deals only with research on an uninhibited polyol ester, trimethylolpropane triheptanoate. Degradation/deposition experiments with this basestock included studies of thermal (inert atmosphere) and oxidative (air atmosphere) stability, using both dry and moist atmospheres for each type of environment. Various chemical analyses were employed to quantitatively and, where possible, qualitatively monitor the reactants and products involved in the deterioration

of the ester. The principal analytical techniques used for this purpose were gas chromatography and combined gas chromatography/mass spectrometry. Values for the energy of activation were also derived from the oxidation tests on the ester. These data were determined from oxygen consumption rates as a function of lubricant film temperature.

One of the initial tasks of this study was the conduct of a literature search pertaining to the analysis and chemistry of ester-base turbine lubricants. The findings of this search are also presented herein.

LITERATURE SEARCH

Objective

The objective of this search, completed in June 1976, was to accumulate a literature reference list pertinent to the chemistry of synthetic, ester-base fluids intended for use as gas turbine engine lubricants, and methods of chemical analysis of such lubricants. The findings of the search, where applicable, would be used in the formulation of lubricant degradation schemes related to the formation of lubricant deposits. Lubricant analytical procedures were sought which might have application in following chemical changes occurring in the deposition process.

Reference Sources

All work dealing with the chemistry of synthetic lubricants may be separated into two categories: 1) work sponsored by various Government agencies and described in appropriate technical reports, and 2) studies supported by private industry and conducted, invariably, within the sponsoring organization's own laboratories.

Information sources related to the first category of work were the Defense Documentation Center (DDC) and the National Technical Information Service (NTIS). Bibliographies from each of these sources were obtained and copies of pertinent reports not already on hand were ordered. Bibliography requests to both DDC and NTIS were submitted with the following descriptions of the subject of interest:

Overall Subject

The chemistry of synthetic, ester-base lubricants and methods of chemical analysis of such lubricants.

Key words

Lubricants
Synthetic
Ester
Dibasic acid ester
Diester
Neopentyl polyol ester
Polyol ester

Chemistry of
Analysis of
Oxidation of
Thermal stability of
Stability of
Degradation of
Deterioration of
Formulation of

Note: Lubricant type refers, almost exclusively, to lubricants employed in aircraft gas turbine (jet) engines.

Two report bibliographies were received from DDC. One compilation, entitled "Chemistry of Synthetic Lubricants," contained 209 abstracts with the earliest report date being November 1950. The second DDC bibliography, with the broad title of "Synthetic Lubricants," contained 656 abstracts with the earliest report date being January 1944. The literature search received from NTIS was entitled "Synthesis and Analysis of Ester Base Lubricants" and included 35 references. This compilation apparently covered the period of 1965 onward.

The primary information source for industrially-sponsored work in this field was Chemical Abstracts published by the American Chemical Society. This source was searched for the period of 1945 to June 1976. Due to possible changes in indexing criteria over this period of time, all subheadings under the principal headings of "Lubricants" and "Lubricating Oils" were scanned for subjects of interest.

The number of pertinent references obtained in the search of Chemical Abstracts was small. References found under the subject headings of interest were frequently patent descriptions concerned with the synthesis of specialized lubricants. It would appear that research by private industry in this area does not normally appear in the open literature because of proprietary considerations. It is conceivable that turbine engine lubricant formulations intended for large-scale production are not even covered by patents, since the complexity of the fluids and additives would probably ensure against full identification and duplication by others.

Development Work

Although esters had been previously used in the plastics industry, the first production of significant quantities of esters intended for use as lubricants is believed to have been carried out by the Germans during World War II. The fluids served as a much sought after supplement to Germany's dwindling petroleum resources. Immediately following the war, research on synthetic diester lubricants in the United States accelerated considerably.

Some of the earliest work^(1,2) in this country on the properties and possible applications of diester lubricants was performed by the Naval Research Laboratory (NRL). This work examined the effects of chain length and branching, concentrating on four primary dibasic acids: azelaic, adipic, glutaric, and sebacic. From this and subsequent investigations, a dibasic acid ester evolved which has been referred to as the "original ester"—di(2-ethylhexyl) sebacate. This ester was extensively employed as the basestock in early lubricant formulations qualified under Military Specification MIL-L-7808.

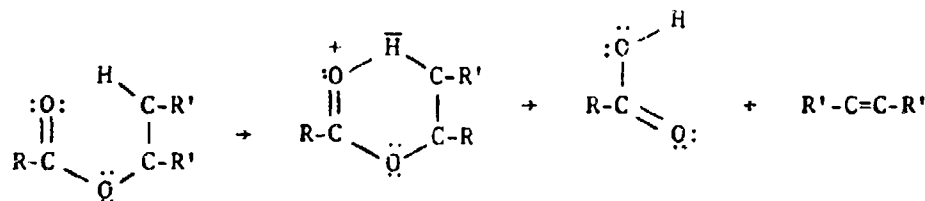
In the search for ester lubricant basestocks of improved oxidative, thermal, and hydrolytic stability, several investigators noted the superior stability exhibited by esters which lacked any hydrogen atoms on the beta-carbon of the alcohol moiety, as typified by neopentyl polyol esters. McTurk⁽³⁾ referred to such compounds as "dense-center esters." Several other workers,^(4,5,6,7) while primarily engaged in exploring the performance properties of the diesters, also reported the superior stabilities of the hindered type esters. Barnes and Fainman⁽⁸⁾ discussed the probable explanation for the improved thermal stability of neopentyl polyol esters and presented results on the physical properties and lubricating capabilities of numerous variations of the esters.

The advantages of the neopentyl polyol esters, coupled with some compromise in low-temperature flow properties, formed the basis for issuance of Military Specification MIL-L-23699 in 1963. Basestocks qualified under this specification are believed to be confined to esters of aliphatic monocarboxylic acids of approximately C₄ to C₁₀ chain length and three neopentyl polyols: trimethylolpropane, pentaerythritol, and dipentaerythritol. The finished basestock may contain one or more of these polyols each esterified with a mixture of acids to achieve some optimization of low-temperature rheological properties.

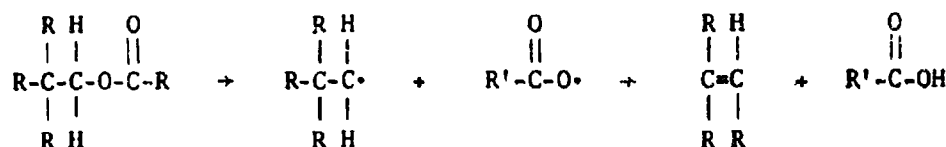
Mechanisms of Degradation

Three separate, but not necessarily independent, mechanisms of ester degradation may be identified. These are pyrolysis (thermal degradation), oxidation, and hydrolysis. Relative to the first two mechanisms, work on the mode of ester hydrolysis has received lesser attention.

The thermal breakdown of esters possessing a beta-hydrogen in the alkyl group, such as diesters, proceeds by a cyclic mechanism to yield the parent acid and a characteristic olefin. It is believed that the original explanation of the mechanism is attributable to Hurd and Blunck⁽⁹⁾ who employed the concept of a "hydrogen bridge" as illustrated here.



In the absence of a beta-hydrogen, such as with the polyol esters, cyclization is blocked and decomposition occurs via a free radical mechanism according to Bilger and Hibbert.⁽¹⁰⁾ The pyrolysis proceeds as follows:

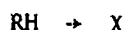


The superior thermal stability of the polyol esters relative to the diesters is attributed to the requirement for a higher initiation energy for the free-radical decomposition mode.

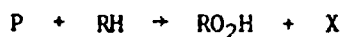
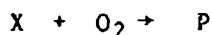
Postulated theories of the oxidative degradation of ester lubricants have been based on analogies with organic oxidation reactions. Murphy and coworkers(11) described a chain mechanism with hydroperoxide consumption as the rate-determining step. Rigg and Gisser(12) studied the oxidation behavior of several dialkyl adipate esters and proposed a two-part oxidation phenomenon consisting of an initial rate and a "steady" rate. A description of the course of the mechanism is quoted directly here: "Oxidation chains are initiated thermally with the formation of hydroperoxide. The hydroperoxide decomposes resulting in free radicals which initiate new oxidation chains. In the initial period, the amount of hydroperoxide which is decomposing is small and most of the oxidation is initiated by thermal means and the rate of oxygen consumption is proportional to the square of ester concentration. As hydroperoxide formation and decomposition continue, free radical initiation competes with thermal initiation, the reaction speeds up and, after a period of time, most of the oxidation chains are initiated by previously formed hydroperoxide. At this stage the rate is again constant and is proportional to the square root of ester concentration." The reaction formulas promulgated by Rigg and Gisser for the two oxidation stages were

Energy Chain

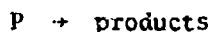
Initiation



Propagation

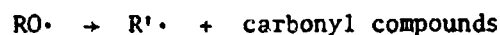


Termination

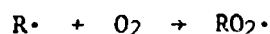
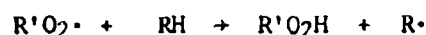
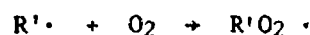


Free-Radical Chain

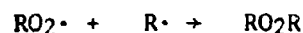
Branching



Propagation



Termination



where RH is the ester, X is an energy-rich ester molecule, and P is an energy-rich complex of the ester and oxygen.

Studies concerned with ester hydrolysis mechanisms have generally been oriented towards investigation of the effect of hydrolysis on lubricant storage stability at ambient temperature conditions. Work at NRL⁽¹³⁾ concluded that low-temperature deterioration of di(2-ethylhexyl) sebacate was due to hydrolysis of the ester which yielded the corrosive acid half ester. Hydrolysis was acid catalyzed by acid phosphates present in the antiwear additive, tricresyl phosphate, or resulting from its hydrolysis. The effectiveness of a low-temperature antioxidant, 2,6-di-tert-butyl- α -dimethylamino-4-methyl-phenol, was attributed to its action as an acid acceptor. Studies by Cuellar and Johnston⁽¹⁴⁾ served to confirm the concept of storage deterioration of ester fluids via hydrolysis, as opposed to oxidation, as well as the efficacy of the above antioxidant in retarding the process.

Chemical Analysis of Lubricants

Recent literature on techniques for chemical analysis of synthetic ester lubricants has generally been related to various spectroscopic or chromatographic procedures. Madison⁽¹⁵⁾ discussed the applicability of infrared and ultraviolet spectroscopy for detection of changes in synthetic basestocks and additives. The use of optical absorption (ultraviolet and visible), optical emission (fluorescence and phosphorescence), and nuclear magnetic resonance spectroscopy was investigated by Rodriguez⁽¹⁶⁾ for characterizing

ester lubricants. It was found that such techniques could be employed for batch control, and showed promise for the monitoring of lubricants in service. An infrared method for the detection of additives in MIL-L-7808 lubricants was described in a recent report by Wright.(17) Differential infrared spectra were employed in the detection of 15 additives with an ultimate sensitivity of 0.02 percent.

The development of a gas-liquid chromatographic method for the analysis of ester lubricant components and certain additives was described by Centers and Rubey.(18) The recommended column liquid phase was the silicone grease, OV-17. Davies(19) reported on a thin layer chromatography separation technique for antioxidants in a synthetic lubricant. Detection by densitometry using fluorescence or fluorescence quenching was used for quantitative determination of phenothiazine, dioctylphenothiazine, phenyl- α -naphthylamine, dioctyldiphenylamine, and benzotriazole. A similar study(20) was conducted at the Air Force Aero Propulsion Laboratory using thin layer chromatography and fluorescence spectroscopy for the qualitative and quantitative determination of MIL-L-7808 lubricant additives. Sniegowski(21) used gas-liquid chromatography in an evaluation of components found in neopentyl polyol ester basestocks. The fluids were analyzed for parent polyol content and identification of acyl groups. A later paper(22) by this author describes derivatization techniques, followed by gas-liquid chromatography, used in observing the oxidative breakdown of a neopentyl hexanoate. The study was aimed at establishing the susceptibility of the ester carbon-hydrogen bonds to oxidative attack.

Several analytical procedures were utilized by Klaus, Tewksbury, et al.(23) in following the products of thermal and oxidative deterioration of two typical ester basestocks, di(2-ethylhexyl) sebacate and trimethylolpropane triheptanoate. Temperature-programmed gas chromatography was the primary technique used in analysis of the degraded esters. Additionally, preparative gas chromatography, elution chromatography, and vacuum distillation were employed in the separation and concentration of some products. Identification methods included infrared spectroscopy, mass spectroscopy, and elemental carbon-hydrogen analysis.

Stavinoha et al.(24) described a sequence of analysis procedures and separation methods for the characterization of synthetic and hybrid lubricants. The recommended sequence for analysis of ester-base fluids utilized, initially, infrared spectrometry for general classification, followed by gel permeation chromatography for separation of high molecular weight additives. Parent ester acids and alcohols were obtained by hydrolysis, derivatized, and identified by gas chromatography.

A recent Russian article(25) dealt with the disintegration patterns of a family of sebacate esters as determined by electron bombardment mass spectrometry. The characteristic dissociation patterns were used to identify the composition of a technical sample of lubricant of unknown structure.

In the course of this search, technical personnel within several prominent organizations which supply ester-base lubricants were contacted. Their advice was sought as to the constitution of such fluids and appropriate

analytical techniques for characterization. Although no open-literature references could be cited, nor chemical data revealed, many of the personnel recommended gas chromatography/mass spectrometry as the most direct and informative method of analysis.

Experimental Work

Numerous studies have been conducted on the thermal and oxidative stability of ester basestock lubricants. However, the major portion of this effort has been devoted to investigation of the effects of environmental conditions on two lubricant properties, viscosity and acidity. Experimental work cited here will be confined to those references in which the chemical reactants or products of degradation were identified and/or measured.

Murphy and Ravner(26) studied the oxidative stability of several diesters in a program conducted at NRL. Absorbed oxygen was compared against the percent of oxygen recovered as peroxide, acid, carbon dioxide, and water. Incomplete oxygen recovery was attributed to the fact that no analysis was performed for alcohols, ketones, and aldehydes.

Klaus et al.(27) studied the thermal stability of diesters, polyol esters, and simple monobasic acid esters, with and without metal catalysts. In tests with di(2-ethylhexyl) sebacate, the extent of ester consumption and resulting products were determined by gas chromatography. Depending on test conditions, three or more of the following liquid products were found: 2-ethyl-1-hexene, polymerized 2-ethyl-1-hexene, the half-acid ester, sebacic acid, and secondary reaction products. A multiplicity of reaction components was obtained in thermal stability experiments with polyol esters. Employing trimethylolpropane triheptanoate, 13 individual components with boiling points less than that of the original ester were noted.

One of the most extensive studies concerned with the thermal and oxidative deterioration of typical esters was reported for a subsequent investigation by Klaus and colleagues.(23) The products of degradation were examined for di(2-ethylhexyl) sebacate and trimethylolpropane triheptanoate. Oxidation and thermal degradation of the diester gave four primary products boiling below the original ester. These were the olefin, 2-ethyl-1-hexene, 2-ethyl-1-hexanol, 2-ethylhexyl pelargonate, and mono-2-ethylhexyl sebacate. Findings suggested that the pelargonate ester is the probable product resulting from the free-radical oxidation reaction. Oxidation experiments with the polyol ester resulted in the formation of diesters and a series of smaller fragments. The primary diester was conjectured to be trimethylolpropane diheptanoate. A number of products boiling above 950°F appeared to be condensation products of the diesters. Thermal degradation of the neopentyl-type ester produced diesters, mono-esters, n-heptanoic acid and smaller fragments, and a group of compounds boiling above 950°F.

An interesting investigation of the effect of neopentyl polyol ester structure on lubricant deposition tendency was reported by D'Orazio et al. (28) A major effect, both quantitatively and qualitatively, was found for the acyl component in deposition tests using pentaerythritol, dipentaerythritol, and trimethylolpropane esters. Deposits increased with increasing acid chain length. The deposition trends established in tests with the neat basestocks agreed with those for fully inhibited lubricants. However, the use of inhibitors resulted in higher overall deposit levels.

ROTATING CYLINDER DEPOSITION TEST RIG AND PROCEDURES

Test Equipment

The device used in conducting oxidative and thermal stability experiments is known as the rotating cylinder deposition test rig. Details of the background and development of the device were originally described in an earlier report.(29)

A schematic of the test rig is shown in Figure 1, with an identifying parts list given in Table 1. To provide for firm mounting and alignment, the assembly is installed on a lathe bed, item 1. The cylinder, item 17, is of stainless steel (Type 304) construction, open at one end and closed at the opposite end by a hemispherical internal surface connected to the drive shaft, item 20. Nominal cylinder dimensions are 4-in. ID with a horizontal surface of 4-1/2 in. At its open end, the cylinder is sealed by means of a carbon-face bellows seal, item 15, and its housing, item 14.

Passing through the seal housing are the oil-in line, item 5, and three bare-wire thermocouples, item 6, which can be positioned in contact with the fluid film on the cylinder ID. To provide hermetic sealing and lateral movement, the thermocouple probes enter the cylinder section through small metal bellows, item 12. All three thermocouples are mounted on micrometer spindles, item 9, to allow for accurate positioning and referencing. Viewed from the cylinder open end, the thermocouple at 0° provides input to a West temperature controller which activates a pair of 8-in. clam-shell heaters (not shown) encircling the cylinder, seal housing, and exposed portion of the cylinder drive shaft. The thermocouple at 120° is used to measure film thickness. Initial film contact by this sensor is indicated by an abrupt temperature rise measured by a potentiometer. Continued insertion to contact with the cylinder wall is evidenced by an electrical resistance measurement between the thermocouple wire and the OD of the cylinder. The thermocouple sensor at the 240° position is used for precise indication of the film temperature. This sensor is a commercial microminiature element with a bead diameter of slightly less than 2 mils. Readout of this thermocouple is by electronic digital indicator.

The cylinder rig lubricant and atmosphere flow systems are illustrated in Figure 2. Both systems are sealed from the environment between the gas-in (air or N₂) and exhaust points. The unheated lubricant reservoir is of borosilicate glass, with provision for magnetic-bar stirring of the fluid. The lubricant-in pump is a Zenith precision gear pump driven by a variable speed motor, with a 10:1 speed reducer to permit stable operation. The lubricant-in line includes a 200-mesh screen filter and an electrically heated preheater coil just before the line enters the cylinder. Preheating of the test lubricant to match the target film temperature is necessary to avoid discontinuities of both film temperature and thickness on the cylinder wall. The lubricant-in temperature is monitored by a bare-wire thermocouple within the cylinder at the exit point of the oil-in line. The test lubricant is scavenged from a groove in the carbon seal counterface,

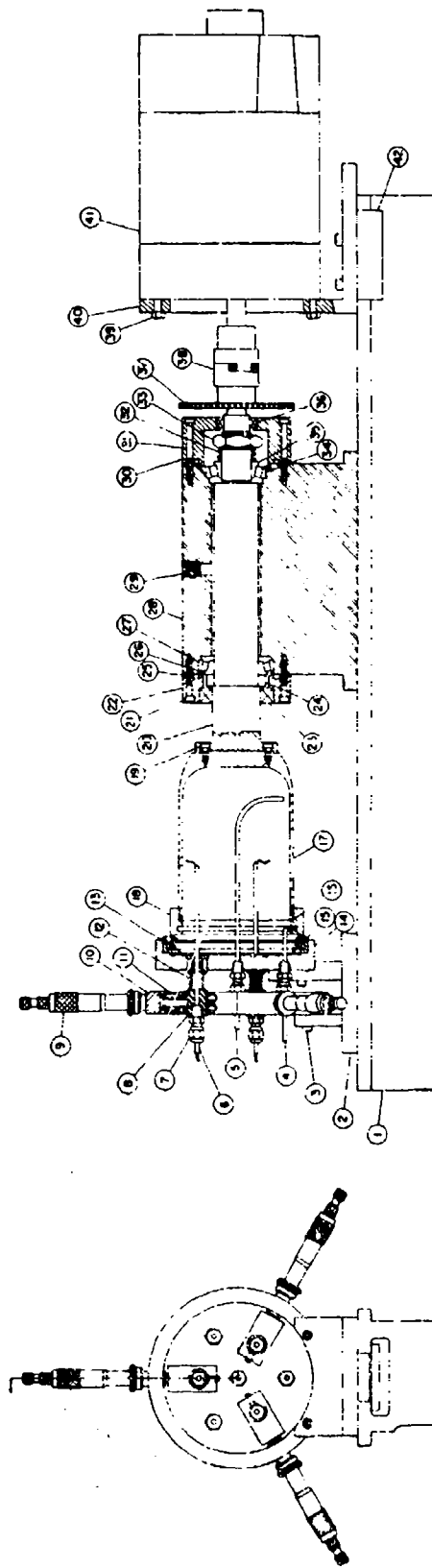


FIGURE 1. SCHEMATIC OF ROTATING CYLINDER RIG

TABLE 1. ROTATING CYLINDER
DEPOSITION RIG—PARTS LIST

Find No.	Part Name	Req'd
1	Lathe bed, Sears L9-1, Model No. 101.21400	1
2	Ring and seal bracket	1
3	1/4-20 x 3/4 hexagon socket cap screw	16
4	Scavenge oil line	1
5	Oil-in line	1
6	Thermocouple probe	3
7	Connector, Gyrolok 2 CMF-2-316	3
8	Connector adapter, SwRI A-3314-13	3
9	Micrometer, Starrett T262L-1	3
10	Micrometer ring, SwRI C-3314-15	1
11	Micrometer adapter, SwRI B-3314-16	3
12	Bellows, Metal Bellows Co. No. 60010-1	3
13	Bellows adapter, SwRI A-3314-18	3
14	Seal housing, SwRI C-3314-6	1
15	Seal, Sealol Inc. No. EJS-102573	1
16	Aluminum wire seal	1
17	Cylinder, SwRI B-3314-1	1
18	Seal counterface, SwRI B-3314-4	1
19	10-32 x 1/2 hexagon socket cap screw	4
20	Shaft, SwRI C-3314-39	1
21	10-24 x 1 hexagon socket cap screw	4
22	Front seal housing, SwRI B-3314-41	1
23	Seal, National No. 450194	1
24	Spacer, SwRI B-3314-42	1
25	O-ring, National No. 623008	2
26	Bearing cone assembly, Timken No. 13889	1
27	Bearing cup, Timken No. 13830	1
28	Bearing housing, SwRI C-3314-38	1
29	1/4-in. pipe plug	1
30	Rear seal housing, SwRI B-3314-40	1
31	10-24 x 1-3/4 hexagon socket cap screw	4
32	Spring	1
33	1-14 jam nut	1
34	Bearing cup, Timken No. 07196	1
35	Bearing cone assembly, Timken No. 07100	1
36	Seal, National No. 450567	1
37	Gear, 60-teeth	1
38	Coupling, Boston Gear No. FCR-FC9B-15	1
39*	3/8-16 x 1 hexagon head cap screw	4
40*	Motor bracket, SwRI D-3314-30	1
41*	Boston Gear, 1/3 HP DC shunt motor	1
42*	Motor bracket clamp	2

* Items not shown in layout schematic.

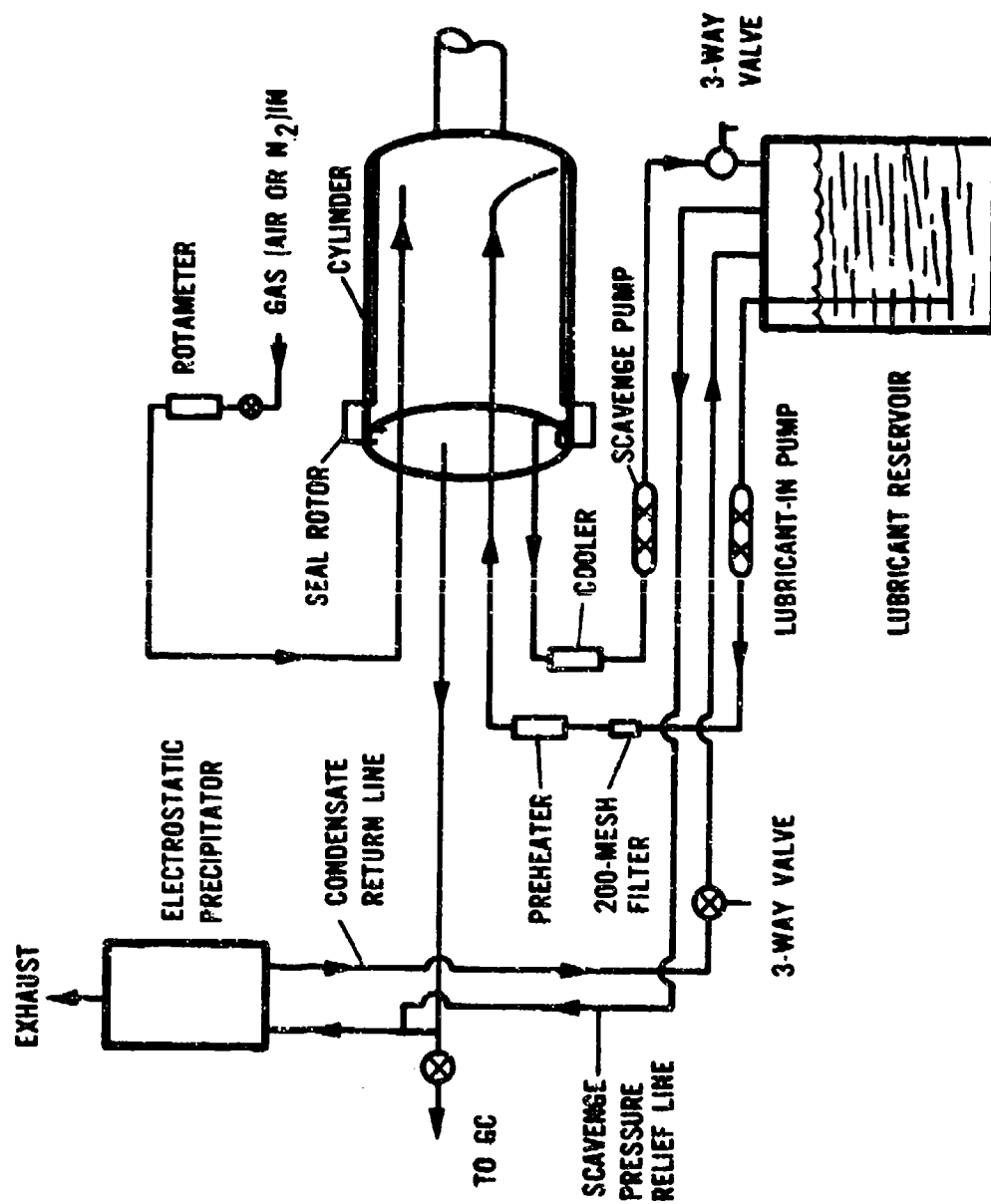


FIGURE 2. ROTATING CYLINDER R/L LUBRICANT/ATMOSPHERE FLOW SYSTEMS

item 18 (Fig. 1). The scavenge line passes immediately through a water-cooled heat exchanger (Fig. 2) to quench the degradation process. The scavenge pump, also a Zenith gear type, directs the fluid through a three-way sampling valve to the reservoir. Since over-scavenging is necessary, scavenged gas flows from the reservoir via a pressure relief line.

Gas (air or N_2) flow to the cylinder is metered through a line which exits nears the closed end of the cylinder. The effluent gas line may be sampled for gas chromatographic (GC) analysis of oxygen content. Downstream of this point, the effluent line from the cylinder and the scavenge pressure relief line merge and flow to an electrostatic precipitator for recovery of condensable vapors. By gravity feed, the condensate is continuously returned to the lubricant reservoir.

The precipitator is composed of a 12-in. section of 2-in. pipe with an insulated precipitator wire centrally mounted within the pipe. In operation, the pipe section is grounded and 9000 volts of negative polarity applied to the wire. The entire device is encased by a short section of 8-in. pipe to contain debris in the unlikely event of a dislodgement within the precipitator.

At the precipitator operating voltage, there was some concern that, under oxidative conditions, a corona discharge capable of ozone generation might occur. Since ozone is highly reactive, oxidative attack of lubricant vapors within the precipitator might occur. However, atmosphere sampling just inside the precipitator exhaust line by means of a highly sensitive ozone detector (0.01 ppm) showed no evidence of the gas.

An overall view of the cylinder rig installation is seen in Figure 3. The gas chromatograph for oxygen analysis of the rig effluent gas is located at the far left. The cylinder, covered with blanket insulation, and the cylinder drive motor are mounted on the table near the photograph center. The high-voltage precipitator is seen to the left and rear of the cylinder. Test lubricant pumps and the lubricant reservoir are mounted beneath the rig table. The rig instrumentation cabinet is at the center right. The bench at the far right supports a strip-chart recorder and digital integrator for recording and processing output from the GC.

Test Procedures and Conditions

Cylinder rig tests reported herein were conducted in multiples of 5 hr of test time. Normally, runs were performed with two-shift operation to obtain 15 hr of continuous run time per day. During a run, verification and recording of flow rates, temperatures, and film thickness were performed at 30-min intervals. Rotational speed of the cylinder was also recorded at this time, but speed adjustments were made, as required, to maintain the desired film thickness. Test lubricant samples (10 cm^3) were taken at 5-hr intervals. A sample of the condensate from the electrostatic precipitator was normally taken at the termination of each test. GC analysis of the cylinder effluent atmosphere was made each 30 min.



FIGURE 3. OVERALL VIEW OF THE ROTATING CYLINDER RIG AND INSTRUMENTATION

Certain test conditions, with values selected on the basis of prior work, (29) were held constant throughout the program. These were:

Film thickness	0.004 in.
Lubricant flow	10 cm ³ /min
Gas (air or N ₂) flow	100 l/hr
Lubricant charge	1000 cm ³

Test duration was generally dictated by the extent of lubricant deterioration. That is, runs were terminated if excessive increases in sample viscosity and/or neutralization number occurred. In all preliminary tests, fresh lubricant additions were made every hour to make up for fluid losses and intermediate samples. This procedure was stopped, commencing with Test No. 24, in order to avoid further complication of the degradation mechanism of the lubricant and interpretation of chemical analyses.

Three major test conditions were varied at two levels each as a subject of investigation in this study. These were atmosphere (oxidative or inert), atmosphere moisture (dry or moist), and film temperature (two levels). Thermal stability experiments were performed with inert gas (N₂) blanketing of the cylinder rig lubricant and atmosphere systems. Oxidative tests employed filtered air as the atmosphere. The presence or absence of moisture was investigated for both atmospheres. Dry atmosphere tests used a gas (air or N₂) of -95°F dewpoint or below. Moist atmosphere runs employed a gas with a moisture content of 10 ± 1 mg/liter. Two film temperature levels for each atmosphere type were selected on the basis of preliminary cylinder rig experiments. The thermal stability test series was conducted at film temperatures of 600° and 650°F; the oxidative test series was performed at film temperatures of 350° and 400°F.

In addition to the specification of test conditions of film temperature, film thickness, and total oil flow rate, calculations were made relative to average and total lubricant residence times. The average residence time was a calculated value for a "single pass" based on the average velocity of the lubricant, which in turn was based on lubricant flow rate and the cross-sectional area of the film. Thus, the following relationships apply:

$$t = l/v \quad (1)$$

$$v = Q/c \quad (2)$$

$$c = \pi/4 [d^2 - (d - h)^2]$$

where t = average residence time, sec

l = cylinder length, cm

v = average film velocity, cm/sec

Q = lubricant flow rate, cm³/sec, corrected for thermal expansion

c = film cross section, cm²

d = cylinder ID, cm

h = film thickness, cm

It is noted that the above relations are simplified in that boundary effects and, possibly, rotational effects are not considered. If one considers a unit volume of lubricant, the volume will be exposed to the high-temperature cylinder surface in one cycle for the duration of the average residence time, t. If it is assumed that each fluid increment has an equal probability of undergoing the same number of cycles during test, a total residence time may be calculated as follows:

$$E = \frac{TQt}{V} \quad (3)$$

where Q and t are as above and

E = total residence time, sec

T = test duration, sec

V = lubricant charge, cm³

In tests employing the oil makeup procedure each hour, there was a negligible change in the lubricant charge volume throughout the run. Thus, a value of 1000 cm³ was used for V in Eq. (3). Upon discontinuance of the oil makeup procedure, Eq. (3) was summed for each 5-hr test period using a mean volume indicated by oil loss measurement and correcting for intermediate lubricant sample withdrawals. Under these circumstances, it is observed that the total residence time per 5-hr period increases with test time. Similarly, unusually high oil losses (e.g., due to improper carbon-seal performance of a temporary nature) increase the total residence time, especially if the losses occur during the early hours of the test.

Deposit Rating Procedure

The deposit rating procedure used to describe numerically the deposits occurring within the cylinder was essentially that used in the 48-hr bearing deposition test⁽³⁰⁾ except that only one surface was inspected, viz., the surface of the cylinder ID.

A demerit rating number was selected to identify the different types and thicknesses of deposits present. Demerit values range from 0 to 20, defined as follows:

<u>Deposit Type</u>	<u>Demerit Rating Number</u>		
	<u>Light</u>	<u>Medium</u>	<u>Heavy</u>
Varnish	1	3	5
Sludge	6	7	8
Smooth carbon	9	10	11
Crinkled carbon	12	13	14
Blistered carbon	15	16	17
Flaked carbon	18	19	20

This demerit number was multiplied by a number from 0 to 10, corresponding to the percent of the area, 0 to 100 percent, covered by that deposit type. In the event that more than one type of deposit was present on the rated area, the deposit rating was then the total of the individual rating values necessary to account for 100 percent of the rated area. In any event, double ratings, such as sludge over varnish, were not used. The deposit rated was that which was visible without the removal of another deposit, except in the case of sludge over carbon. In such instances, the more severe deposit type was used in the rating calculations.

LUBRICANT ANALYSIS PROCEDURES

All intermediate and final lubricant samples taken during the cylinder rig tests were routinely analyzed for kinematic viscosity by ASTM Method D 445 and for neutralization number (total acid number) by ASTM Method D 664. All samples were likewise analyzed by GC, except for most preliminary tests.

GC was the principal tool used in following changes in the major ester component of the lubricant basestock, as well as other significant constituents in the new or used samples. The analysis was performed with an instrument equipped with a hydrogen flame ionization detector (FID). The conditions and column materials used with the procedure are summarized here:

Liquid phase	OV-17, 2%
Solid phase	Gas Chrom Q, 60/80
Column length	17 ft
Column tubing	0.125-in. OD x 0.093-in. ID S.S.
Column efficiency	1025 theor. plates
Oven temperature	
Initial	210°C
Final	320°C
Program rate	8°C/min
Injector temperature	320°C
Detector temperature	340°C
Carrier gas (He) flow	25 cm ³ /min
Sample size	0.2 µl
Internal standard	n-tridecane, 10 wt %
Injection procedure	On-column

Considerable effort was expended in the development of suitable GC conditions and techniques for analysis of lubricant samples. Because of the significant changes in the various basestock components seen in degraded lubricant samples, it was apparent that an internal standard GC method would be necessary to quantify individual components. However, anomalous results were obtained with the use of n-tridecane (n-C₁₃) as the internal standard. This material was chosen because of its relatively high boiling point (455°F), its noninterference with component peaks in the polyol ester basestock, and its availability in high-purity form. Experiments to establish ester response factors relative to n-C₁₃ repeatedly showed excessively low GC detector response for the ester.

It was suggested that the cause of the observed effect might be selective fractionation of the n-C₁₃ standard from the syringe needle upon injection of the n-C₁₃/sample mixtures into the high-temperature GC injector zone. This phenomenon was subsequently verified by analyses of n-C₁₃ mixtures in a fluid composed of oligomers of decene-1. The latter material spans a wide boiling range encompassing that of the ester basestocks and, relative to n-C₁₃, has a response factor of one. Thus, GC detector outputs could be directly related to weight concentrations. Multiple analyses of these

mixtures indicated that at a mixture concentration of 10 wt percent n-C₁₃, the injected concentration was approximately 11.5 percent. Similarly, a mixture concentration of 20 percent n-C₁₃ yielded an injected value of about 24.5 percent. Attempts to reduce these variations by different injection techniques, e.g., reducing the injected sample size, repumping the syringe plunger, holding the syringe needle for an extended period within the injector, etc., were all unsuccessful. However, it was found that for a given injection technique, the apparent n-C₁₃ concentration was highly consistent. As a consequence, it appeared feasible to apply a weight correction factor. This factor, coupled with the application of a dilution factor and a detector response factor, allowed for the use of n-C₁₃ as an internal standard for the GC analysis of used lubricant samples.

Initially, GC output was measured by use of a Vidar Autolab 6300 digital integrator, and GC peak concentrations were calculated using appropriate factors. Approximately mid-way through the program necessary instrumentation was provided by SWRI for access to a Hewlett-Packard 3354A laboratory data system. This is a computer controlled system for chromatographic data collection and analysis, and report generation via terminal printer. The availability of this system to the program significantly benefitted the effort with regard to the accuracy and speed of GC data processing.

Because of the unavailability of suitable standards and, in some cases, of full knowledge of chemical structure, a common GC response factor relative to n-C₁₃ was used for all basestock components. It should also be noted that component concentrations for degraded samples, reported as weight percent, are subject to some error since no attempt was made to achieve total recovery of gaseous degradation products such as moisture, CO, or CO₂. However, it is believed that the error introduced by the lack of a material balance determination would not be appreciable.

The TMP triheptanoate basestock, selected degraded samples thereof, and selected deposit samples were also analyzed by various other methods in an effort to characterize the chemical structure of these materials. Analytical techniques utilized for this purpose included infrared spectrophotometry, X-ray fluorescence spectrometry, gel permeation chromatography, reversed-phase high performance liquid chromatography, mass spectrometry, and combined gas chromatography/mass spectrometry (GC/MS). Analyses by GC/MS were performed with a Finnigan Model 3300F instrument interfaced with a computer for both instrument control and data acquisition and analysis. The GC procedures and conditions used with the GC/MS instrument were similar to those previously described for GC analysis of lubricant samples. The GC/MS instrument may be operated by use of an electron impact ionization source (70 electron volts) or a chemical ionization source (methane reagent gas), each equipped with a quadrupole mass filter. The GC/MS facility has access to the Cyphernetics spectra library known as the mass spectral search system (MSSS).

Selection of the analysis procedures used in this study was based principally on prior knowledge of the field and the findings of the literature search presented in a previous section of this report.

CHARACTERIZATION OF TRIMETHYLOLPROPANE TRIHEPTANOATE BASESTOCK

Two heptanoate samples, coded O-71-8 and O-76-5, were used in this study. The fluids are different batches of a commercially available material supplied by the same manufacturer, and contain no additives. No attempt was made to purify the samples before use since it was considered more realistic to employ a basestock of typical composition. The following basic properties were determined for the two samples:

	<u>O-71-8</u>	<u>O-76-5</u>
100°F Vis, cs	15.08	15.23
210°F Vis, cs	3.51	3.53
Neut. No., mg KOH/g	0.06	0.02
Gravity, °API/60°F	15.4	15.2

Lubricant O-71-8, available in only small quantity, was used solely for preliminary experiments to investigate appropriate cylinder rig test conditions. Following preliminary tests, further work was performed with O-76-5 which was supplied in drum quantity. All detailed characterization of the ester basestock was conducted on O-76-5.

Figure 4 shows a GC chromatogram of O-76-5 with the internal standard present. Some 33 distinguishable component peaks were consistently detected in the basestock. Of these, seven constituents (one a combination peak) indicated a concentration of 0.5 wt percent, or greater, and characterization studies concentrated on those seven. The combination peak is labeled peaks 1 and 1a in Figure 4. The latter is seen as a trailing shoulder on peak 1.

Infrared spectrometry examination of O-76-5 indicated appropriate absorption for the ester with evidence of free water or alcoholic functionality.

The alcoholysis and esterification procedure of reference 21 was used to identify parent alcohols present in O-76-5. The alcohols were determined by GC as valerates. The analysis yielded the results shown in Table 2.

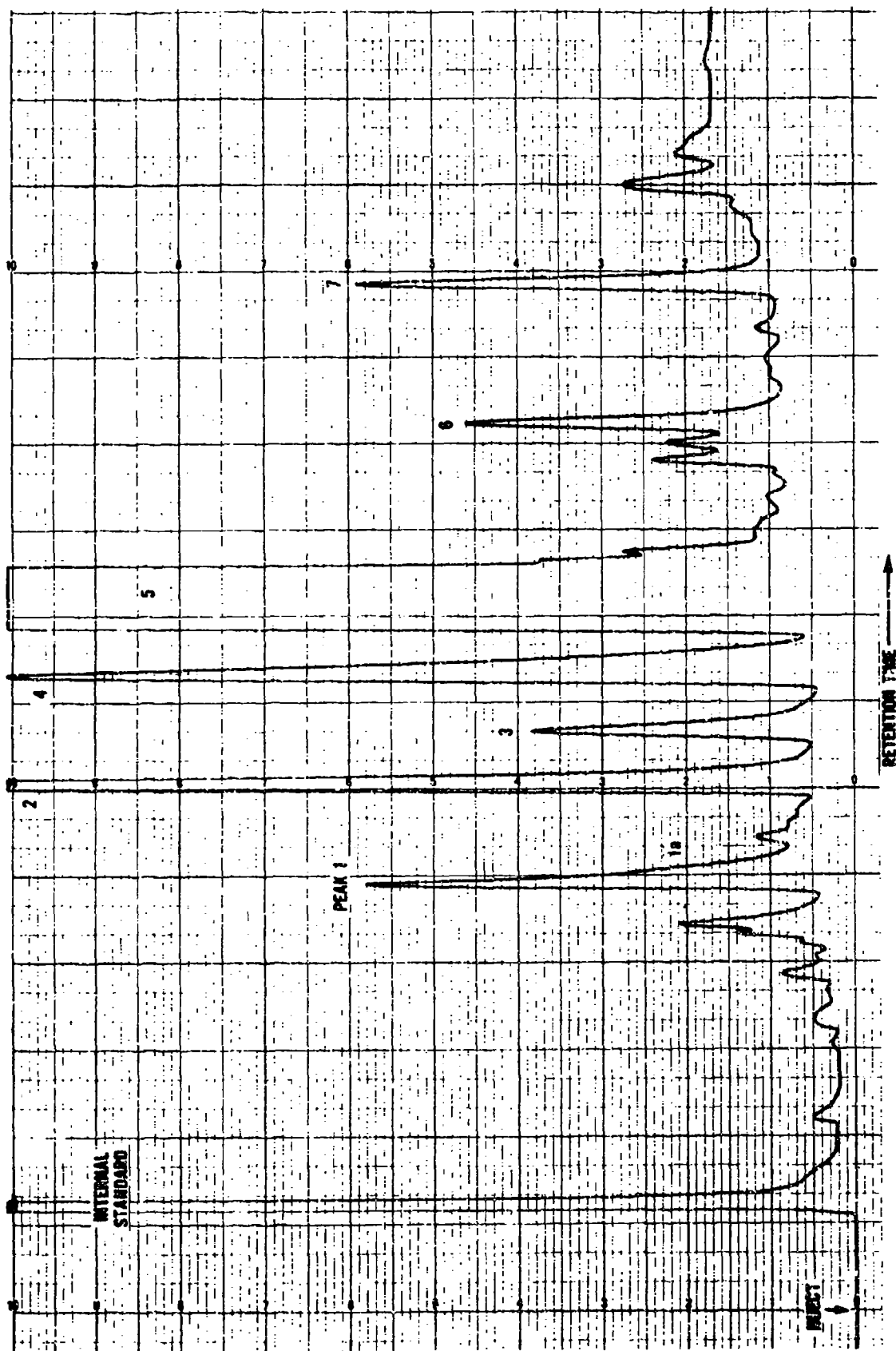


FIGURE 4. GAS CHROMATOGRAM OF O-76-5

TABLE 2. ANALYSIS FOR PARENT ALCOHOLS IN O-76-5

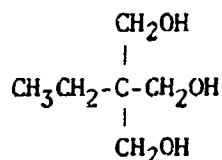
<u>Valerate Ester</u>	<u>Content, wt %^(a)</u>
Unknown 1	0.9
Trimethylolpropane (TMP)	93.7
Pentaerythritol (PE)	0.6
Dipentaerythritol (DPE)	1.8
Unknown 2	3.0

(a) Calculated as the valerate; GC response factors were not determined.

The compounds are listed in the order of GC retention time. No information regarding the identity of the first unknown was obtained. It is suspected that the second unknown is the original ester, due to incomplete valeration, as its GC retention time compared closely with the heptanoate ester. If this assumption is correct, the TMP concentration would be closer to 96-97 percent.

Parent acids contained in O-76-5 were determined by two hydrolysis methods. In both methods, the free acids, following hydrolysis of the ester, are measured by GC. Acid contents derived from these analyses are given in Table 3. The two methods are essentially the same, with the final step in acid recovery being an ether extraction. In method 1, virtually complete ether removal is performed to permit a determination of percent recovery. With method 2, GC analysis of the ether extract is run as is. Method 2 was applied because of the suspicion that ether removal using method 1 might result in losses of the more volatile acids. However, the data of Table 3 indicate the reverse effect. With the exception of the C₇ and trace C₁₀ acids, method 2 showed reduced acid contents. No comment regarding the accuracy of data for either method of analysis can be offered. However, as subsequently discussed, the values obtained by method 2 more closely agree with GC data for O-76-5.

The TMP alcohol possesses three hydroxyl group sites for esterification as shown by its structural formula



Esterification of pure TMP with pure heptanoic acid would yield acyl carbon lengths of seven at each site (777). In the event of an acid mixture, various ester species will occur. Sniegowski⁽²¹⁾ has shown that experimental results agree with the calculated random probability of forming the different acyl combinations. The calculation is based on the multinomial distribution formula

$$P = 100 \left(\frac{n! p_1^{k_1} p_2^{k_2} \dots p_r^{k_r}}{k_1! k_2! \dots k_r!} \right) \quad (4)$$

where p is the mole percent of the ester specie; n is the number of acyl sites (three for TMP); the p's are the acid mole percentages expressed as a decimal fraction; and the k's are the number of times the acyl groups are present in one ester molecule.

TABLE 3. ANALYSIS FOR PARENT ACIDS IN O-76-5

Parent Acid (Carbon No.)	Acid Analysis, mole %	
	Method 1(a)	Method 2(b)
Butyric (C ₄)	3.1	1.6
i-Pentanoic (i-C ₅)	1.0	nil
Pentanoic (C ₅)	0.5	0.3
Hexanoic (C ₆)	1.9	0.9
Heptanoic (C ₇)	93.3	97.2
Octanoic (C ₈)	0.2	nil
Nonanoic (C ₉)	0.4(c)	nil
Decanoic (C ₁₀)	0.4(c)	0.1

(a) Reference 24.

(b) Reference 21.

(c) Approximation.

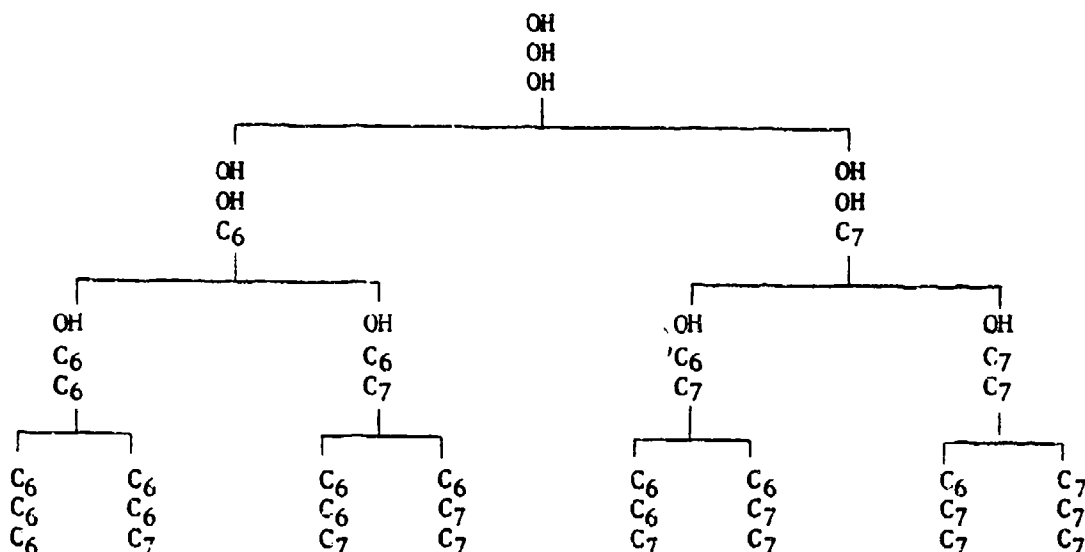
By use of the probability calculation, an interesting result is demonstrated by considering TMP esterification with two acids, say, hexanoic (C₆) and heptanoic (C₇) of equal mole percentages (50 percent each). The acyl group combinations which are possible are 666, 777, 667, and 677. The calculated probability for the 666 or 777 combination is the same for each

$$P = 100 \left(\frac{3! (0.5)^3}{3!} \right) = 12.5\%$$

Likewise, the probability for the two dissimilar acyl combinations is identical for each

$$P = 100 \left(\frac{3! (0.5)^2 (0.5)}{2! 1!} \right) = 37.5\%$$

The process may be demonstrated pictorially by considering a sequence of hydroxyl replacements by the two acids, each with equal probability, neglecting any differences in reactivity:



Combining like groups, it is seen that the yield would be one molecule each of the 666 and 777 combinations and three molecules each of the 667 and 677 combinations. Thus, dissimilar acyl combinations would dominate by a ratio of 3:1, as also shown by the previous probability calculations.

A calibration mixture of normal paraffins was analyzed by GC to obtain the boiling point calibration curve of Figure 5. These data permit the

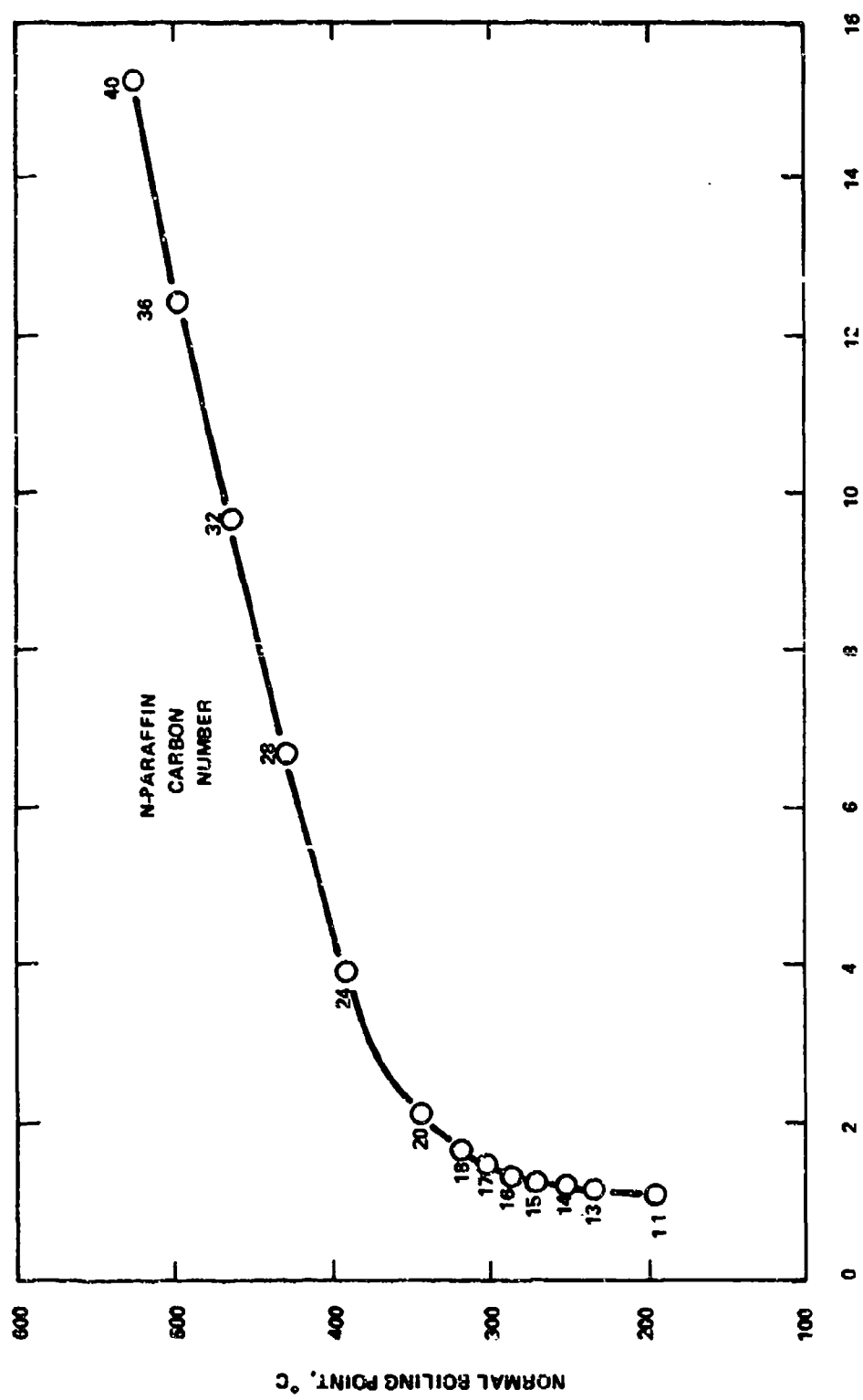


FIGURE 5. BOILING POINT CALIBRATION CURVE

assignment of boiling point values to the seven major components found in O-76-5. These values, as well as the component concentrations obtained by GC, are given in Table 4. The primary ester, TMP triheptanoate, constitutes approximately 90 percent of the basestock.

Several inferences were made in the interpretation of data to identify the lesser GC peaks in O-76-5. Of the TMP ester specie variations possible, it appeared necessary that a minimum of two C7 acyl groups must be present to yield an appreciable quantity of compound. For example, aside from C7 acid, the highest acid amount in Table 3 was 3.1 mole percent for C₄ acid using method 1. The calculated percentage of a 447 acyl combination would be

$$P_{447} = 100 \left(\frac{3! (0.933) (0.031)^2}{1! 2!} \right) = 0.3\%$$

roughly half the amount of any of the significant GC peaks. Calculated values for TMP triheptanoate (777) using the two C7 values shown in Table 3 gives 81.2 mole percent for method 1 and 91.8 mole percent for method 2. Because of the better agreement between the method 2 value and the GC value (89.9 wt percent), acid analysis data by method 2 were assumed to be of greater accuracy and peak identification proceeded on this basis. (It is noted that, at this point, comparisons between calculated mole percentages and GC wt percentages are being made. However, as will be shown later, conversion of one to the other has only a slight effect.)

Assuming at least two C7 acyl groups must be present to yield a significant quantity of material, parent acid data by method 2 indicated the following possible acyl combinations: 477, 577, 677, 777, and 7710. Calculated percentages for these combinations, and boiling point ranking, gave very satisfactory agreement with GC analysis for peaks 2 through 6, respectively. Structural assignments for peaks 1 and 1a considered three possible compounds: (1) a TMP diheptanoate resulting from incomplete esterification such that one hydroxyl group remains, (2) a diheptanoate from esterification of the aldehyde, 2, 2-dimethylolbutanal, an intermediate in the synthesis of TMP, and (3) a diheptanoate from esterification of an acid-alcohol which is a secondary product in the synthesis of TMP. The latter compound (prior to esterification) has the following structure:

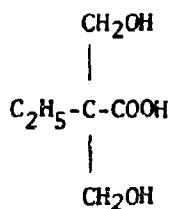


TABLE 4. GAS CHROMATOGRAPHY ANALYSIS
OF BASESTOCK O-76-5

<u>GC Peak</u>	<u>Concentration, wt %</u>	<u>Approximate BP, °C</u>
1 + 1a	0.9	410
2	2.9	430
3	0.6	440
4	2.5	445
5	89.9	450-460
6	0.7	480
7	<u>0.9</u>	500
	98.4	

The presence of this compound in appreciable quantity was thought to be improbable. Accordingly, it was assumed that the ester-alcohol and ester-aldehyde compounds could be attributed to the combination peak (Klaus, et al.(23) also presumed the presence of 2, 2-dimethylolbutanal in TMP triheptanoate).

In an effort to distinguish or verify the identity of the two compounds thought to be associated with the combination peak, a derivatization procedure was used with a sample of O-76-5. A silylation technique(24) was employed which causes replacement of an active hydrogen by a trimethylsilyl (TMS) group. The procedure is often used to obtain volatile derivatives for GC analysis of parent compounds. It was reasoned that the hydroxyl group hydrogen of the ester-alcohol would indicate reactivity with TMS, whereas the ester-aldehyde would not. GC analysis of the sample after derivatization showed complete removal of peak 1a. No other peak in the sample indicated a quantitative change.

Identification of peak 7 considered the possibility of TMP trinonanoate (tripelargonate) or pentaerythritol (PE) tetraheptanoate. This feasibility was investigated by comparing GC retention time with samples of these materials provided by AFAPL. The comparison, and subsequent "spiking" of O-76-5 with 1 percent of each of the fluids, indicated identical retention with peak 7 for both materials. The possibility of the trinonanoate, however, appeared to be inconsistent with the C₉ acid contents found by either acid analysis method. A TMP ester with an acyl combination of 999 would require a C₉ acid content of approximately 21 mole percent to yield 0.9 mole percent of the ester, roughly the peak 7 concentration.

In this regard, one aspect of the GC analysis for the various acyl combinations should be noted. The analysis cannot distinguish acyl combinations, of the same parent alcohol, with equal total acyl carbon numbers. For example, a TMP ester with a 4710 acyl combination (total carbon number 21) will be included in the same GC peak as a 777 combination, as well as all other possible combinations of 21. With respect to alternatives to a 999 combination, only a 71010 combination could be expected to contribute to peak 7; and the calculated yield for that combination is only 0.0003 mole percent. As a consequence, peak 7 was tentatively identified as PE tetraheptanoate, and additional characterization work was conducted using gas chromatography/mass spectrometry as the analytical tool.

Several generalized remarks regarding the findings of the GC/MS analyses can be made. The total ion chromatograms (TIC) did not exhibit the peak sensitivity shown in the chromatogram of Figure 4. Nevertheless, the significant peaks of interest were easily distinguishable, as seen in the TIC of Figure 6. Using electron impact ionization (EI), all fluid components gave numerous fragment ions, generally at low masses (less than m/e 200). Molecular ions were not obtained for any component. Because of the absence of molecular ions or other high mass ions, it was not possible to acquire structural information from neutral fragment losses; therefore, little or no information could be obtained relative to the structure of the parent ester. A brief investigation of a chemical ionization (CI) procedure was made in an effort to reduce the

816K03 X-1012 THP-TRIHEPTANOATE GC/EI
TOTAL ION CHROMATOGRAM

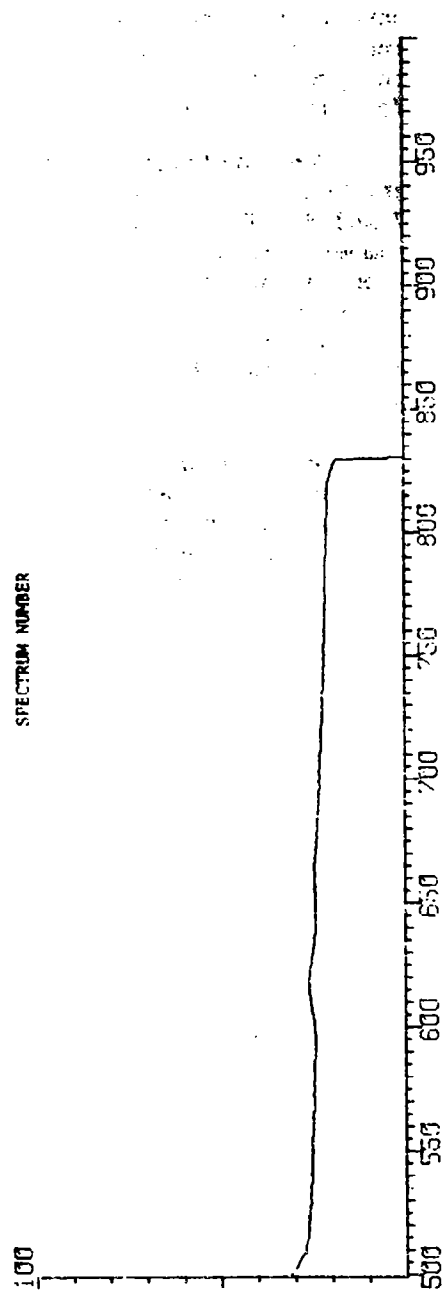
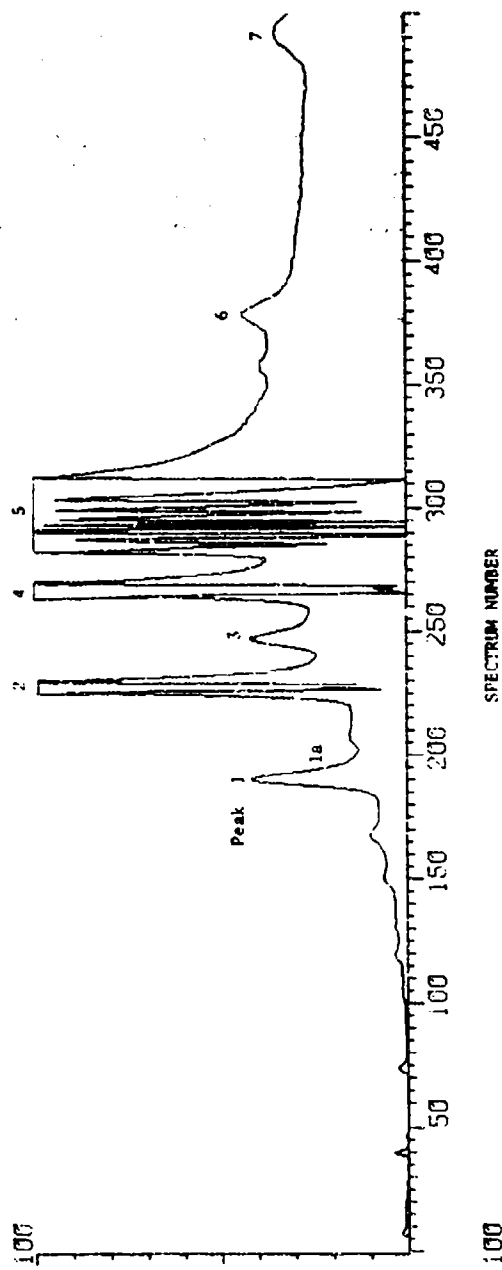
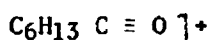


FIGURE 6. TOTAL ION CHROMATOGRAM FOR O-76-5

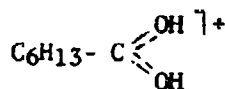
extent of fragmentation and identify molecular ions. The technique indicated some promise using methane as the reagent gas; however, the program schedule and complexity of the CI spectra did not allow for closer examination of the technique.

The complexity of the EI mass spectra obtained with O-76-5 is illustrated by the spectra for the major ester peak (peak 5) shown in Figures 7 and 8. The spectra were obtained at spectrum numbers 283 and 305, which numbers are a function of the frequency of scanning and identify the position on the TIC (Fig. 6) at which the scan was made. Both spectra are characterized by the alkyl chain ions (m/e 43, 57, 71, 85) and the C₇ acyli ion (m/e 113). A fragment at m/e 114 also shows a high abundance in the spectra, possibly due to a hydrogen rearrangement which yields the C₇ acyl plus one.

Computer analysis of mass spectra with the spectra library of the mass spectral search system provided no useful comparisons. Consequently, interpretation of mass spectra proceeded largely on the basis of first principles. Postulated fragment ions were derived characterizing one and two acid side chains in the fragmentation of TMP triheptanoate. For a single acid side chain, the following ions were deduced:

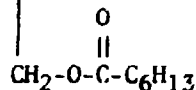
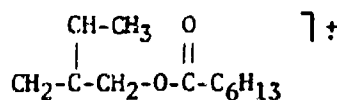


m/e 113

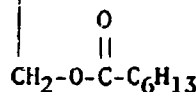
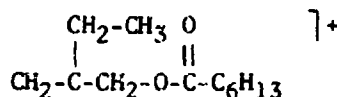


m/e 131

Major fragment ions derived for two acid side chains were:



m/e 340



m/e 341

Spectra for the significant peaks in O-76-5 were then scanned and noted for variants of the four ions listed above, for all possible acid combinations of C₄ through C₁₀. Because masses greater than m/e 200 were few in number, the results of this effort for two acid side chains were inconsequential. Instances for which both of the postulated single acid ions were found showed the presence of the following acids in the peaks of interest:

816K03 X-1012 TMP-TRIHEPTANOATE GC/EI
* 283 -280 RT=10.21 MIN

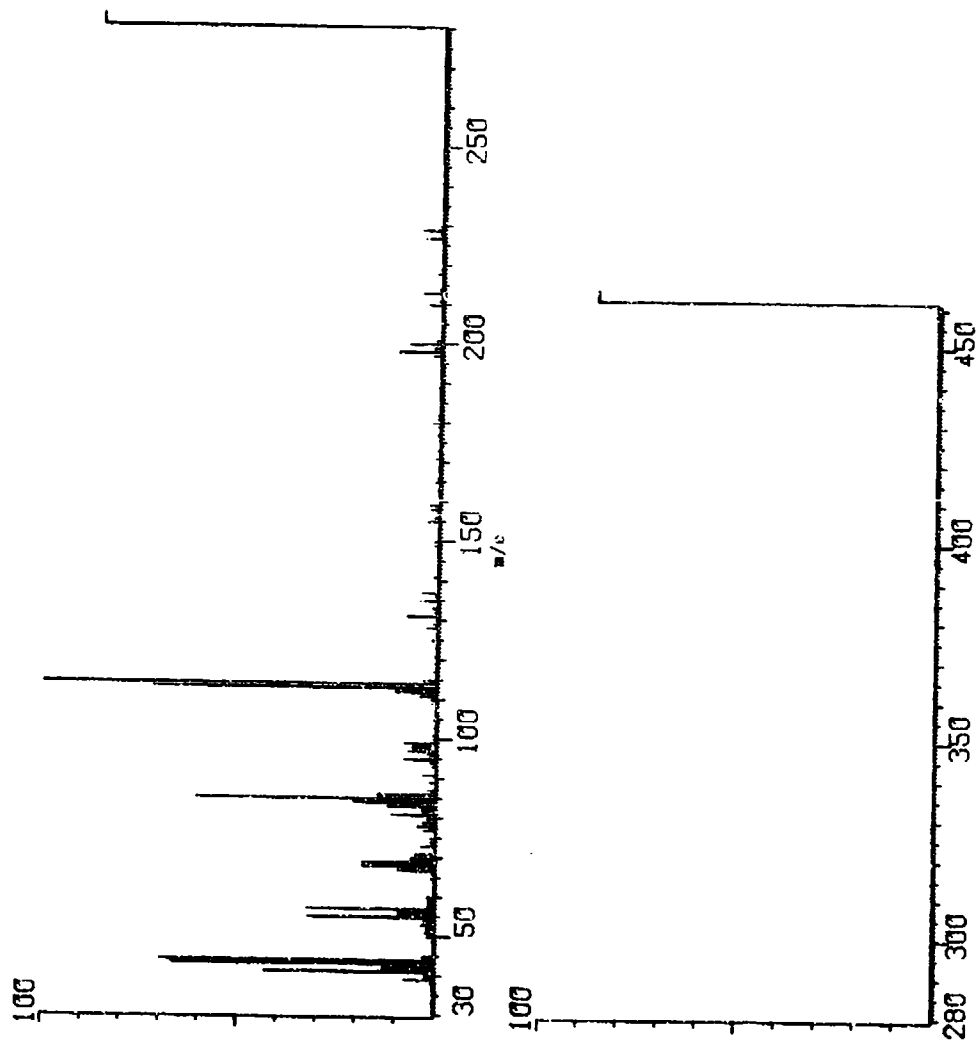


FIGURE 7. MASS SPECTRUM OF O-76-5 (PEAK 5) AT SPECTRUM NUMBER 283

816X03 X-1012 TMP-TRIHEPTANOATE GC/EI
305 -280 RT=11.00 MIN

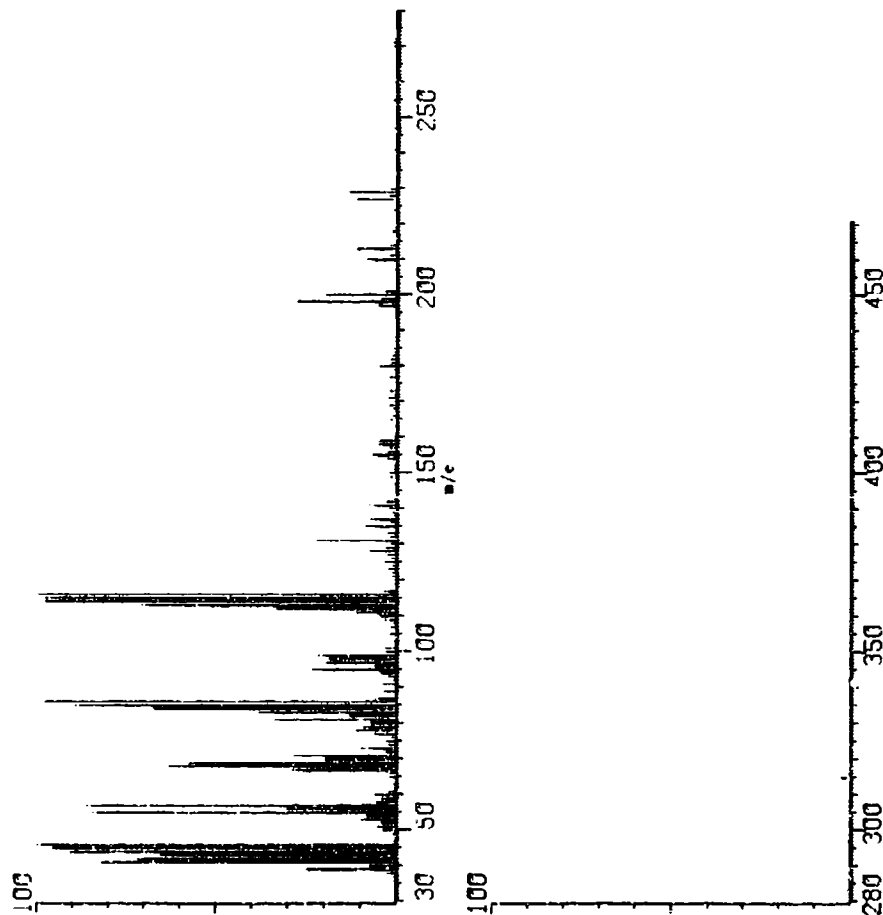


FIGURE 8. MASS SPECTRUM OF 0-76-5 (PEAK 5) AT SPECTRUM NUMBER 305

Peak	Acid Carbon Number						
	4	5	6	7	8	9	10
1 + 1a	X	X	X	X	X	X	X
2	X	X	X	X	X	X	X
3	X	X	X	X	X	X	X
4		X	X	X	X	X	X
5	X	X		X	X	X	X
6	X		X	X	X		
7	X			X			X

The multiplicity of acyl groups present is due to the various combinations possible for a given total carbon number.

To identify the primary acyl groups present in the GC peaks, the acyl group ion series for C_4 through C_{10} acids were utilized. The series consists of ions m/e 71 (C_4), 85 (C_5), ..., 155 (C_{10}). It was recognized that the C_4 and C_5 acyl ions overlap with the alkyl chain ions which were evident in all spectra due to primary or secondary fragmentation of the acid chains. Nevertheless, the relative abundances of the m/e 71 and 85 ions were significantly greater for the tentatively identified GC peaks 2 and 3, respectively. A high relative abundance was also obtained for the C_6 acyl ion (m/e 99) in peak 4.

Because of earlier difficulty in interpreting the acyl combinations of the longer chain acids, single ion scans of the 0-76-5 chromatogram were made for m/e 113, 127, 141, and 155 corresponding to the C_7 through C_{10} acyl ions. The presence of heptanoic acyl group throughout the 0-76-5 sample is shown by the m/e 113 ion scan of Figure 9. The octanoic acyl group is indicated in the scan of Figure 10. The C_8 chain was primarily found in peaks 5 and 6, and a small peak between 5 and 6. The C_9 and C_{10} acyl groups are identified in Figures 11 and 12, respectively. These acid chains were located principally in peak 5, and to a lesser extent in components boiling below peak 5. A significant quantity of C_9 or C_{10} acid chains was not indicated for peaks 6 or 7, as had been originally conjectured on the basis of inference.

Since peak 7 appeared to contain C_7 acyl groups exclusively, an effort was made to verify the composition as PE tetraheptanoate. Comparison of the peak 7 mass spectra and spectra for the major peak in a sample of PE tetraheptanoate did show similarities. In particular, a unique ion at m/e 184, of unknown derivation, was evident in both spectra. The structure of the ion suggests that it cannot be generated by primary scission of the molecule; consequently, the ion is thought to be the result of secondary fragmentation.

816K03 X-1012 TMP-TRIHEPTANOATE GC/EI
SIS 113 AMU

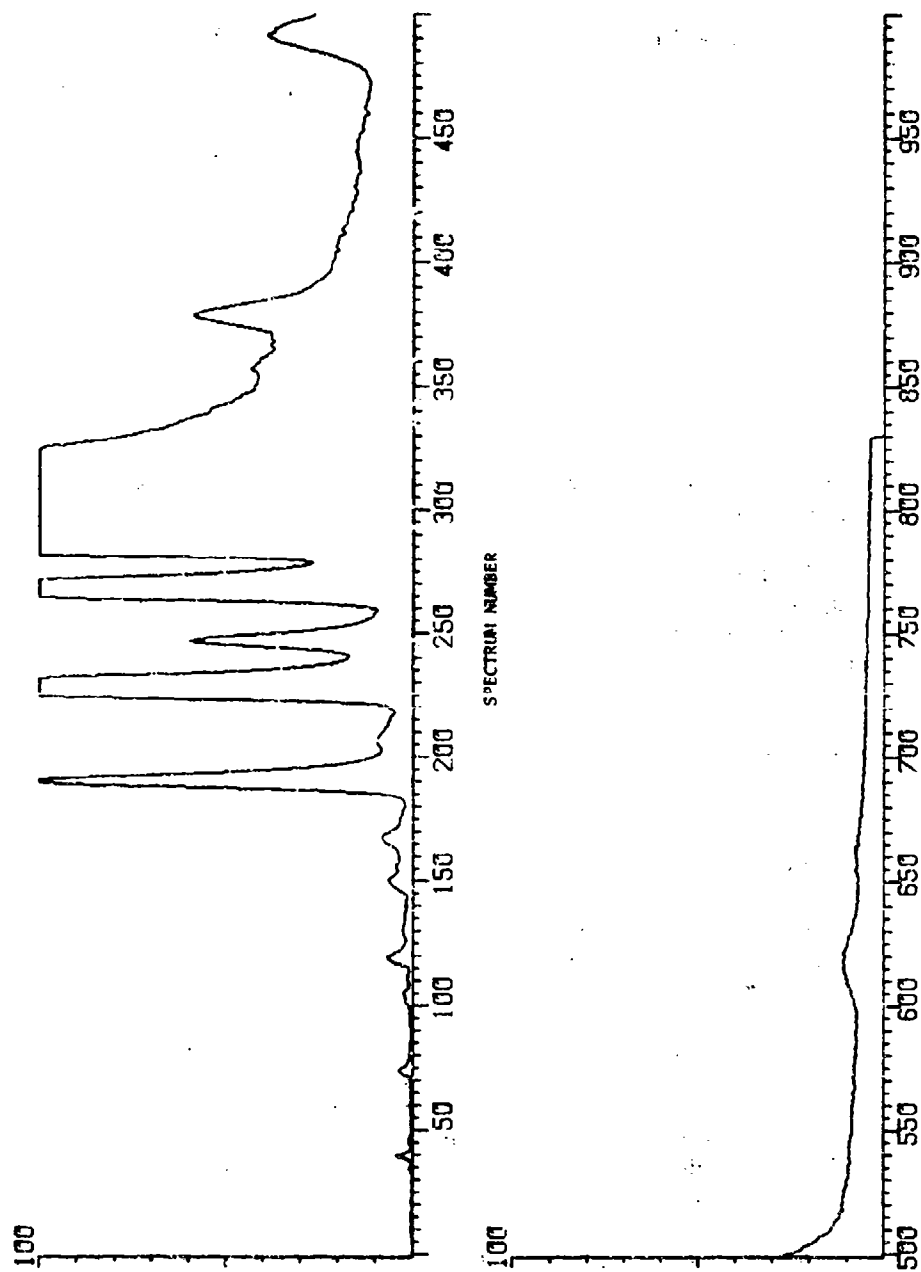


FIGURE 9. SINGLE ION CHROMATOGRAM OF 0-76-5 AT m/e 113

816K03 X-1012 TMP-TRIHEPTANOATE GC/EI
SIS 127 AMU

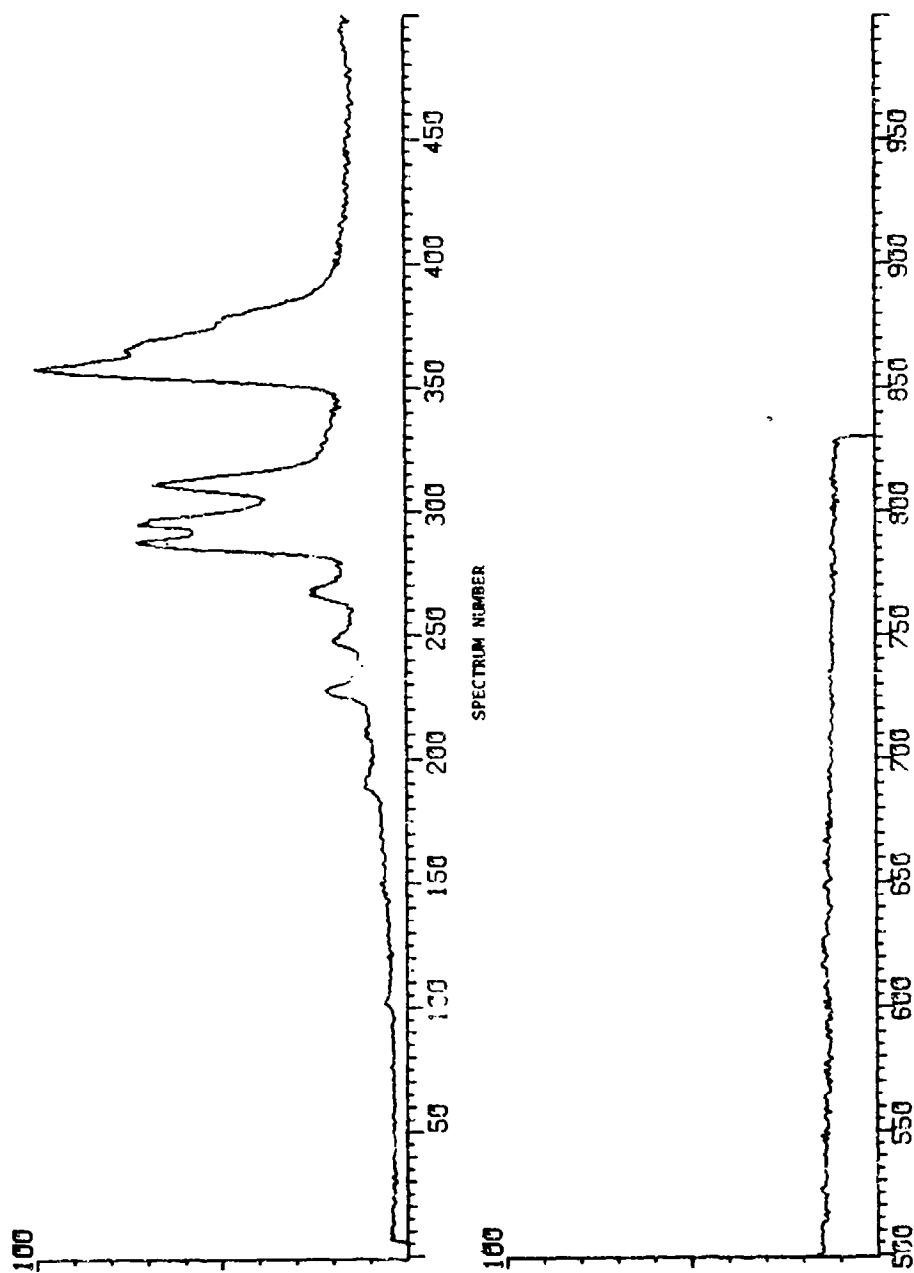


FIGURE 10. SINGLE ION CHROMATOGRAM OF O-76-5 AT m/e 127

816K03 X ¹³C12 TMP-TRIHEPTANOATE GC/EI
IS 141 AMU

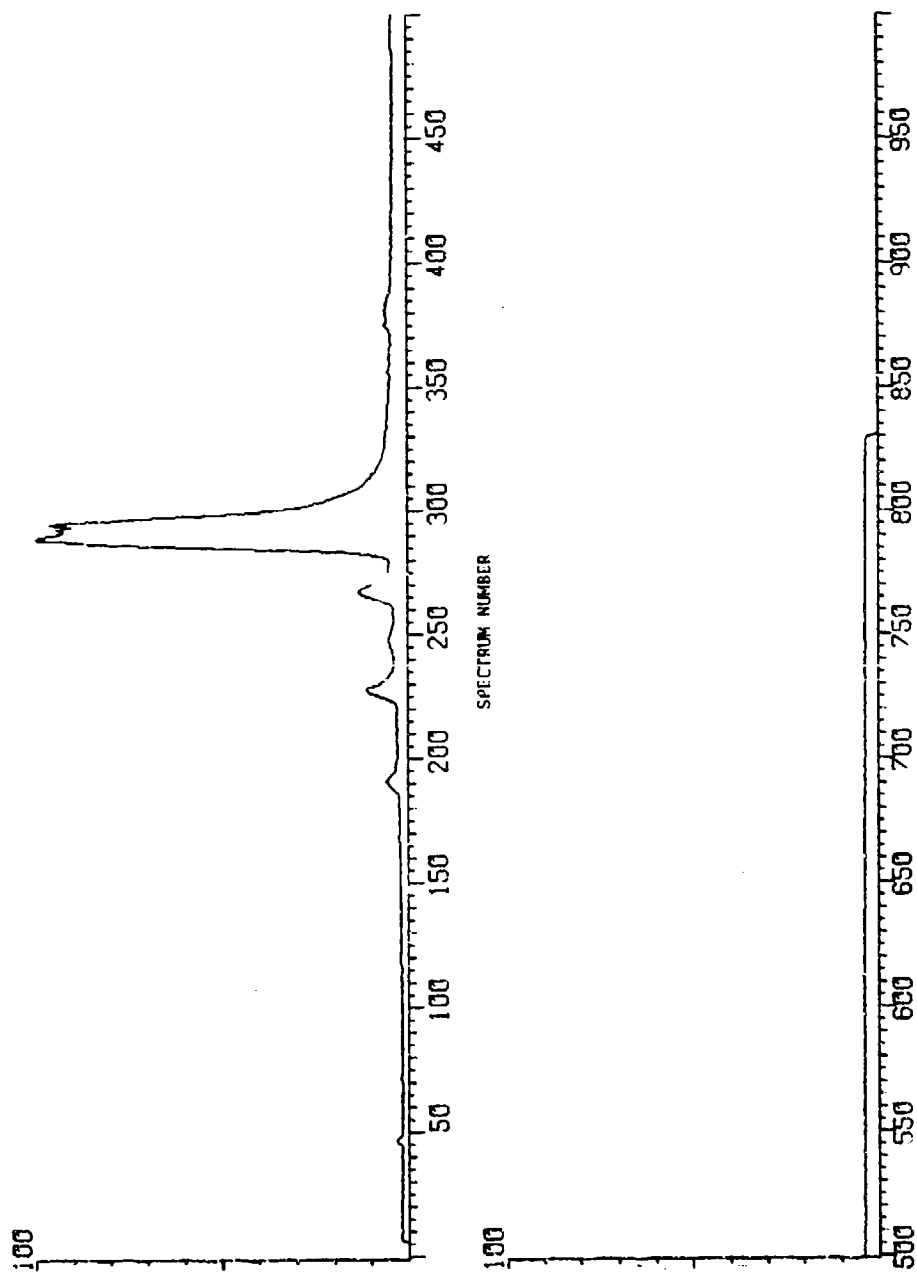


FIGURE 11. SINGLE ION CHROMATOGRAM OF O-76-5 AT m/e 141

818K03 X-1012 TMP-TRIHEPTANOATE GC/EI
SIS 155 AMU

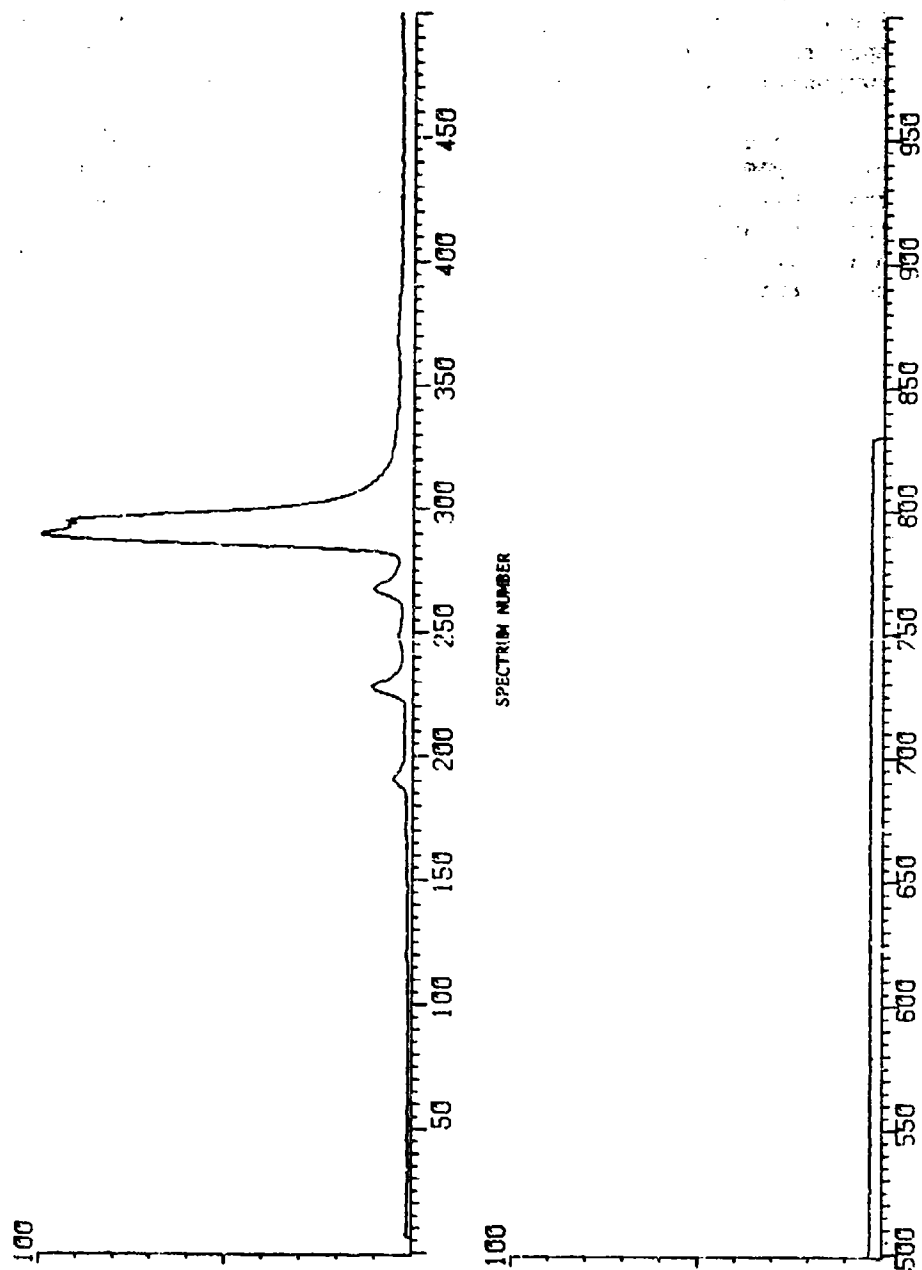


FIGURE 12. SINGLE ION CHROMATOGRAM OF 0-76-5 AT m/e 155

An attempt to confirm by GC/MS the identity of peak 1 as a diester-aldehyde was not conclusive. Two ions were postulated by first principles for fragmentation of the compound, m/e 198 and 327. Only the lower mass ion was evident in the peak 1 spectrum, but it was also found in the spectra of several other peaks. Nevertheless, it is believed that the supposition of a diester-aldehyde is indicated.

Table 5 presents the analysis data and suggested identification derived from the characterization of the O-76-5 basestock. It is observed that this final identification for the TMP acyl combinations still suggests that the analysis of method 2 (Table 3) more accurately defined the parent acid composition of the ester, except for the presence of the C8 acid component.

TABLE 5. O-76-5 BASESTOCK CHARACTERIZATION
FOR MAJOR COMPONENTS

<u>Peak</u>	<u>Concentration by GC</u>		<u>Primary Compound</u>
	<u>Wt %</u>	<u>Mole %</u>	
1	0.7*	1.0*	TMP diester-aldehyde
1a	0.2*	0.3*	TMP diester-alcohol
2	2.9	3.2	TMP-477
3	0.6	0.6	TMP-577
4	2.5	2.6	TMP-677
5	89.9	90.8	TMP-777
6	0.7	0.7	TMP-778
7	0.9	0.7	PE-7777

* Approximation.

EXPERIMENTAL RESULTS AND DISCUSSION

General

Individual data sheets for all rotating cylinder rig tests are included in the Appendix hereto. These data summaries are arranged in order of test number and include pertinent test conditions, the cylinder rig deposit rating, and basic lubricant performance data. In oxidative (air) tests, oxygen consumption values are expressed in liters at operating temperature and pressure (OPT), corresponding to ambient atmospheric pressure and temperature (75° to 80°F). Data for the amount of unreacted ester remaining, determined by GC, refer only to the major ester component (peak 5) present in the basestock.

Tests No. 20 through 23 were performed with lubricant O-71-8, primarily to establish appropriate test conditions for use with the polyol ester basestock. The remaining tests were conducted in the study of the thermal and oxidative degradation of the primary TMP triheptanoate basestock, G-76-5. Duplicate runs were made at two temperature levels with both an inert and oxidative atmosphere and both a dry and moist atmosphere, for a total of 16 determinations. (Test numbers for the O-76-5 series are not consecutive throughout because of interspersed runs on another fluid and one aborted test.)

Preliminary Test Results

Three cylinder rig tests (Tests No. 20-22) using a dry air atmosphere were performed with O-71-8 to examine the effect of film temperature on the oxidative deterioration of the fluid. With all other conditions held constant, tests on O-71-8 were conducted at film temperatures of 400°, 425°, and 450°F. As shown by the summary of Table 6, all three runs were continued to a relatively high level of fluid degradation as evidenced by viscosity and neutralization number values. However, lubricant deposits were negligible in all cases despite the extent of lubricant deterioration.

Oxygen absorption data for the three tests with O-71-8 are plotted in Figure 13. A consistent and logical effect for film temperature is illustrated by these results. Neglecting a brief induction period, the line slopes in Figure 13 yield the following rate values:

<u>Film Temp, °F</u>	<u>O₂ Consump, l/hr</u>
400	0.83
425	1.10
450	1.48

Using the average residence time per cycle (from test data sheets in the Appendix) and assuming an exposure of 600 cm³ (10 cm³ per min for 1 hr), the

TABLE 6. SUMMARY OF OXIDATIVE CYLINDER
RIG TEST RESULTS ON O-71-8

<u>Film Temp, °F</u>	<u>Test Duration, hr</u>	<u>100°F Vis Increase, %</u>	<u>NN Change, mg KOH/g</u>	<u>Deposit Rating</u>	<u>Test No.</u>
400	75	92	18.5	14	21
425	50	150	10.8	10	20
450	35	105	14.4	10	22

Film thickness 4×10^{-3} in.
Lubricant flow $10 \text{ cm}^3/\text{min}$
Airflow 100 l/hr , dry
Lubricant charge 1000 cm^3

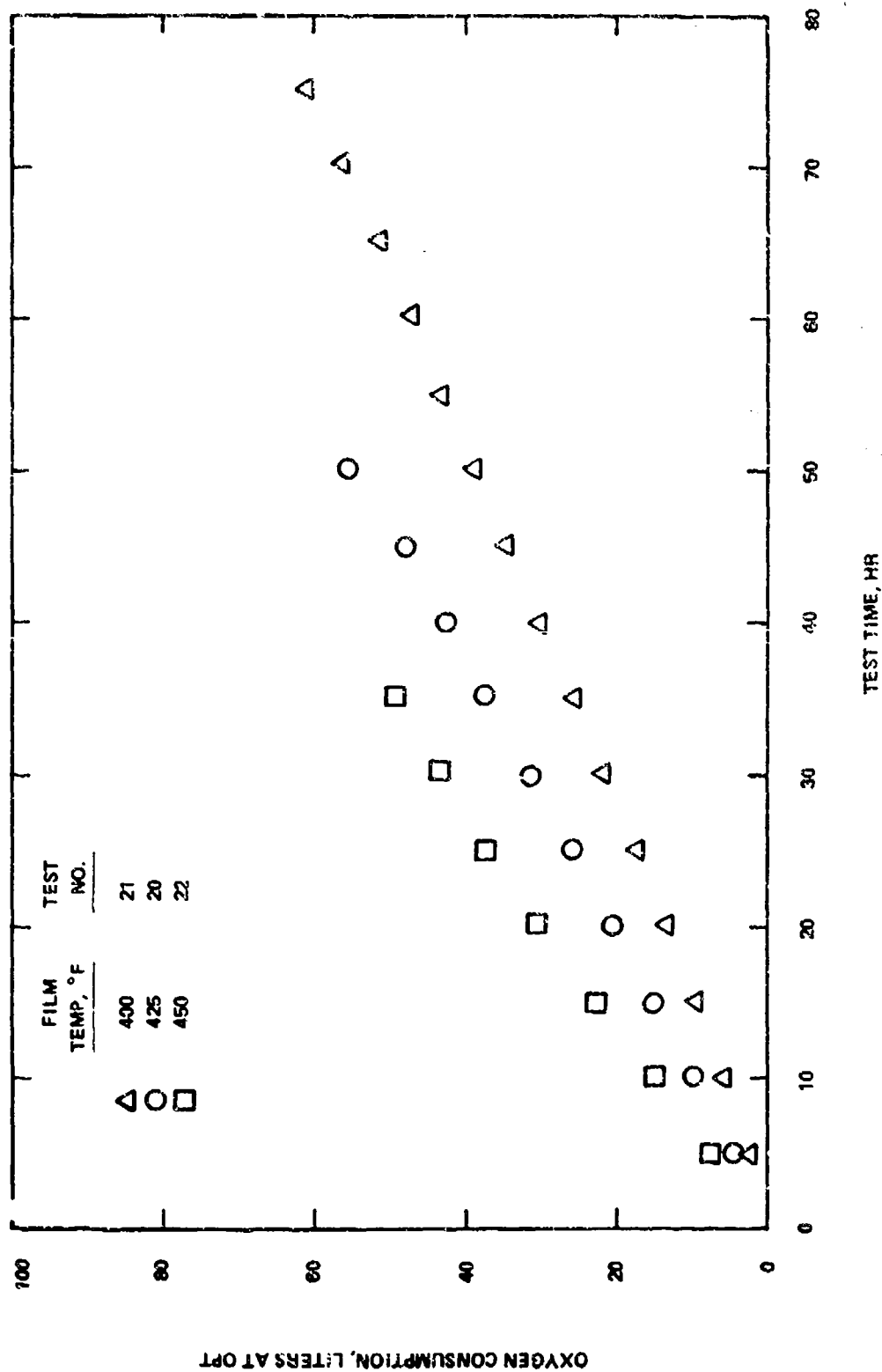


FIG. 13. OXYGEN CONSUMPTION VALUES FOR LUBRICANT 0-71-8

above values were converted to moles O₂ per mole of ester per sec for calculation of the energy of activation by the Arrhenius equation. Figure 14 shows the rate data versus the reciprocal of absolute temperature, and compares the rates with data for three dialkyl adipate esters obtained by Rigg and Gisser.⁽¹²⁾ It is apparent that oxygen consumption rates for O-71-8 were appreciably higher than would be expected, particularly in view of the fact that the hindered polyol ester should exhibit the superior oxidative stability.

The slope of the line shown in Figure 14 for O-71-8 also yields a low value for the energy of activation for this ester. Utilizing the Arrhenius equation, the slope gives an activation energy of 10.1 Kcal/mole. This compares with the following values given by Rigg and Gisser for the diesters listed in Figure 14:

<u>Dialkyl Adipate</u>	<u>Activation Energy, Kcal/mole</u>
1-ethylpropyl	26.3
n-pentyl	26.1
3-methylbutyl	21.9

In view of the low energy of activation obtained for the polyol ester, alternate methods for the calculation of the oxygen consumption rate were attempted, e.g., using total oxygen consumption and total residence time. None of the alternate techniques resulted in a significant change in the computed energy value.

Several factors could be responsible for the disparity of reaction data relative to the work of Rigg and Gisser. Their experiments were conducted over a much lower range of oxidation temperatures, and in classical glassware apparatus with continuous exposure of a discrete fluid quantity. While it is believed that the lubricant residence time within the cylinder rig is accurately defined, the necessity for preheating the fluid prior to its entry into the cylinder may be a significant complicating factor in any comparison. Thus, energies of activation shown by oxidative cylinder rig experiments may represent a combination of thermal and oxidative processes.

Preliminary investigation of the thermal stability characteristics of O-71-8 was carried out using a dry nitrogen atmosphere in the cylinder rig. To maximize the information to be gained by a single test, film temperature and lubricant-in temperature were varied according to the following schedule: 0-30 hr, 500°F; 30-60 hr, 550°F; 60-100 hr, 600°F. The results of this run are given for Test No. 23 in the Appendix. An intermediate inspection at 30 hr and the final 100-hr inspection showed no deposits present on the cylinder surface. Lubricant performance data indicated a negligible fluid viscosity change throughout the run. Neutralization number change was also insignificant up to 60 hr of test time. From 60 to 100 hr, corresponding to the test interval at 600°F film

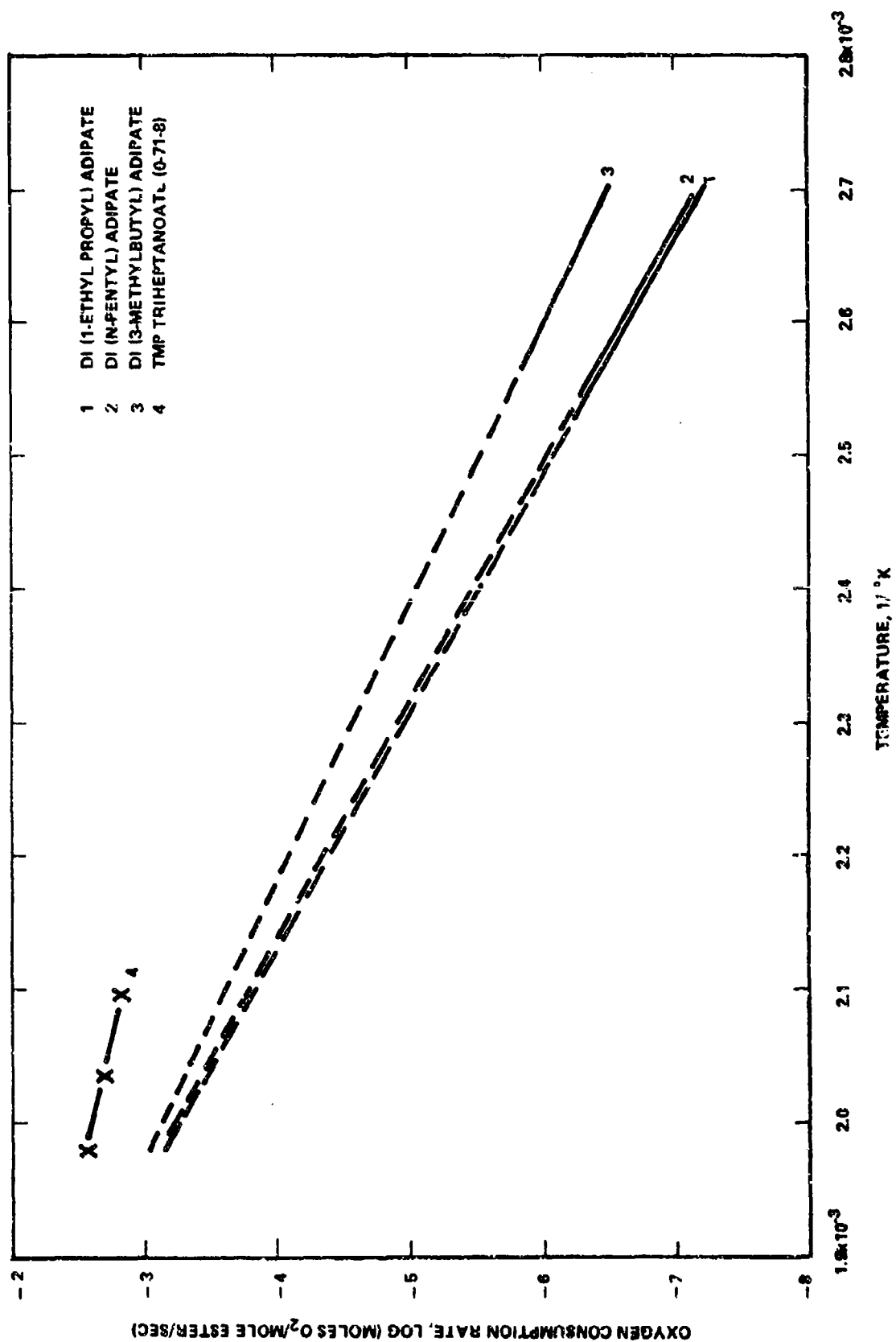


FIGURE 14. ESTER OXIDATION RATES

temperature, the acid number change rose from 0.06 to 0.40 mg KOH/g. GC analysis for the major ester component also showed insignificant changes in concentration at the end of the three test intervals.

All of the foregoing discussion suggests that fluid deterioration was not significant in the test performed, although the 600°F film condition appeared to show incipient property changes within the 40-hr period at that temperature. Since the upper temperature capability of the cylinder rig is in the range of 650°-700°F, it was decided that subsequent thermal stability experiments with the primary polyol ester basestock would be run at the temperatures of 600° and 650°F.

Thermal Stability

A summary of cylinder rig results for the thermal stability test series with O-76-5 is presented in Table 7. At the 600°F film temperature, lubricant property changes were slight and no cylinder deposits (100 percent clean) were formed in 100-hr tests either with the dry or moist atmosphere. Attack of the primary ester component was also slight at 600°F, with concentration reductions ranging from about 2 to 6 wt percent.

With a dry N₂ atmosphere, increase of the lubricant film temperature from 600° to 650°F did not produce a significant increase in O-76-5 degradation. Fluid property changes were generally comparable, although a very light varnish deposit occurred at the higher temperature. Using a moist atmosphere, a marked deleterious effect for the presence of water was shown by the polyol basestock at 650°F. Appreciable changes in viscosity, acidity, and ester consumption were noted. In addition, some medium and heavy varnish deposits were formed with moisture present at 650°F.

The apparent lack of repeatability of viscosity and acidity data for the duplicate tests at 650°F with moisture is not believed to be severe. Examination of the Appendix data sheets for Tests No. 33 and 34 indicates that the former showed a viscosity maximum at about 80 hr, after which fluid viscosity rapidly decreased while neutralization number increased. There was no corresponding acceleration shown in consumption of the basestock. The phenomenon appeared to be associated with secondary breakdown of high boiling components. These degradation products are measured indirectly as compounds not eluting from the GC column (GC residue). As shown in Table 7, such products were significant for some tests and the amounts correlated closely with the degree of primary ester attack. The viscosity decrease and neutralization number increase occurring in Test No. 33 suggested degradation resulting in smaller acidic fragments. The source of such fragments appeared to have been secondary reaction of high-boiling products. Measured GC residues in this run showed a consistent increase in concentration to about 12 percent at 75 hr. Throughout the remainder of the test, the residue amount stayed in the range of 10 to 12 percent.

Since ester deterioration was negligible at the 600°F film temperature but, aside from severity, comparable to the mode of degradation at 650°F, subsequent discussion will be largely restricted to findings at the higher temperature.

TABLE 7. THERMAL STABILITY END-OF-TEST RESULTS FOR LUBRICANT O-76-5

Atmosphere	Film Temp, °F	Test Duration, hr	Total Res Time, sec	100°F Vis Incr, %	NN Change, mg KOH/g	Deposit Coverage	Unreacted Ester, wt%	GC Residue, wt %	Test No.
Dry N ₂	600	100	1450	5	2.49	100% C1	94.4	4.1	24
	600	100	1525	3	0.53	100% C1	98.4	0.4	25
	650	100	1287	5	2.26	100% LV	92.6	5.1	26
	650	95	1402	7	3.35	100% LV	88.9	7.4	27
Moist N ₂	600	100	1308	1	2.92	100% C1	93.6	5.1	31
	600	100	1431	4	1.58	100% C1	94.1	3.5	32
	650	100	1404	-7	20.8	25% LV 75% HV	74.3	11.3	33
	650	100	1444	15	8.05	25% LV 10% MV	80.3	10.4	34
						65% HV			

Film thickness 4 x 10⁻³ in.
Lubricant flow 10 cm³/min
N₂ flow 100 s/hr
Lubricant charge 1000 cm³

Table 8 lists the compositional changes in significant constituents of the polyol ester basestock at 650°F. Except for approximately 5 percent consumption of the TMP-777 ester and formation of a diester corresponding to the TMP diester-alcohol, no other noticeable concentration changes were evident with the dry atmosphere. With air atmosphere conducive to hydrolytic breakdown, several components indicated compositional changes. The longer chain triesters, TMP-777, TMP-778, and to a lesser extent TMP-677, showed measurable consumption. Increases in the amounts of the aldehyde and alcohol diesters were of such magnitude as to represent, in conjunction with GC residue, the principal reaction products. The formation of appreciable amounts of diesters suggests that the high-boiling products may be principally condensation products of the diesters.

Figure 15 illustrates the reaction of the primary ester component (TMP-777) as a function of test residence time. The deleterious effect of moisture is again demonstrated. It is also noted that, in the moist atmosphere tests, ester consumption was moderated in the latter half of the test period when viscosity and neutralization number changes were largest, evidential of secondary reaction processes.

Other than the diester compounds and GC residue constituents, no other thermal breakdown products were indicated by GC analysis at appreciable concentrations. Traces of low-boiling components adjacent to the n-C₁₃ internal standard were observed and GC comparisons were made to determine the presence, in particular, of free heptanoic acid. The C₇ acid was identified in all 650°F tests at trace levels except Test No. 33 which showed an acid concentration of 0.8 wt percent for the 100-hr sample.

Since the acid is relatively volatile (434°F boiling point vs 453°F for n-tridecane), analyses were performed on selected end-of-test condensate samples taken from the precipitator return line to the lubricant sump. Table 9 shows, firstly, a comparison between the bulk fluid and condensate properties. As normally found, the condensate samples exhibited reduced viscosity and much higher neutralization numbers relative to the bulk lubricant. Results for heptanoic acid content in the condensate samples indicated that the acid was a major product being generated in basestock degradation. The close agreement between actual and theoretical neutralization numbers suggests that heptanoic acid accounts for virtually all of the acidic components in the condensate. Apparently the dilution effect of the bulk lubricant resulted in much lower C₇ acid concentrations for the lubricant samples. Further, it is seen that the theoretical neutralization numbers were significantly lower than the actual for the lubricant samples. Presumably, some high-boiling acidic materials were also present which because of volatility effects were not found in appreciable quantity in the condensate samples.

As previously noted, cylinder rig deposits when present were limited to varnish-type materials. Nevertheless, in an effort to characterize the nature of the varnish, analytical work was performed with the light varnish formed in the cylinder from Test No. 27. The deposit was collected using acetone-wetted cotton swabs. The swabs were rinsed with additional acetone

TABLE 8. COMPOSITIONAL CHANGES IN 650°F THERMAL STABILITY TESTS WITH O-76-S

Time, hr	Component Concentration, wt %			
	Dry Nitrogen		Moist Nitrogen	
	Test No. 26	Test No. 27	Test No. 33	Test No. 34
<u>TMP diester-aldehyde</u>				
0	0.7	0.7	0.7	0.7
100	0.8	0.6*	3.0	3.3
<u>TMP diester-alcohol</u>				
0	0.2	0.2	0.2	0.2
100	1.0	1.2*	2.4	1.6
<u>TMP-477</u>				
0	2.7	2.7	2.7	2.7
100	2.4	2.4*	3.1	2.5
<u>TMP-577</u>				
0	0.6	0.6	0.6	0.6
100	0.6	0.7*	0.9	0.7
<u>TMP-677</u>				
0	2.5	2.5	2.5	2.5
100	2.2	2.2*	2.3	2.1
<u>TMP-777</u>				
0	89.9	89.9	89.9	89.9
100	84.5	81.1*	67.8	73.3
<u>TMP-778</u>				
0	0.7	0.7	0.7	0.7
100	0.6	0.5*	0.1	0.4
<u>PE-7777</u>				
0	0.9	0.9	0.9	0.9
100	1.0	1.1*	0.8	1.2

* 95-hr test time.

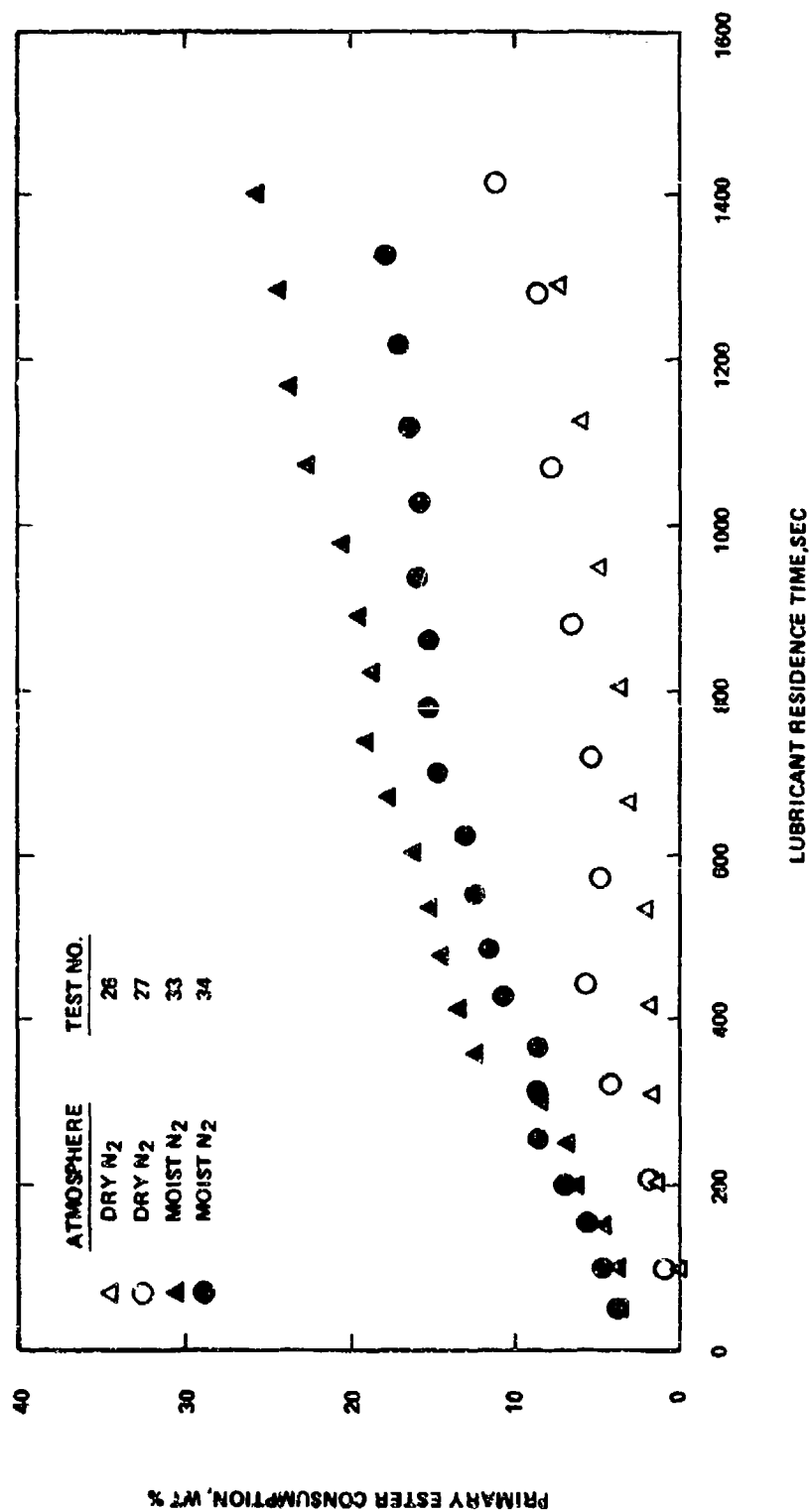


FIGURE 15. PRIMARY ESTER CONSUMPTION DATA FOR THERMAL STABILITY TESTS ON O-76-5 AT 650°F

TABLE 9. O-76-5 LUBRICANT PROPERTIES AT TEST TERMINATION
FOR SELECTED 650°F THERMAL STABILITY TESTS

<u>N₂</u> <u>Atmosphere</u>	<u>100°F Vis,</u> <u>cs</u>	<u>Heptanoic</u> <u>Acid, wt%</u>	<u>Neut. No., mg KOH/g</u> <u>Theor.*</u>	<u>Actual</u>	<u>Test</u> <u>No.</u>
<u>Lubricant Sample</u>					
Dry	16.27	0.14	0.6	3.4	27
Moist	14.12	0.8	3.5	20.8	33
<u>Condensate Sample</u>					
Dry	8.73	14.5	63	78	27
Moist	6.59	29.3	126	121	33

* Theoretical neut. no. based on heptanoic acid content.

to free the varnish particles. The solvent was then stripped with dry nitrogen and an infrared absorption spectrum obtained on the dried residue (9.5 mg).

The IR spectrum indicated little total carbon-hydrogen. Carbonyl group absorption was present but weak. The strongest absorption was a broad peak at 1000 to 1100 cm^{-1} . Absorption in this region may be indicative of phosphates or metal compounds. X-ray fluorescence analysis of the deposit confirmed the presence of phosphorous, as well as iron, potassium, and aluminum. Quantitative values for these elements could not be obtained with any accuracy because of the small quantity of residue available. Subsequent destructive analysis of the deposit showed the following composition: 31.2 percent carbon, 3.8 percent hydrogen, and 55.8 percent ash. The high ash content identifies the deposit as principally inorganic.

The presence of iron and aluminum in the deposit suggests corrosive wear of the cylinder rig system materials, probably by the heptanoic acid formed, and subsequent deposition. Phosphorous is present in some stainless steel alloys used in the system, but at very low concentrations. It is believed more likely that measurable amounts of phosphorous and potassium were probably due to trace contamination from the rig cleaning materials. It should be emphasized that any interpretation of analytical data for the deposit residue should be tempered by the fact that only a very small quantity was obtainable for analysis.

Oxidative Stability

The results of the cylinder rig oxidation tests series with O-76-5 are summarized in Table 10. As evidenced by all performance criteria, the test conditions resulted in severe fluid degradation. Approximately one-half of the primary ester component was consumed, and viscosity and neutralization number increases were appreciable. In addition, significant GC residue values were recorded for all tests in the oxidative series.

The effect of the 50°F film temperature differential was significant for both the dry and moist air conditions. At 350°F, test durations ranged from 70 to 100 hr, whereas all 400°F runs were terminated at 50 hr with deterioration levels comparable to the lower temperature tests. There was no clear-cut effect for moisture on the oxidation stability of the basestock at either temperature, as indicated by the lubricant sample properties measured. However, the deposit types formed at 350°F appeared to show some influence for moisture--light varnish (LV) for dry air tests, light sludge (LS) with moisture present. It should be observed that all deposit coverages rated as light sludge were of very slight severity with negligible thickness.

The data in Table 10 for the 350°F film temperature using dry air indicate poor repeatability of results for this test pair. Test No. 37 was terminated at a total lubricant residence time of 1144 sec with a degree of degradation noticeably greater than Test No. 36 terminated with 1658 sec

TABLE 10. OXIDATION END-OF-TEST RESULTS FOR LUBRICANT O-76-5

Atmosphere	Film Temp., °F	Test Duration, hr	Total Res Time, sec	100°F Vis Incr, %	NN Change, mg KOH/g	Oil Loss, cm ³ /hr	Deposit Coverage	O ₂ Consump, l at OPT	Unreacted Ester, wt%	GC Residue, wt %	Test No.
Dry Air	350	100	1658	62	12.22	3.2	100% LV	24.2	47.0	35.8	36
	350	70	1144	86	15.21	6.2	100% LV	33.9	33.9	44.2	37
	400	50	634	90	13.75	4.6	100% LS	43.4	46.2	22.5	35
	400	50	727	101	14.34	7.7	100% LS	42.9	37.7	38.8	38
Moist Air	350	90	1693	68	11.58	4.5	100% LS	22.1	46.7	40.3	40
	350	100	1800	73	13.18	4.1	100% LS	26.6	44.2	42.2	43
	400	50	632	79	10.83	3.7	100% LS	39.3	43.5	42.9	41
	400	50	651	60	9.85	3.7	20% LV 80% LS	33.3	46.8	40.0	42

Film thickness 4×10^{-3} in.
 Lubricant flow $10 \text{ cm}^3/\text{min}$
 Airflow 100 l/hr
 Lubricant charge 1000 cm^3

residence time. A review of recorded test parameters for both tests produced no evidence of a discrepancy for either run. An overall examination of results for the entire series suggests that data for Test No. 37 are at variance.

Further discussion of oxidation of the 0-76-5 basestock will be confined to the 400°F test data which, aside from severity, were representative of 350°F results. Compositional basestock changes at 400°F are listed in Table 11. The formation of diester reaction products was extensive in all 400°F experiments, such that the diester-alcohol GC peak merged with the diester-aldehyde peak and could not be resolved by the normal GC conditions. Significant consumption of the TMP-777 ester was observed. Changes in the other lesser concentration esters were not of sufficient magnitude that a specific trend may be cited. The TMP-677 ester component was partially consumed in all tests, while a reaction product with a boiling point coincident with the TMP-778 ester was formed in all tests.

Figure 16 illustrates the consumption rate of the TMP-777 ester in the 400°F oxidation tests. Comparable ester loss was shown in all tests, particularly by data at residence times greater than 400 sec, and no effect for moist versus dry air was apparent. It is observed that after approximately 50 percent consumption, reduced reaction rates for the primary ester were exhibited. The effect was shown at residence times in the range of 400 to 500 sec, or 35 to 40 hr test time. There was some reduction in oxygen consumption rates at the corresponding time in the moist air tests, but not in the dry air determinations.

In addition to the oxidation products noted in Table 11, several low-boiling compounds of very low concentration were generated. Two major products of about 0.7 percent concentration were also shown by GC. The components eluted in the region between the TMP-777 and TMP-778 esters. The product peaks were not new but represented increases in concentration of two minor peaks in the undegraded basestock. The location of the compounds was in the area where single ion scans by MS had indicated prominent C₈ acyl peaks (Fig. 10).

As with the thermal stability studies, the oxidation test data of Table 12 show some heptanoic acid present in the test lubricant samples but at insufficient concentration to account for the sample neutralization number. C₇ acid amounts in oxidation test condensate samples did correlate with neutralization number. In these tests, acid concentration in the condensate was very high, constituting almost 50 percent of the material present.

Since GC residue values had shown that these unrecovered compounds constituted a significant portion of the oxidation products, an effort was made to characterize the material using high performance liquid chromatography techniques.⁽²⁴⁾ The end-of-test sample for Test No. 35, which showed a GC residue of 22.5 percent, was investigated using the HPLC procedures. The results of analysis by gel permeation chromatography revealed two high molecular weight minor components present in the sample,

TABLE 11. COMPOSITIONAL CHANGES IN 400°F
OXIDATION TESTS WITH O-76-5

Time, hr	Component Concentration, wt %			
	Dry Air		Moist Air	
	Test No. 35	Test No. 38	Test No. 41	Test No. 42
<u>TMP diester-aldehyde</u>				
0	0.7	0.7	0.7	0.7
50	9.8	7.9	6.5	6.1
<u>TMP diester-alcohol</u>				
0	0.2	0.2	0.2	0.2
50	Peak not resolved by GC			
<u>TMP-477</u>				
0	2.7	2.7	2.7	2.7
50	2.5	2.1	1.8	1.9
<u>TMP-577</u>				
0	0.6	0.6	0.6	0.6
50	1.4	1.2	0.8	0.8
<u>TMP-677</u>				
0	2.5	2.5	2.5	2.5
50	1.7	1.7	1.3	1.5
<u>TMP-777</u>				
0	89.9	89.9	89.9	89.9
50	41.5	33.9	38.6	42.1
<u>TMP-778</u>				
0	0.7	0.7	0.7	0.7
50	3.0	2.1	1.4	1.6
<u>PE-7777</u>				
0	0.9	0.9	0.9	0.9
50	0.6	1.5	0.3	0.4

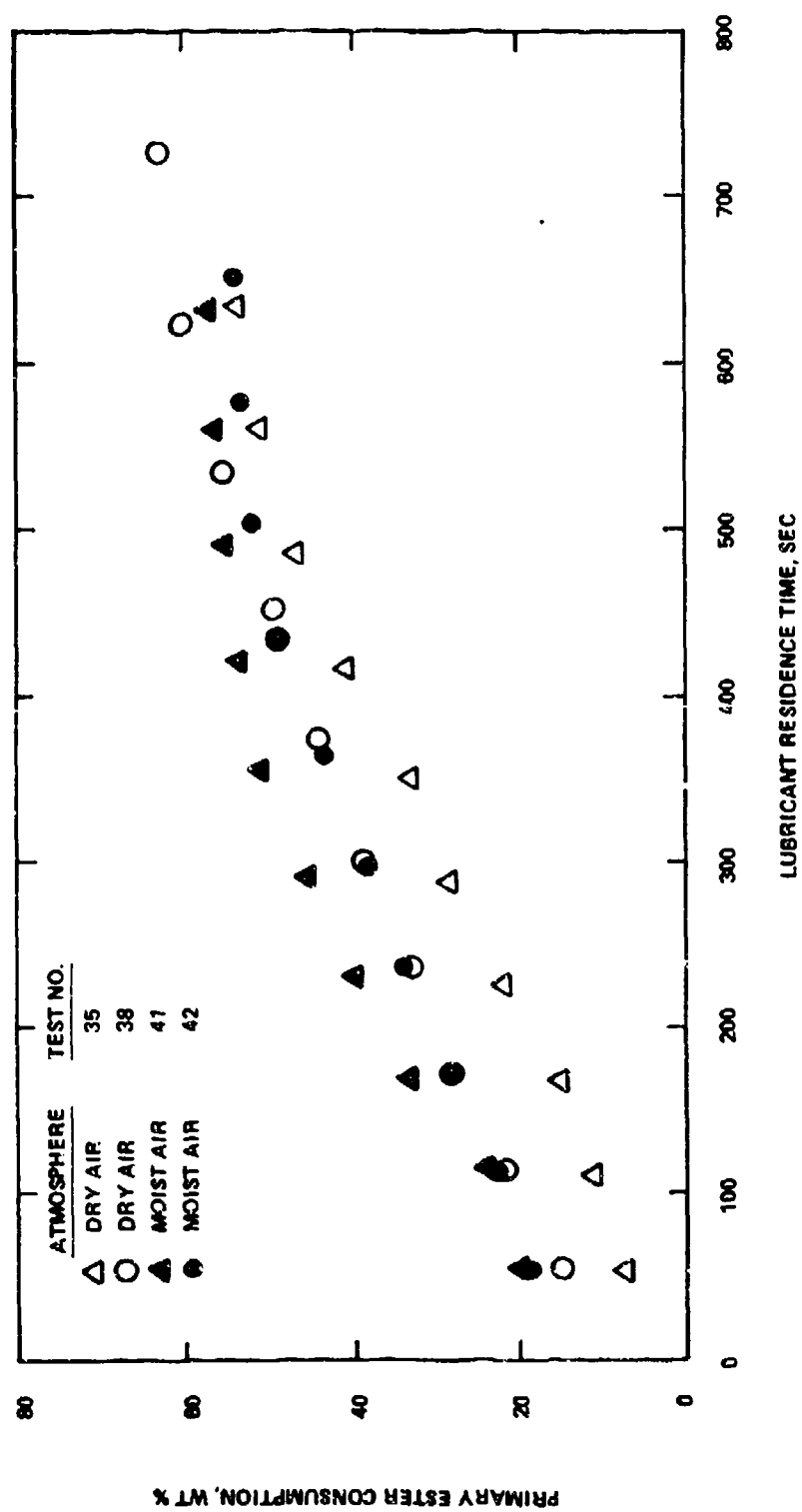


FIGURE 16. PRIMARY ESTER CONSUMPTION DATA FOR OXIDATION TESTS ON 0-76-5 AT 400°F

TABLE 12. O-76-5 LUBRICANT PROPERTIES AT TEST TERMINATION
FOR SELECTED 400°F OXIDATION TESTS

<u>Air</u> <u>Atmosphere</u>	<u>100°F Vis,</u> <u>cs</u>	<u>Heptanoic</u> <u>Acid, wt%</u>	<u>Neut.No., mg KOH/g</u>		<u>Test</u>
			<u>Theor.*</u>	<u>Actual</u>	<u>No.</u>
<u>Lubricant Sample</u>					
Dry	28.92	0.9	3.9	13.77	35
Moist	27.23	0.7	3.0	10.85	41
<u>Condensate Sample</u>					
Dry	4.36	48.0	207	214	35
Moist	**	46.2	199	210	41

* Theoretical neut. no. based on heptanoic acid content.

** Insufficient sample.

not found in the unused basestock. These components indicated "equivalent molecular weights" of approximately 700 and >975. Both materials appeared as merged shoulders on the primary ester peak. Thus, preparative techniques for separation were not practical. Further analysis of the sample by reversed-phase chromatography showed the dissimilarity of the new and used lubricant samples, as also shown by GC, but the RPC procedure did not permit identification of constituents which could be associated with the GC residue.

Figure 17 illustrates oxygen consumption data for the dry air determinations at 350° and 400°F. After a brief induction period, consumption rates remained relatively constant. As previously noted for other performance results, Figure 17 also shows the disparity of data between the duplicate tests at 350°F. Figure 18 presents oxygen data for the moist air runs. Neglecting Test No. 37, oxygen consumption rates were similar to those with dry air. However, with moist air, it is observed that all four runs indicated some reduction of the consumption rate in the later hours of the tests.

Average oxygen consumption rate values were derived from the data of Figure 17 and 18 to permit calculation of the energy of activation for the polyol ester basestock. For the dry air tests average data were used following the induction period time. Average values for the moist air determination were developed for data after the induction period, but before the reduction in consumption rate shown by these curves, i.e., in the region of the curve inflection point. On these bases, the following rate data were derived:

<u>Air</u>	<u>Film Temp, °F</u>	<u>O₂ Consump Rate, l/hr</u>	<u>Test No.</u>
Dry	350	0.30	36
	350	0.68	37
	400	1.09	35
	400	0.98	38
Moist	350	0.56	40
	350	0.48	43
	400	1.03	41
	400	0.91	42

Using average rate values for each of the test pairs at the same condition, the Arrhenius equation yields an energy of activation of 11.8 Kcal/mole for the dry air condition, and 9.9 Kcal/mole for moist air. These values compare favorably with the value of 10.1 Kcal/mole obtained in preliminary work with lubricant O-71-8. Because of the lack of agreement between the dry air tests at 350°F with O-76-5, energies of activation were calculated by omitting each test individually instead of using a mean rate for both. Rejecting data for Test No. 37, a value of 19.4 Kcal/mole was obtained. Rejecting results for Test No. 36 gave 6.8 Kcal/mole. These values appear to indicate that the mean data for these duplicate determinations are of better accuracy than results for either of the individual tests.

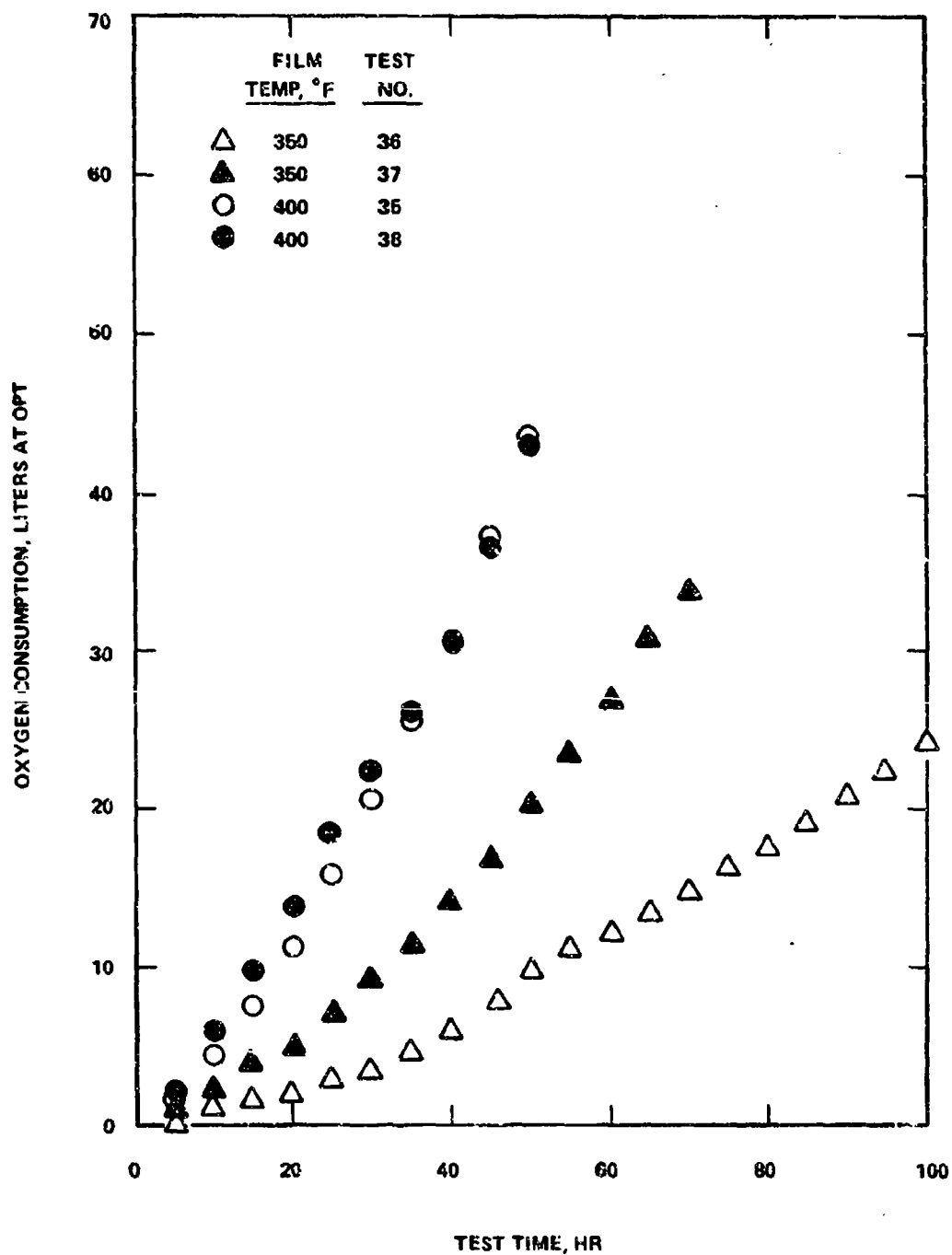


FIGURE 17. OXYGEN CONSUMPTION DATA FOR O-76-5 USING DRY AIR

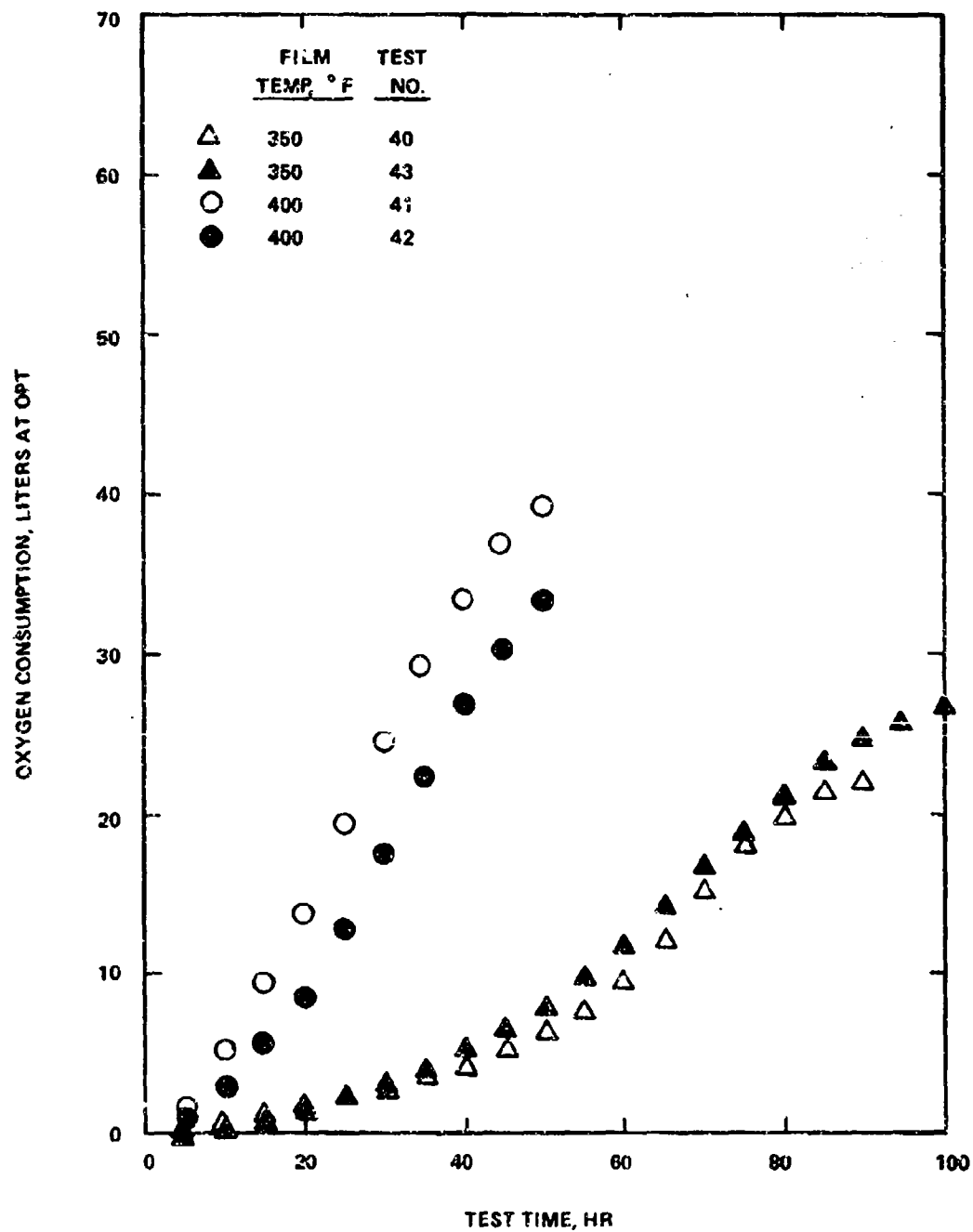


FIGURE 18. OXYGEN CONSUMPTION DATA FOR O-76-5 USING MOIST AIR

Various analyses were performed on sludge deposit samples recovered from the oxidation tests. X-ray fluorescence was used for elemental analysis of many samples, and extensive investigation was performed with the fluid and deposit samples from Test No. 35. All deposit samples showed iron as the major inorganic present, with concentrations as high as 16.3 percent for Test No. 38 and 21.4 percent for Test No. 40. Though not consistently present, lesser amounts of aluminum, phosphorous, chromium, nickel, and silicon were also found by XRF. The iron content of the sludge removed from Test No. 35 was 6.4 percent with significant, but lesser amounts of phosphorous and potassium. Trace amounts of several other metals were also found in the deposit. After repeated solvent washings, infrared analysis of the deposit indicated very little carbon-hydrogen structure present. The spectrum did show the possibility of phosphate absorption. X-ray diffraction analysis of the deposit did not produce a clear diffraction pattern which would permit interpretation. By solid probe insertion, the material was next examined by mass spectrometry. This analysis confirmed that the deposit contained very little organic material. The main feature of the mass spectrum obtained was a fragment ion characteristic of the C7 acyl group (m/e 113).

Comparative work on suspended material in the end-of-test fluid for Test No. 35 was also carried out. This material was obtained by filtering a 100-cm³ sample through a 0.45- μ m membrane filter. Microscopic examination of the cylinder rig deposit and the filter residue indicated the two materials were identical in appearance. The particles were several micrometers in major dimension and ranged in color from very light straw to black, with numerous shades between. By visual estimation, the particles were generally amorphous in structure. The material showed no response to a magnetic field, indicating that the iron present was reacted. The compositional similarity of inorganics between the filter residue and the cylinder wall deposit was also confirmed by XRF "fingerprinting" of the samples.

The final step in the investigation of Test No. 35 consisted of XRF analysis for inorganics in the lubricant samples taken throughout the run. Iron was the only significant element found by this analysis. The 5 through 35-hr samples showed iron contents of ≤ 5 ppm. The 40, 45, and 50 hr samples indicated iron contents of 10, 105, and 340 ppm, respectively. Analysis of the highly acidic condensate sample gave an iron value of 1360 ppm.

CONCLUSIONS

Characterization of the polyol ester basestock by GC/MS was based principally on fragment ions for the acyl groups present. Electron impact ionization resulted in extensive fragmentation such that no molecular ions were evident. In addition to the primary ester component, TMP-777, significant TMP triester concentrations were found which apparently consisted of two C7 acyl groups and one C4, C5, C6, or C8 group. Pentaerythritol tetraheptanoate was also identified as a major (>0.5 wt percent) basestock component. Based on lesser analytical evidence, a combination GC peak composed of TMP diheptanoate-aldehyde and TMP diheptanoate-alcohol was inferred.

In the absence of an oxidizing atmosphere, thermal degradation of the TMP triheptanoate basestock was slight at 600°F film temperature. Cylinder rig tests at 650°F showed increased ester breakdown, especially with a moist atmosphere. For this condition, the principal degradation products were diesters, heavy constituents indicated by GC residue, and, as found in condensate samples, heptanoic acid. Only varnish-type deposits were formed in the thermal stability test series. Chemical analysis of the varnish recovered from one run (Test No. 27) showed the composition of the material was primarily inorganic; however, the quantity of the deposit available for analysis was extremely small.

Employing film temperatures of 350° and 400°F, oxidative deterioration of the polyol ester was significant. Use of a moist air atmosphere did not accelerate degradation, probably because the intensity of the oxidative attack was so severe that any hydrolytic effect was obscured. Aside from quantitative differences, the products of ester oxidation were similar to those found in the thermal stability experiments, i.e., compounds postulated to be C7 diesters, GC residue components, and heptanoic acid. In addition, the oxidation experiments showed the apparent formation of triesters in the gas chromatogram region associated with the presence of C8 acyl groups. A possible explanation for this phenomenon might be associated with a recombination of free C8 acid and partially hydrolyzed esters.

On the basis of average oxygen consumption rate data, calculated energies of activation for the polyol ester were 9.9 Kcal/mole with moisture present, and 11.8 Kcal/mole for dry air. The fact that these values are considerably lower than expected is thought to be the result of the "rig dependence" of data obtained.

Elemental analysis of various sludge deposits from the oxidation experiments indicated a high inorganic content, primarily iron and other metals. Mass spectrometry confirmed the inorganic nature of the deposit samples and also showed the presence of the C7 acyl ion (m/e 113). Analysis of fluid samples taken for Test No. 35 revealed a rapid buildup in iron contents in the later hours of the test (35 to 50 hr), with the highest iron concentration found in the acidic condensate sample taken at 50 hr. Microscopic examination and X-ray fluorescence "fingerprinting" of the Test No. 35

deposit and suspended matter in the test fluid indicated the materials were of similar structure and metal content.

The foregoing findings suggest that, under the conditions investigated, the mechanism of deposit formation by the polyol ester was through a corrosive wear process. Attack of system metals by the acidic constituents generated, primarily heptanoic acid, apparently produced metallo-organic compounds which were subsequently deposited on the cylinder wall. It is unclear, however, whether the corrosion process occurs mainly in the high temperature region of the cylinder or, because of the relatively high volatility of the organic acids, in the lower temperature condensing areas of the test apparatus. If the latter case is applicable, deposits adhering to the cylinder wall would presumably be introduced via the influent lubricant and deposited, possibly, by some polar attraction, or simply due to the centrifugal force imposed by cylinder rotation.

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APPENDIX
ROTATING CYLINDER DEPOSITION TEST
SUMMARY DATA

TEST NO. 20

 OXIDATIVE
 ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
 ON LUBRICANT O-71-8

Test Conditions

Film temp., °F 425 Lubricant-in temp., °F 425
 Film thickness, in, $\times 10^{-3}$ 4 Airflow, liters/hr 100, dry
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 17.9 Test duration, hr 50
 Total res. time, sec 538.1

Deposit Rating

Deposit Type	Area, λ	Demerits
L varnish	100	10

Overall Rating: 10

Test Lubricant Performance

Test Time, hr	100°F Vis, cs	100°F Vis Increase, λ	210°F Vis, cs	NN Change, mg KOH/g	Oxygen Consumption, l at OPT
0	15.08	-	3.51	0.06	-
5	16.99	12.7	3.73	1.15	4.56
10	18.07	19.8	3.87	2.34	9.94
15	19.33	28.2	4.00	3.57	15.22
20	20.20	34.0	4.12	4.72	20.57
25	21.03	39.5	4.24	5.88	25.79
30	23.08	53.1	4.45	7.24	31.32
35	24.48	62.1	4.62	8.19	36.87
40	25.08	66.3	4.70	11.62	42.55
45	26.83	91.2	5.12	9.91	48.12
50	37.85	150	5.91	10.79	54.82

Lubricant loss, cm³/hr 4.6

TEST NO. 21

 OXIDATIVE
 ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
 ON LUBRICANT O-71-8

Test Conditions

Film temp., °F 400 Lubricant-in temp., °F 400
 Film thickness, in, $\times 10^{-3}$ 4 Airflow, liters/hr 100, dry
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 18.1 Test duration, hr 75
 Total res. time, sec 815.2

Deposit Rating

Deposit Type	Area, λ	Demerits
L varnish	95	9.5
L smooth carbon	5	4.5

Overall Rating: 14

Test Lubricant Performance

Test Time, hr	100°F Vis, cs	100°F Vis Increase, λ	210°F Vis, cs	NN Change, mg KOH/g	Oxygen Consumption, l at OPT
0	15.08	-	3.51	0.06	-
5	16.70	10.7	3.69	1.59	2.63
10	17.42	15.5	3.76	2.48	5.88
15	18.16	20.4	3.86	3.65	9.64
20	18.94	25.6	3.94	4.95	13.55
25	19.43	28.8	4.03	6.60	17.38
30	20.22	34.1	4.08	8.44	21.76
35	21.20	40.6	4.22	9.27	25.78
40	21.63	43.4	4.27	10.66	30.00
45	22.60	49.9	4.39	11.53	34.50
50	23.20	53.8	4.49	12.58	38.66
55	24.39	61.7	4.58	14.20	42.66
60	25.47	68.9	4.73	15.79	46.62
65	26.68	76.9	4.98	16.33	50.76
70	28.20	87.0	5.08	18.07	56.10
75	28.95	92.0	5.17	18.52	61.04

Lubricant loss, cm³/hr 4.9

TEST NO. 22

OXIDATIVE
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT C-711-8

Test Conditions

Film temp, °F 450 Lubricant-in temp, °F 450
 Film thickness, in, X 10⁻³ 4 Airflow, liters/hr 100, dry
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 17.8 Test duration, hr 35
 Total res. time, sec 372.1

Deposit Rating

Deposit Type	Area, %	Demerits
L varnish	100	10

Overall Rating: 10

Test Lubricant Performance

Test Time, hr	100°F Vis, cS	100°F Vis Increase, %	210°F Vis, cS	NN Change, mg KOH/g	Oxygen Consumption, % at Opt
0	15.08	-	3.51	0.06	-
5	17.59	16.6	3.79	2.02	7.30
10	19.14	26.9	3.98	4.10	14.92
15	20.47	36.4	4.14	5.87	22.32
20	21.96	45.6	4.33	8.71	30.04
25	23.20	67.1	4.69	11.00	36.96
30	27.83	84.5	5.00	12.57	41.02
35	30.98	105	5.36	14.59	49.40

Lubricant loss, cm³/hr 5.4

TEST NO. 23

THERMAL STABILITY
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT C-711-8

Test Conditions

Film temp, °F variable* Lubricant-in temp, °P variable*
 Film thickness, in, X 10⁻³ 4 Nitrogen blanket dry
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle variable Test duration, hr 100
 Total res. time, sec 1024.6

Deposit Rating

Deposit Type	Area, %	Demerits
Clean	100	0

Overall Rating: 0

Test Lubricant Performance

Test Time, hr	100°F Vis, cS	100°F Vis Increase, %	210°F Vis, cS	NN Change, mg KOH/g	Unreacted Ester, wt %
0	15.08	-	3.51	0.06	100
5	15.29	1.4	3.52	0.00	-
10	15.30	1.5	3.52	0.00	-
15	15.28	1.3	3.52	0.00	-
20	15.28	1.3	3.52	0.00	-
25	15.25	1.1	3.52	0.00	-
30	15.28	1.3	3.52	0.00	-
35	15.28	1.3	3.52	0.00	-
40	15.29	1.3	3.51	0.00	-
45	15.25	1.1	3.53	0.00	-
50	15.22	1.6	3.52	0.03	-
55	15.21	1.5	3.53	0.06	-
60	15.31	1.5	3.52	0.06	-
65	15.34	1.7	3.53	0.12	-
70	15.29	1.4	3.53	0.19	-
75	15.33	1.7	3.54	0.24	-
80	15.38	2.0	3.54	0.26	-
85	15.34	1.7	3.53	0.32	-
90	15.37	1.9	3.54	0.35	-
95	15.37	1.9	3.54	0.38	-
100	15.40	2.1	3.54	0.40	-

Lubricant loss, cm³/hr 5.0

* Film and lubricant-in temperatures varied as follows: 0-30 hr, 500°F; 30-60 hr, 550°F; 60-100 hr, 600°F.

TEST NO. 24

THERMAL STABILITY
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT O-76-5

Test Conditions

Film temp., °F 600 Lubricant-in temp., °F 400
 Film thickness, in, X 10⁻³ 4 Nitrogen blanket dry
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 16.8 Test duration, hr 100
 Total res. time, sec 1449.7

Deposit Rating

Deposit Type	Area, %	Demerits
Clean	100	0

Overall Rating: 0

Test Lubricant Performance

Test Time, hr	100°F Visc, cps	100°F Visc Increase, %	210°F Visc, cps	HN Change, mg KOH/g	Unreacted Ester, wt %
0	15.22	-	3.53	0.02	100
5	15.39	1.1	3.54	0.08	-
10	15.37	0.9	3.53	0.14	100
15	15.41	1.2	3.55	0.20	-
20	15.44	1.4	3.54	0.24	100
25	15.45	1.4	3.54	0.29	-
30	15.43	1.3	3.54	0.35	98.5
35	15.54	2.0	3.56	0.32	-
40	15.57	2.2	3.56	0.46	92.3
45	15.61	2.5	3.58	0.52	-
50	15.59	2.4	3.56	1.05	97.3
55	15.57	2.2	3.56	1.29	-
60	15.60	2.4	3.57	1.46	95.1
65	15.63	2.4	3.57	1.59	-
70	15.62	2.4	3.58	1.72	94.8
75	15.83	3.9	3.60	1.43	-
80	15.82	3.9	3.59	1.67	94.8
85	15.84	4.0	3.61	1.84	-
90	15.87	4.2	3.61	2.29	94.6
95	15.92	4.5	3.61	2.29	-
100	15.96	4.7	3.61	2.49	94.4

Oil loss, cm³/hr : 7

TEST NO. 25

THERMAL STABILITY
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT O-76-5

Test Conditions

Film temp., °F 600 Lubricant-in temp., °F 600
 Film thickness, in, X 10⁻³ 4 Nitrogen blanket dry
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 16.8 Test duration, hr 100
 Total res. time, sec 1525.4

Deposit Rating

Deposit Type	Area, %	Demerits
Clean	100	0

Overall Rating: 0

Test Lubricant Performance

Test Time, hr	100°F Visc, cps	100°F Visc Increase, %	210°F Visc, cps	HN Change, mg KOH/g	Unreacted Ester, wt %
0	15.23	-	3.53	0.02	100
5	15.37	0.9	3.53	0.08	-
10	15.44	1.4	3.53	0.11	99.1
15	15.38	1.0	3.54	0.15	-
20	15.43	1.3	3.54	0.23	98.7
25	15.45	1.4	3.54	0.24	-
30	15.45	1.4	3.54	0.29	97.9
35	15.43	1.3	3.54	0.32	-
40	15.50	1.8	3.54	0.35	98.7
45	15.48	1.6	3.55	0.38	-
50	15.45	1.6	3.55	0.39	90.8
55	15.52	1.9	3.56	0.41	-
60	15.57	2.2	3.56	0.43	98.2
65	15.57	2.2	3.57	0.44	-
70	15.53	2.3	3.57	0.43	98.0
75	15.63	2.6	3.57	0.45	-
80	15.67	2.9	3.58	0.46	98.7
85	15.70	3.1	3.52	0.48	-
90	15.68	3.0	3.58	0.50	98.4
95	15.72	3.2	3.59	0.52	-
100	15.74	3.3	3.58	0.53	98.4

Oil loss, cm³/hr 4.6

TEST NO. 26

THERMAL STABILITY
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT O-76-5

Test Conditions

Film temp, °F 650 Lubricant-in temp, °F 650
 Film thickness, in, $\times 10^{-3}$ 4 Nitrogen blanket dry
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 16.2 Test duration, hr 100
 Total res. time, sec 1287.3

Deposit Rating

Deposit Type	Area, μ	Demerits
L varnish	100	10

Overall Rating: 10

Test Lubricant Performance

Test Time, hr	100°F Visc, cs	100°F Visc Increase, μ	210°F Visc, cs	MN Change, mg KOH/g	Unreacted Ester, wt %
0	15.23	-	3.53	0.02	100
5	15.34	0.7	2.53	0.26	-
10	15.35	0.8	3.54	0.43	100
15	15.36	0.9	3.54	0.48	-
20	15.32	0.6	3.53	0.56	98.7
25	15.35	0.8	3.53	0.59	-
30	15.39	1.1	3.54	0.64	98.4
35	15.39	1.1	3.54	0.74	-
40	15.41	1.2	3.55	0.81	98.1
45	15.43	1.3	3.54	0.93	-
50	15.46	1.5	3.54	1.03	97.9
55	15.48	1.6	3.55	1.10	-
60	15.52	1.9	3.55	1.23	96.8
65	15.54	2.0	3.57	1.36	-
70	15.60	2.4	3.57	1.49	96.2
75	15.63	2.6	3.57	1.59	-
80	15.65	3.0	3.60	1.76	95.1
85	15.56	4.0	3.61	1.85	-
90	15.86	4.1	3.61	1.97	94.0
95	15.91	4.5	3.61	2.23	-
100	16.00	5.1	3.63	2.26	92.6

Oil loss, cm³/hr 2.6

TEST NO. 27

THERMAL STABILITY
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT O-76-5

Test Conditions

Film temp, °F 650 Lubricant-in temp, °F 650
 Film thickness, in, $\times 10^{-3}$ 4 Nitrogen blanket dry
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 16.2 Test duration, hr 95
 Total res. time, sec 1408.0

Deposit Rating

Deposit Type	Area, μ	Demerits
L varnish	100	10

Overall Rating: 10

Test Lubricant Performance

Test Time, hr	100°F Visc, cs	100°F Visc Increase, μ	210°F Visc, cs	MN Change, mg KOH/g	Unreacted Ester, wt %
0	15.23	-	3.53	0.02	100
5	15.31	0.5	3.53	0.27	-
10	15.37	0.9	3.54	0.49	99.0
15	15.38	1.0	3.53	0.64	-
20	15.39	1.1	3.54	0.75	93.2
25	15.43	1.3	3.55	0.88	-
30	15.48	1.6	3.55	0.99	95.7
35	15.51	1.8	3.55	1.06	-
40	15.58	2.3	3.57	1.16	94.4
45	15.63	2.6	3.56	1.21	-
50	15.68	3.0	3.57	1.25	95.2
55	15.71	3.2	3.59	1.39	-
60	15.78	3.6	3.59	1.44	94.7
65	15.89	4.3	3.61	1.52	-
70	15.93	4.6	3.62	1.78	93.3
75	15.96	4.8	3.63	1.97	-
80	16.09	5.6	3.63	2.02	92.3
85	16.18	6.7	3.65	2.16	-
90	16.26	6.8	3.66	2.33	91.5
95*	16.27	6.9	3.66	3.35	88.9

Oil loss, cm³/hr 6.6

* Test terminated at 95 hr due to clogging of test-oil jet.

TEST NO. 31

THERMAL STABILITY
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT O-7-15

Test Conditions

Film temp, °F 600 Lubricant-in temp, °F 600
 Film thickness, in, X 10⁻³ 4 Nitrogen blanket moist
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 10.8 Test duration, hr 100
 Total res. time, sec 1107.6

Deposit Rating

Deposit Type Clean Area, sq 100 Deposits 0

Overall Rating: 0

Test Lubricant Performance

Test Time, hr	100°F Visc, cps	210°F Visc, cps	Vis. Chg, %	Unreacted Ester, wt %
0	15.23	3.53	0.02	100
5	15.31	3.52	0.04	97.9
10	15.37	3.5	0.20	97.5
15	15.34	3.53	0.27	96.5
20	15.34	3.53	0.33	95.4
25	15.34	3.53	0.42	96.4
30	15.34	3.53	0.47	96.0
35	15.34	3.53	0.54	95.5
40	15.34	3.53	0.73	96.8
45	15.34	3.53	0.76	97.5
50	15.34	3.53	0.79	98.2
55	15.34	3.52	1.01	97.0
60	15.34	3.53	1.10	97.0
65	15.35	3.53	1.37	96.9
70	15.35	3.53	1.62	95.0
75	15.34	3.53	1.90	96.6
80	15.34	3.53	2.16	96.0
85	15.34	3.53	2.36	95.3
90	15.35	3.53	2.61	95.0
95	15.36	3.53	2.79	95.0
100	15.38	3.53	2.92	93.6

Oil loss, cm³/hr 2.8

TEST NO. 32

THERMAL STABILITY
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT O-76-5

Test Conditions

Film temp, °F 600 Lubricant-in temp, °F 600
 Film thickness, in, X 10⁻³ 4 Nitrogen blanket moist
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 16.0 Test duration, hr 100
 Total res. time, sec 1440.0

Deposit Rating

Deposit Type Clean Area, sq 100 Deposits 0

Overall Rating: 0

Test Lubricant Performance

Test Time, hr	100°F Visc, cps	210°F Visc, cps	Vis. Chg, %	Unreacted Ester, wt %
0	15.23	3.53	0.02	100
5	15.29	3.53	0.18	97.1
10	15.27	3.51	0.20	96.8
15	15.30	3.54	0.31	97.1
20	15.40	3.54	0.34	96.9
25	15.47	3.54	0.37	97.2
30	15.47	3.54	0.44	96.4
35	15.48	3.54	0.46	96.9
40	15.50	3.55	0.52	96.4
45	15.50	3.55	0.71	96.6
50	15.51	3.55	0.67	97.0
55	15.52	3.55	0.67	96.7
60	15.56	3.55	0.70	97.0
65	15.58	3.56	0.88	96.2
70	15.63	3.57	1.02	96.5
75	15.64	3.57	1.21	95.1
80	15.66	3.57	1.24	95.9
85	15.69	3.58	1.27	96.3
90	15.72	3.58	1.29	93.6
95	15.81	3.60	1.52	91.7
100	15.92	3.61	1.58	94.1

Oil loss, cm³/hr 3.8

TEST NO. 33

THERMAL STABILITY
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT O-76-5

Test Conditions

Film temp., °F 650 Lubricant-in temp., °F moist
 Film thickness, in, X 10⁻³ 4 Nitrogen blanket
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 16.2 Test duration, hr 100
 Total res. time, sec 1404.1

Deposit Rating

Deposit Type	Area, Å	Demerits
I varnish	25	2.5
H varnish	75	37.5

Overall Rating: 40

Test Lubricant Performance

Test Time, hr	100°F Visc, cP	100°F Visc Increase, Å	210°F Visc, cP	MM Change, mg KOS/g	Unreacted Ester, wt %
0	15.23	-	-	0.02	100
5	15.42	1.2	-	0.22	96.2
10	15.45	1.5	-	0.30	96.1
15	15.56	2.3	-	0.41	95.1
20	15.72	3.2	-	0.70	93.5
25	15.78	3.6	3.61	0.84	93.0
30	16.04	5.3	3.64	0.96	91.5
35	16.21	6.4	3.66	1.39	87.5
40	16.38	7.6	3.68	1.68	86.4
45	16.52	8.5	3.70	1.79	85.6
50	16.78	10.2	3.74	1.89	84.7
55	16.94	11.2	3.77	2.07	83.7
60	17.16	12.7	3.79	2.38	82.3
65	17.41	14.3	3.82	2.74	81.0
70	17.59	15.5	3.86	3.20	81.6
75	17.61	15.6	3.86	3.61	80.6
80	17.62	15.7	3.87	4.27	79.6
85	17.31	13.7	3.80	6.73	77.3
90	17.07	12.1	3.78	8.56	76.4
95	15.39	1.1	3.52	15.72	75.9
100	14.12	-7.3	3.33	20.8	74.3

Oil loss, cm³/hr 4.5

TEST NO. 34

THERMAL STABILITY
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT O-76-5

Test Conditions

Film temp., °F 650 Lubricant-in temp., °F moist
 Film thickness, in, X 10⁻³ 4 Nitrogen blanket
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 16.2 Test duration, hr 100
 Total res. time, sec 1444.2

Deposit Rating

Deposit Type	Area, Å	Demerits
L varnish	25	2.5
M varnish	10	2
H varnish	65	32.5

Overall Rating: 38

Test Lubricant Performance

Test Time, hr	100°F Visc, cP	100°F Visc Increase, Å	210°F Visc, cP	MM Change, mg KOS/g	Unreacted Ester, wt %
0	15.23	-	-	0.02	100
5	15.31	0.5	3.53	0.41	96.5
10	15.34	0.7	3.53	0.74	95.4
15	15.43	1.3	3.54	0.96	94.5
20	15.48	1.6	3.55	1.23	93.2
25	15.59	2.4	3.57	1.51	91.3
30	15.66	2.8	3.57	1.82	91.7
35	15.76	3.5	3.59	1.96	91.3
40	15.86	4.1	3.61	2.30	89.5
45	15.97	4.9	3.64	2.70	88.6
50	16.35	7.4	3.67	2.18	87.8
55	16.51	8.4	3.70	2.31	87.0
60	16.58	8.9	3.71	2.77	85.7
65	16.72	9.8	3.73	2.79	85.0
70	16.81	10.4	3.74	3.18	85
75	16.83	10.5	3.75	3.16	84.2
80	16.90	11.0	3.76	4.24	84.2
85	17.10	12.3	3.78	4.37	83.9
90	17.36	14.0	3.82	4.63	83.0
95	17.43	14.4	3.85	5.91	82.3
100	17.58	15.4	3.87	8.05	80.3

Oil loss, cm³/hr 3.8

TEST MC. 36

OXIDATIVE
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT O-76-S

Test Conditions

Film temp., °F	350	Lubricant-in temp., °F	350
Film thickness, in. $\times 10^{-3}$	4	Airflow, liters/hr	100, dry
Lubricant flow, cm ³ /min	4	Lubricant charge, cm ³	1000
Average -ca. time, sec/cycle	18.5	Test duration, hr	100
Total test time, sec	1658.1		

Deposit Rating

10
Drerits

Overall Rating: 10

Test Lubricant Performance

Test Time, hr.	100°F V ₁ /C ₂	100°F V ₁ Increase, %	NH Change, mg KCH ₃ S	Unreacted Fater, wt%	Oxygen Consumption, % at 60°C
0	13.23	-	0.02	100	0
5	15.42	1.2	0.06	99.8	0.13
10	15.66	2.8	0.42	88.3	1.15
15	15.90	3.7	0.48	80.5	2.60
20	16.06	5.4	0.59	86.2	2.08
25	16.41	7.7	0.86	84.5	2.96
30	16.84	9.3	1.15	83.1	3.72
35	17.06	12.0	1.46	81.2	4.64
40	17.42	14.4	2.07	78.4	6.14
45	17.86	17.3	2.63	75.2	7.98
50	18.46	21.2	3.57	74.5	9.90
55	18.98	24.6	4.20	70.8	11.06
60	19.46	27.8	5.06	68.2	12.22
65	19.97	31.2	5.63	65.9	13.48
70	20.51	34.7	6.78	63.3	14.70
75	20.95	37.6	7.74	60.1	16.17
80	21.61	41.9	8.43	59.6	17.72
85	22.25	46.1	9.72	54.5	19.19
90	23.23	52.5	11.26	53.2	20.83
95	23.95	56.6	11.82	49.2	22.46
100	24.70	62.2	12.22	47.0	24.18

Oil loss, cm³/hr 3.2

TEST NO. 37

OXIDATIVE
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT O-76-5

Test Conditions

Film temp, °F 350 Lubricant-in temp, °F 100, dry
 Film thickness, in $\times 10^{-3}$ 4 Airflow, liters/hr 100, dry
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 18.5 Test duration, hr 70
 Total res. time, sec 1143.5

Deposit Rating

Deposit Type L varnish
 Area, in² 100
 Demerits 10

Overall Rating: 10

Test Lubricant Performance

Test Time, hr	100°F Visc, cSt	100°F Visc Increase, %	MN Change, mg KOH/g	Unreacted Ester, wt %	Oxygen Consumption, l at 100°C
0	15.23	-	0.02	100	0
5	15.53	2.0	0.25	88.9	1.16
10	15.89	4.1	0.62	85.6	2.49
15	16.23	6.6	1.07	81.1	3.99
20	16.63	9.2	1.55	80.5	5.10
25	17.12	12.4	2.36	76.2	7.06
30	17.72	16.3	3.28	72.5	9.44
35	18.60	17.5	3.93	69.6	11.46
40	19.67	22.7	5.63	65.4	14.14
45	20.57	33.7	7.45	61.0	16.96
50	21.56	41.7	8.74	55.2	20.32
55	22.75	49.4	11.28	49.3	23.56
60	25.09	64.7	14.63	44.5	26.58
65	28.40	86.5	15.21	40.6	30.77
70				39.4	33.93

Oil loss, cm³/hr 6.2

TEST NO. 38

OXIDATIVE
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT O-76-5

Test Conditions

Film temp, °F 400 Lubricant-in temp, °F 400
 Film thickness, in $\times 10^{-3}$ 4 Airflow, liters/hr 100, dry
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 18.1 Test duration, hr 50
 Total res. time, sec 726.7

Deposit Rating

Deposit Type L sludge
 Area, in² 100
 Demerits 60

Overall Rating: 50

Test Lubricant Performance

Test Time, hr	100°F Visc, cSt	100°F Visc Increase, %	MN Change, mg KOH/g	Unreacted Ester, wt %	Oxygen Consumption, l at 100°C
0	15.23	-	0.02	100	0
5	15.96	4.8	0.62	85.0	2.30
10	16.71	9.7	1.64	77.9	5.97
15	17.75	16.5	2.73	71.7	9.90
20	18.61	22.2	4.20	66.9	13.95
25	19.47	27.8	5.73	60.8	18.44
30	20.50	34.8	7.64	56.1	22.28
35	21.70	42.5	9.44	50.9	26.28
40	22.69	49.0	11.41	45.1	30.56
45	26.92	76.8	14.03	40.3	36.36
50	30.65	101	16.34	37.7	42.69

Oil loss, cm³/hr 7.7

TEST NO. 40

 OXIDATIVE
 ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
 ON LUBRICANT O-76-5

Test Conditions

Film temp, °F 350 Lubricant-in temp, °F 350
 Film thickness, in. $\times 10^{-3}$ 4 Airflow, liters/hr 100, moist
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 18.5 Test duration, hr 90
 Total res. time, sec 1693.2

Deposit Type	Deposit Rating	Area, μ	Demerits
L sludge		100	60

Overall Rating: 60

Test Lubricant Performance

Test Time, hr	100°F Vis. cs	100°F Vis. Increase, μ	NW Change, mg KOH/g	Unreacted Ester, wt %	Oxygen Consumption, l at CPT
0	15.23	-	0.02	100	0
5	15.33	0.7	0.04	84.0	0.31
10	15.42	1.2	0.12	83.8	0.72
15	15.53	2.0	0.17	82.8	1.24
20	15.69	3.0	0.27	81.8	1.70
25	15.87	4.2	0.48	80.6	2.22
30	16.09	5.6	0.65	79.7	2.83
35	16.41	7.6	0.99	77.4	3.48
40	16.69	9.6	1.32	75.4	4.21
45	17.14	12.5	1.82	74.1	5.14
50	17.55	15.2	2.57	70.9	6.26
55	18.03	18.4	3.24	68.2	7.62
60	18.60	22.1	4.48	64.6	9.48
65	19.59	28.6	6.30	59.3	12.21
70	20.64	35.5	8.46	55.4	15.13
75	22.34	46.7	9.81	51.0	17.95
80	23.69	55.5	11.03	48.0	19.95
85	24.94	63.8	11.25	47.2	21.26
90	25.63	68.3	11.58	46.7	23.12

Oil loss, cm³/hr 4.5

TEST NO. 41

 OXIDATIVE
 ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
 ON LUBRICANT O-76-5

Test Conditions

Film temp, °F 400 Lubricant-in temp, °F 400
 Film thickness, in. $\times 10^{-3}$ 4 Airflow, liters/hr 100, moist
 Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
 Average res. time, sec/cycle 18.1 Test duration, hr 50
 Total res. time, sec 631.7

Deposit Type	Deposit Rating	Area, μ	Demerits
L sludge		100	60

Overall Rating: 60

Test Lubricant Performance

Test Time, hr	100°F Vis. cs	100°F Vis. Increase, μ	NW Change, mg KOH/g	Unreacted Ester, wt %	Oxygen Consumption, l at CPT
0	15.23	-	0.02	100	0
5	15.83	3.9	0.52	80.1	1.72
10	16.82	10.4	1.63	76.1	5.17
15	17.85	17.2	2.90	66.6	9.31
20	18.33	21.7	4.63	60.3	13.94
25	19.84	30.3	5.73	54.5	19.25
30	21.68	42.4	7.07	48.9	24.64
35	23.05	51.3	8.22	46.2	29.40
40	24.64	61.8	9.04	45.1	33.50
45	25.99	70.7	10.39	43.5	36.77
50	27.23	78.2	10.83	42.9	39.26

Oil loss, cm³/hr 3.7

TEST NO. 42

OXIDATIVE
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT O-76-S

Test Conditions

Film Temp., °F 400 Lubricant-in temp., °F 400
Film thickness, in. $\times 10^{-3}$ 4 Airflow, liters/hr 100 moist
Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
Average test time, sec/cycle 18.1 Test duration, hr 50
Total test time, sec 650.7

Deposit Rating

Demerits

Area, in.²

Deposit Type

L varnish

L sludge

2

43

Overall Rating: 50

Test Lubricant Performance

Test Time, hr	100°F Visc, cps	100°F Visc Increase, %	NN Change, mg KOH/g	Unreacted Ester, wt %	Oxygen Consumption, % at 0.1% O ₂
0	15.23	-	0.02	100	0
5	15.56	2.2	0.27	91.4	0.88
10	15.21	5.8	0.78	77.9	2.82
15	17.02	11.8	1.71	71.9	5.60
20	17.61	15.6	2.81	66.3	8.64
25	18.38	20.6	4.63	61.3	11.70
30	19.63	28.9	7.11	56.3	12.52
35	20.96	37.6	7.03	51.5	22.32
40	22.16	45.5	8.12	48.1	26.81
45	23.36	53.4	9.27	47.3	30.34
50	24.35	59.9	9.65	46.8	33.18

Oil loss, cm³/hr 3.7

TEST NO. 43

OXIDATIVE
ROTATING CYLINDER DEPOSITION TEST SUMMARY DATA
ON LUBRICANT O-76-S

Test Conditions

Film Temp., °F 350 Lubricant-in temp., °F 350
Film thickness, in. $\times 10^{-3}$ 4 Airflow, liters/hr 100 moist
Lubricant flow, cm³/min 10 Lubricant charge, cm³ 1000
Average test time, sec/cycle 18.5 Test duration, hr 100
Total test time, sec 1800.3

Deposit Rating

Demerits

Area, in.²

Deposit Type

L sludge

100

Overall Rating: 60

Test Lubricant Performance

Test Time, hr	100°F Visc, cps	100°F Visc Increase, %	NN Change, mg KOH/g	Unreacted Ester, wt %	Oxygen Consumption, % at 0.1% O ₂
0	15.23	-	0.02	100	0
5	15.28	0.3	0.09	83.5	0.18
10	15.52	1.9	0.23	82.9	0.54
15	15.77	3.5	0.36	82.7	0.92
20	15.88	4.3	0.60	81.7	1.44
25	16.15	6.0	0.90	77.3	2.20
30	16.45	8.0	1.17	77.7	3.03
35	16.83	10.5	1.72	76.0	4.11
40	17.26	13.3	2.28	72.6	5.11
45	17.57	15.4	3.04	69.4	6.47
50	17.99	18.3	3.67	67.9	7.94
55	18.56	21.9	4.67	63.8	9.79
60	18.92	24.2	5.73	61.5	11.66
65	19.43	27.6	7.21	57.7	14.26
70	20.33	33.5	8.60	55.6	16.66
75	21.19	39.1	9.97	52.9	18.36
80	22.47	47.5	10.60	49.1	21.27
85	23.44	53.7	11.58	46.8	21.07
90	24.59	60.1	12.44	44.9	24.77
95	25.28	66.0	12.82	44.6	25.69
100	26.33	72.9	13.18	44.2	26.56

Oil loss, cm³/hr 4.1