

N85 - 33523**THE USE OF PERFLUOROETHER LUBRICANTS
IN UNPROTECTED SPACE ENVIRONMENTS**

Bryan H. Baxter*, Barry P. Hall*

ABSTRACT

This paper describes a series of ball bearing tests in simulated space environment to determine durability of perfluoroether lubricants. The results of the examination of the test bearings for each stage are described and experimental techniques designed to overcome lubricant degradation are outlined.

INTRODUCTION

The perfluoroether (PFE) group of lubricants, which is manufactured by a variety of companies around the world, has unique physical properties suggesting that they would be ideal for space applications.

The available range of products in this class of fluids is very large indeed and is complicated by the fact that several different manufacturing routes are used, resulting in different families of product.

To illustrate the physical properties which are relevant to space component lubrication, typical data are presented in Table I for two members of representative series, designated Z and Y.

These properties have encouraged designers to consider the use of such lubricants in space mechanisms, and in order to establish design rules and life data, several research programmes have been initiated.

At the European Space Tribology Laboratory (ESTL) established at the National Centre for Tribology, Risley, England, considerable research effort has been expended on studies of lubrication in the space environment, supported by the European Space Agency (ESA).

Part of this ESTL research programme has involved long term studies of the PFE lubricants, running in test ball bearings under ambient pressures of 10^{-6} torr or less.

At the Materials Science Group, in British Aerospace, Stevenage we have established a small working group which has specialized for several years in studies of lubrication mechanisms. As a result of this specialization we have been pleased to assist ESTL and ESA in the studies of test bearings with the aim of improving the understanding of lubricant degradation studies.

Over the past two to three years, we have been closely associated with a series of studies on the PFE lubricants and this paper describes the sequence of tests involved, the results of examining the test bearings and the conclusions we have drawn from the data.

* British Aerospace plc. Stevenage England

LIFE STUDIES WITH Z25 LUBRICATED BALL BEARINGS, RUNNING IN VACUUM

Summary of Tests

In this work, carried out by Mr. K. Stevens at ESTL (1,2), the test bearings were 42 mm o.d. 10 ball angular contact. Raceways and balls were in 440C, and a one-piece fabric reinforced retainer was fitted.

Four bearings were used in this first test, run as preloaded pairs within the vacuum chambers (10^{-6} torr), one at 200 rpm and the other at 1400 rpm, for a total for each pair of 10^8 revolutions.

It was observed during this test that the running torque of both bearing pairs fell steadily, reaching a minimum after 10^6 revolutions. If the tests were stopped for 15 minutes, the torque on restarting was found to be equal to that at the start of the test, but this fell rapidly to the minimum level within a short time.

Bearing noise increased with this fall in running torque, and bearing surface temperature also increased slightly as the minimum torque level was reached.

On completion of the tests it was found that all the bearings were contaminated with brown/black deposits along each ball track and in the ball pockets of the phenolic retainers.

Examination of Bearings

The samples submitted were as follows:

1. An inner race washed free of unchanged oil and contaminant.
2. A sample of contaminant washed free of unchanged oil using trichlorotrifluoroethane (F113).
3. A complete test bearing (1400 rpm) with lubricant and lubricant-degradation products intact.

Preliminary compositional analysis on the contaminant, after washing free of unchanged oil, had been carried out by ESTL, and the results are shown in Table II.

These indicated that the deposits from both the 200 and 1400 rpm bearings were rich in Fe and Cr, both contained a significant level of organic material and that no significant 'foreign' elements were present.

Microscopic examination of the ball track on the raceway of the washed inner bearing (sample 1) showed a well defined wear track with surface pitting. The surface within the wear track carried a very thin, highly adherent film which could not be removed by repeated washing in solvent.

The complete bearing (sample 3) was disassembled and examined microscopically with the lubricant intact on the raceways.

Both inner and outer raceways were heavily contaminated with the black contaminant which had spread on either side of the ball tracks. At higher magnification this contaminant which appeared red/brown in transmitted light was seen to be confined to an immiscible phase separated by clearly visible boundaries from the colourless transparent Z25 film (Figure 1).

Analysis of Deposits

Because of the particular chemical structure of the PFE lubricants, they are totally insoluble in common flushing solvents such as toluene or benzene, chloroform, trichloroethane, etc, and can only be dissolved in fluorinated solvents such as chlorotrifluoroethane (F113). Therefore, if a sample of mixed Z25 oil and contaminant was flushed repeatedly with F113, it was found that all the free Z25 could be removed, leaving dense dark solid which was completely insoluble in Freon 113.

Micro infra-red spectroscopy was used as a preliminary method of characterization of the sample, and the results showed that the material was free of carbon hydrogen absorption, and had a strong carbon fluorine absorption. This indicated that the contaminant was derived directly from the perfluoroether lubricant and was not a 'foreign' product, such as phenolic polymer constituents of the retainer, or residues of cleaning agents remaining in the bearing.

Since the contaminant was a non-volatile 'polymeric' material it was decided to apply pyrolysis gas chromatography mass spectrometry (PGC MS) both to the sample and the unchanged Z25 oil in an attempt to establish the structure of both and hence the mechanism of formation of the contaminant.

The technique of PGC MS involves the process of rapid heating of a polymeric sample within the carrier gas stream of a gas chromatograph. This heating, typically within the range 700 to 900°C, causes thermal "cracking" of the sample to produce a series of stable compounds of lower molecular weight and hence of much greater volatility than the parent compound. These compounds are formed in the carrier gas stream of the chromatograph and are carried onto the column and separated in the conventional way. By the use of carefully controlled conditions the products of a given polymer are both reproducible and characteristic of the parent polymer and the technique finds widespread use in polymer characterization and identification.

By combining a fast scanning mass spectrometer with the gas chromatograph, it is possible to obtain the mass spectrum of each component of the pyrogram as it leaves the gas chromatograph, and thus a rapid identification of each fragment can be obtained.

The equipment used for this work at B.Ae Stevenage was a Finnigan 4021 GC/MS which is coupled to a Digilab Nova 4 computer. This data processor is used to control the operation of the equipment and also for the identification of compounds separated chromatographically.

In Figure 2 the PGC MS output obtained by the pyrolysis of unused Z25 is shown. It is presented in the form known as the reconstructed ion chromatogram (RIC). This is a plot of the ion current at the mass spectrometer detector as the vertical axis, against the time as the horizontal axis. The form of the RIC shown in Figure 2 is immediately recognizable as a typical gas chromatograph since it is generated by using the mass spectrometer as a GC detector. As each component of the pyrolysis leaves the gas chromatograph and enters the mass spectrometer, the ion current rises, reaching a maximum and then falls as the concentration of the component decays, thus building up the type of output shown in Figure 2.

Despite the apparent simplicity of the output, each pyrogram RIC carries an immense amount of information. Typically, using a mass spectrometer scanning rate of 1 Hz, each RIC contains up to 3000 individual mass spectra, each of which can be recalled from memory, searched against a reference library of some 30,000 standard compounds and identified.

Examination of the output obtained from the pyrolysis of Z25 in Figure 2, shows that it comprises two main parts, a single large component at or near scan number 43, followed by a series of closely spaced, barely resolved peaks numbering some 50 components.

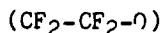
Interpretation of the computer identification of the mass spectrum of the component at scan 43 showed that it was a fluoroalkene, tetrafluoroethene, as shown by the printout in Table III.

When the computer identification was applied to each of the later components from scan 150 to scan 1000, a problem was encountered. Each component when recalled from the computer memory was found to have the same mass spectrum (Figure 3) such that when a computer identification was run each gave exactly the same search. Typical printouts are shown in Table IV from two well separated components, both of which are identified as chloropentafluoroethane.

This apparent anomaly is resolved if the structure of the oil is considered. Since it is a polymer, i.e., a chain of repeating identical units, then the pyrolytic fragments will each be very similar in structure, differing only in their chain length. In the mass spectrum each fragment will ionize to give a relatively small number of ions common to each fragment and independent of the chain length of the fragment.

Thus in the mass spectrum in Figure 3 it is possible to identify the ions CF_2^+ (50), CF_3^+ (69), C_2F_4^+ (100), C_2F_5^+ (119), $\text{C}_2\text{F}_5\text{O}$ (135) and $\text{C}_2\text{F}_5\cdot\text{O}\cdot\text{CF}_2^+$ (185).

The significant information in this series is the pair of ions $C_2F_5^+$ at a.m.u. 119 and $C_2F_5O^+$ a.m.u. 135. This indicates that the repeat unit in the polymer contains two carbons and one oxygen atom, and thus the polymer structure is:



This structure satisfies the pyrolytic fragments obtained, i.e., the first component C_2F_4 , followed by a series of fragments of the polymer chain, made up of $CF_2.CF_2.O$ units.

On applying the pyrolytic technique to the washed contaminant, the output shown in Figure 4 was obtained. If this is compared with the pyrogram of the unused oil in Figure 2, it will be seen that only the early compound was obtained; the system of multiple peaks from about scan number 100 to scan number 1000, so characteristic of the Z25 oil was only barely detectable.

Computer searching of the early compound gave an identical output to that obtained from the corresponding component in the Z25 output, namely tetrafluoroethene.

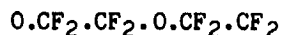
Discussion of Analytical Data

The output obtained from the washed contaminant, namely tetrafluoroethene alone, could only be interpreted as indicating that the "oxygen component" of the polymer had been lost in some way. In simple terms, if the product was a perfluorohydrocarbon, i.e., $CF_2 - CF_2 - CF_2 - CF_2$, then pyrolysis would give the result obtained.

As an example of this, the pyrogram of a sample of polytetrafluoroethylene (Fluon, Teflon, etc.) prepared under identical conditions to those used on the contaminant is shown in Figure 5. This also consisted of a single component searching as tetrafluoroethene.

However, a simple model comprising a perfluorohydrocarbon would not satisfy all the data. For example, the intense color and the very high content could not be satisfactorily explained.

It is proposed therefore that the contaminant consisted of a product formed by interaction between the lubricant and the wearing surface of the bearings. It was further argued that the proposed linear structure of the oil, i.e.,



could render the material particularly sensitive to adsorption to a wearing surface, owing to the unprotected nature of the oxygen atoms in the structure. Sufficient work was not done on the product to establish whether this was a true compound, or a complex formed by the adsorption of the lubricant onto wear debris, but it appears likely that pyrolysis of such a

product would result in the release of the tetrafluoroethene, leaving the oxygen component bound firmly to the inorganic residue remaining after pyrolysis.

The formation of such a surface film would help to explain the loss of running torque which developed during the test. This loss of torque could be explained as being due to loss of the viscous drag component of the total running torque of the bearing pair, and the development of a surface film on the ball track could well cause the loss of the oil film due to non-wetting and retraction. On stopping the bearing, slow flow back would occur, allowing the temporary re-establishment of the hydrodynamic condition, before oil retraction recurred and the viscous drag component was lost again.

Thus this initial test suggested that under the conditions used, namely low pressure (zero oxygen, moisture etc.), the Z25 test lubricant was liable to form a surface 'reaction' product which would wear away sacrificially, building up within the bearing as described.

REPEAT OF BEARING TESTS

Introduction

Following the results obtained in the first test, ESTL prepared and ran a second bearing life test, which was identical in all respects to the first run, except that the bearings, to the same specification, were obtained from a different source.

The results were quite different. The torque level remained constant throughout the 10^8 revolutions of the test, and on disassembly of the test rig no trace of the black contaminant could be found in the bearings.

Examination of Test Bearing

As before, a single bearing was submitted for examination and analysis. On disassembly and microscopic examination at low power (Figure 6), the oil film in the raceways was seen to be cloudy. No trace of the black contaminant could be found, and the ball tracks were smooth and free of any of the pitting wear seen previously.

At higher magnification (Figure 7) it was revealed that the cloudiness of the oil film was due to the presence of two immiscible fluids in the bearings, one in the form of a dispersion of droplets in the second fluid, thus causing light scattering and the cloudiness observed.

Analysis of Bearing Lubricants

Without the 'target' of the insoluble contaminant found in the first test bearings, it was obviously necessary to change the method of analysis. Because of the presence of two mutually insoluble fluids, one of which must have been the test oil Z25, it was almost certain that the second fluid would be a nonfluorinated material such as an hydrocarbon or diester oil.

Therefore by flushing down the bearings with Freon 113 in which both components would be soluble, it was possible to concentrate the lubricant in one region of the bearing and obtain a representative sample for PGC MS.

The output obtained is shown in Figure 8. If one compares this output with that from the unused Z25 standard in Figure 2, it can be seen that although the pyrogram starts with a similar early component, identifiable as tetrafluoroethene as before, the later portion was quite different. In contrast to the close spaced components of the Z25 pyrogram, the output obtained showed a different series of well resolved compounds. The computer search data for three typical samples at scan Nos. 138, 600 and 656, are shown in Table V, proving unequivocally that hydrocarbon oil was present. The output in figure 8 also showed the typical pattern of the PFE oil lying beneath the strong output from the hydrocarbon.

(Due to the ease of pyrolysis and lower ionization potential of the hydrocarbon, PGC MS of a mixture of hydrocarbon tends to result in the exaggeration of the level of the hydrocarbon components in the mixture).

Discussion of Data from Second Bearing Life Test

The reason for the difference in bearing performance between the first and second test runs was obvious following the examination of the bearings. The presence of a second hydrocarbon oil would have successfully decoupled the Z25 from the surface and thus prevented any disruption of the PFE lubricant.

Normally when cross contamination of liquid lubricants occurs, the effects are minimized due to the immiscibility of commonly used systems. Because hydrocarbons and PFE systems are so completely insoluble, one with another, each can act independently when present together in a bearing.

Whichever component has the greatest tendency to wet the bearing surface will be the dominant lubricant in the behaviour of the test bearing.

This result did little to resolve the problem of the apparent sensitivity of the Z lubricant to active metal surfaces, and in fact could have been seen as supporting the theory since decoupling by the accidental use of a second lubricant had completely prevented a recurrence of the degradation.

EXPERIMENTAL METHODS TO VERIFY THEORY

Introduction

Two techniques were investigated to overcome the apparent difficulties associated with the use of the Z series oil.

Non-metallic Coating on Test Bearing Surfaces

The first was to decouple the lubricant from the wearing metal surface by the application of non-metallic layers to the bearing surfaces. The system

chosen by Mr. Stevens at ESTL was to use tungsten carbide balls which had been coated with titanium carbide, running against raceways which had been coated with zirconium nitride. In all other respects the bearings were exactly as used in the previous test runs

The results of running the coated bearings in preloaded pairs at 10^{-6} torr as before were excellent. A total bearing life of 10^8 revolutions was achieved without any change in running torque, and on completion of the test, no evidence of oil degradation could be found.

One of the pair of bearings was submitted for analysis as before, and microscopic examination confirmed that no oil degradation resembling the original result could be detected. The zirconium nitride layer had been worn away from the central high load region of bearing raceways, and a low level of solid debris had been generated as a result. The appearance of the nitride layer and the worn track are shown in Figure 9, which shows the junction between the bright, worn ball track and the partially worn nitride layer. The titanium carbide surface of the balls had not been destroyed.

PGC MS of the very low level of Freon residues gave the output shown in Figure 10. Owing to the extremely small sample size, the output was poorly resolved with respect to the PFE fragments which appeared as the ill-defined, broad peak with a maximum near scan number 800.

The information available from this analysis was improved by performing ion specific searches on the data. By this means known or suspected impurities can be identified by feeding in search ions specific to the unknown. This is demonstrated in Figures 11, and 12, in which the search for hydrocarbons, mass numbers 41, 43 and 57, in conjunction with the RIC and a similar search for the PFE fragments, mass numbers 119, 135 and 185, are shown.

This technique showed clearly that the sample was composed of a very low level of Z25 and hydrocarbon oils, at levels insignificant to the result of the bearing test.

Test of an Oil With Different Chemical Structure

The second part of the hypothesis concerning the sensitivity of the Z type of oil to decomposition in ball bearings was that the particular linear structure of the polymer could contribute to the effect.

Other types of perfluoroether lubricant are available, one of which a member of the Y series; YVAC 40/11 is also recommended for instrument bearing use. As shown in the table of comparative physical data in Table I, certain penalties would be incurred in substitution for Z25, such as an increased viscosity, a higher vapour pressure at a given temperature and a higher pour point.

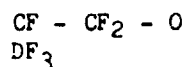
The final ESTL bearing test in this series was identical with the first test, except that YVAC 40/11 was substituted for the Z25 lubricant.

As before, the test duration was 10^8 revolutions at 200 and 1400 rpm, and both were completed without change in running torque.

A test bearing (200 rpm) was submitted for study and was found to be in perfect condition. The oil was unchanged and no wear track was visible on either raceway. The precise ball track was only identified on the inner raceway by the use of a surface topography enhancement technique (Nomarski interferometry), which enables very light surface brinells to be detected (Figure 13).

GC MS of the unrun lubricant YVAC 40/11 gave the output shown in figure 14, in which only the polymer fragmentation pattern from scan 300 to about scan 1000 is shown. Comparison of this with the same region in figure 2, the pyrogram of Z25, shows that the YVAC 40/11 gave a more complex pattern.

As before, computer searching of the mass spectra (figure 15) obtained was unsatisfactory due to the uniformity of successive outputs. However a manual interpretation allows the structure of the lubricant to be estimated; e.g., the ions identified were CF_3^+ (60), $C_2F_3^+O$ (97), $C_2F_4^+$ (100), $C_2F_5^+$ (119), $C_3F_5^+O$ (147) and $C_3F_7^+$ (169). The presence of the two ions with three carbons was a very strong indication that the lubricant had the structure.



i.e., a branched chain lubricant in contrast to the linear form of the Z series.

DISCUSSION AND CONCLUSIONS

In the in vacuo testing of bearings lubricated with Z25, the evidence of the test results and the post-test examination of bearings point unequivocally to the fact that the lubricant suffered considerable chemical decomposition which had clearly occurred in the contact regions between ball and raceway.

The major difficulty is to explain the cause of the decomposition.

The evidence available at present suggests that the operating bearings in-vacuo, i.e., in "zero" oxygen conditions results in the interaction between the lubricant and the wearing surface. A problem arises in establishing a detailed mechanism for this surface effect since in the first ESTL test, both the 200 rpm test bearing (boundary conditions) and the 1400 rpm test bearing (hydrodynamic) appeared to be equally contaminated, when in fact the boundary condition would be expected to be the most severe with respect to a surface-wear-generated effect. Despite these limitations, each

of the subsequent experiments supported the hypothesis that the lubricant was decomposed by the wearing surface, e.g., the accidental contamination of test bearings with a second oil, and the use of nonmetallic surface coatings both resulted in remarkable improvements in lubricant life.

The final experiment using the second, Y series, oil was also consistent with the surface interaction theory, if the stereo chemistry of the lubricant could have the effect proposed, although in this instance the higher viscosity lubricant could have a significant effect on film thickness and stability and could result in improved lubricant life.

Much more investigation will be necessary before a clear understanding is available of the complex mechanisms involved in the tribology of the perfluoroether lubricants. The test described herein were carried out at low pressure (10^{-6} torr) and thus the wearing surface would be low in oxygen and thus chemically active. However other work (not reported) has shown that PFE lubricants can decompose in bearings operating in ambient atmosphere.

This work is also concerned exclusively with PFE lubricants of European origin; other sources, using different synthetic methods of manufacture, could give different results.

At this stage of the work, it appears that bearing surface modification with an inert substance, resulting in "decoupling" of the lubricant from the active wear region of the bearing surfaces, offers the best course to ensure maximum lubricant life.

REFERENCES

1. The performance of Z25 oil in ball bearings operating in vacuum.
E.S.A. (ES1L) 056 January 1983. European Space Agency.
2. Some observations on the performance of Fomblin Z25 oil and Drayco 3L-38-RP in ball bearings and gearboxes.

Proceedings of the 1st European Symposium on Space Mechanisms and Tribology.

Neuchatel 12th -14th October 1983 (E.S.A. SP196, 12/83).

ACKNOWLEDGEMENTS

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Table I Typical Physical Properties for a Z and a Y Type Oil

OIL TYPE	KINEMATIC VISCOSITY Cst 20°C	VISCOSITY INDEX ASTM D2270	VAPOUR PRESSURE mm Hg 20°C	POUR POINT OC	VOLATILITY LOSS % BY WT. 149°C
Z25	233	348	5 X 10 ⁻¹²	-60	0.1
YVAC 40/11	462		2 X 10 ⁻¹¹	-32	

Table II Composition of Bearing Contaminant

COMPONENT	200 RPM	1400 RPM
Fe	20 - 30%	90%
Cr	10% of Fe	10% of Fe
Cl	trace	2%
Minor element	trace	trace
Organic	balance	balance

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Table III C₂F₄ Computer Library Search

LIBRARY SEARCH DATA: INNER • 42 BASE P/E: 81
06/11/81 11:26:00 + 0:42 CALI: C18 • 1 RIC: 434173.
SAMPLE: SAMPLE FROM INNER WASHED SEVERAL TIMES IN FREON 113 (ESTL JOB)
• 42 - • 32 - • 73 X1.00

25418 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
147 MATCHED AT LEAST 4 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1 1437 1-PROPENE,1,1,2,3,3,3-HEXAFLUORO-
2 1436 ETHENE,TETRAFLUORO-
3 2132 BUTANAL,HEPTAFLUORO-
4 1418 CYCLOBUTANE,OCTAFLUORO-
5 2189 PROPANAL,PENTAFLUORO-
6 2031 OCTANAL,PENTAFLUORO-
7 2134 BUTANOICACID,HEPTAFLUORO-
8 2071 BUTANE,DECAFLUORO-
9 2138 CYCLOPENTANE,NONAFLUORO-

RANK	FORMULA	M.WT	S.PK	PURITY	FIT	RFIT
1	C3.F6	150	100	585	848	881
2	C2.F4	100	81	366	834	880
3	C4.H.O.F7	198	100	583	677	825
4	C4.F8	200	100	486	717	812
5	C3.H.C.F5	148	100	488	714	488
6	C8.H.O.F15	398	63	447	612	581
7	C4.H.O2.F7	214	119	384	529	484
8	C4.F10	238	69	382	529	382
9	C5.H.F9	232	60	359	693	372

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Table IV Computer Library Search of Two Z25 Pyrolytic Fragments

LIBRARY SEARCH DATA: RES * 289 BASE M/E: 119
06/05/81 13:58:00 + 4:49 CALI: C10 * 1 RIC: 25983.
SAMPLE: RESIDUE FROM Z25 SAMPLE
* 289 - * 288 - * 298 X1.00

25410 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
961 MATCHED AT LEAST 2 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1 332 ETHANE, CHLOROPENTAFLUORO-
2 333 ETHANE, HEXAFLUORO-
3 3175 BUTANE, 1,1,1,2,3,3,4,4,4-NONAFLUORO-2-(TRIFLUOROMETHYL)-
4 3822 DISULFIDE, BIS(PENTAFLUOROETHYL)
5 14885 BENZENEPROPANOIC ACID, .BETA., .BETA.-DIMETHYL-, METHYLESTER
6 3821 PENTANE, DODECAFLUORO-
7 2871 BUTANE, DECAFLUORO-
8 2683 BENZAMIDE, 2-METHYL-
9 24281 BENZAMIDE, 3-METHYL-N-(PHENYLAMINO)THIOXOMETHYL-

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C2.CL.F5	154	119	177	761	180
2	C2.F6	138	119	177	949	181
3	C5.F12	288	119	157	819	189
4	C4.S2.F10	382	119	141	518	182
5	C12.H16.O2	192	119	135	681	165
6	C5.F12	288	119	134	782	98
7	C4.F10	238	69	126	679	72
8	C8.H9.O.N	135	135	121	647	64
9	C15.H14.O.N2.S	278	119	128	631	179

LIBRARY SEARCH DATA: RES * 318 BASE M/E: 119
06/05/81 13:58:00 + 5:18 CALI: C10 * 1 RIC: 26847.
SAMPLE: RESIDUE FROM Z25 SAMPLE
ENHANCED (S 158 2H 0.7)

25410 SPECTRA IN LIBRARY SEARCHED FOR MAXIMUM PURITY
55 MATCHED AT LEAST 3 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1 332 ETHANE, CHLOROPENTAFLUORO-
2 15372 MOLYBDENUM, TETRACARBONYLBIS(HEXAMETHYLPHOSPHOROUSTRIAMIDE-P)-
3 19633 PYRROLO[1,2-B][1,2,4-OXADIAZOLE-2(1H)-THIONE, TETRAHYDRO-5,5-DIMETHYL-
4 4216 PHENOL, 2-(4-HYDROXYPHENYL)-1-METHYLETHYL-
5 599 BENZENACETAMIDE, .ALPHA., -ETHYL-
6 1733 1,6,10-DODECATRIEN-3-OL, 3,7,11-TRIMETHYL-, .S-(Z)-
7 11886 MOLYBDENUM, PENTACARBONYL(HEXAMETHYLPHOSPHOROUSTRIAMIDE-P)-, (OC-6-22)-
8 19634 PYRROLO[1,2-B][1,2,4-OXADIAZOLE-2(1H)-THIONE, TETRAHYDRO-5,5,7,7-TETRAM
9 6526 SILANE, (ERGOSTA-5,7,22-TRIEH-3.BETA.-YLOXY)TRIMETHYL-

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C2.CL.F5	154	119	178	626	266
2	C16.H36.O4.N6.MO.P2	536	119	146	632	286
3	C13.H16.O.N2.S	248	119	146	494	273
4	C15.H16.O2	229	119	132	495	212
5	C18.H13.O.N	163	119	117	474	215
6	C15.H26.O	222	119	99	364	287
7	C11.H18.O5.N3.MO.P	481	119	93	426	219
8	C15.H20.O.N2.S	276	69	85	312	193
9	C31.H52.O.S1	468	69	74	289	197

Table V Computer Library Search of Three Hydrocarbon Impurities

LIBRARY SEARCH DATA: RISRES2 * 138 BASE M/E: 56
 09/07/02 15:25:00 + 2:10 CALI: AGD1 * 3 RIC: 6687.
 SAMPLE: RISLEY A OUTER LUB RESIDUE
 * 138 - * 130 - * 150 X1.01

25409 SPECTRA IN LIBRARYND SEARCHED FOR MAXIMUM PURITY
 87 MATCHED AT LEAST 8 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
 1 3131 1-HEXENE
 2 1288 CYCLOHEXANE
 3 7349 2H-PYRAN-2-ONE, TETRAHYDRO-3,6-DIMETHYL-
 4 4011 1-PENTENE, 2-METHYL-
 5 768 CYCLOPENTANE, METHYL-

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C6.H12	84	41	952	976	978
2	C6.H12	84	56	913	936	935
3	C7.H12.O2	128	42	984	937	942
4	C6.H12	84	56	895	917	928
5	C6.H12	84	56	895	919	923

LIBRARY SEARCH DATA: RISRES2 * 600 BASE M/E: 56
 09/07/02 15:25:00 + 10:00 CALI: AGD1 * 3 RIC: 8399.
 SAMPLE: RISLEY A OUTER LUB RESIDUE
 * 600 - * 592 - * 608 X1.01

25409 SPECTRA IN LIBRARYND SEARCHED FOR MAXIMUM PURITY
 145 MATCHED AT LEAST 8 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
 1 4250 1-DECENE
 2 1374 1-DECANOL
 3 8192 1-OCTENE, 3,7-DIMETHYL-
 4 1745 1-NONANOL
 5 1389 1-DODECANOL

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C10.H20	140	41	686	996	687
2	C10.H22.O	158	41	679	961	679
3	C10.H20	140	43	669	972	675
4	C9.H20.O	144	56	662	979	666
5	C12.H26.O	186	41	659	958	671

LIBRARY SEARCH DATA: RISRES2 * 606 BASE M/E: 43
 09/07/02 15:25:00 + 11:26 CALI: AGD1 * 3 RIC: 5119.
 SAMPLE: RISLEY A OUTER LUB RESIDUE
 * 606 - * 676 - * 694 X1.01

25409 SPECTRA IN LIBRARYND SEARCHED FOR MAXIMUM PURITY
 220 MATCHED AT LEAST 8 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
 1 4157 1-UNDECENE
 2 1383 1-UNDECANOL
 3 1374 1-DECANOL
 4 1745 1-NONANOL
 5 1389 1-DODECANOL

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C11.H22	154	41	847	991	848
2	C11.H24.O	172	41	835	988	835
3	C10.H22.O	158	41	828	978	825
4	C9.H20.O	144	56	818	985	818
5	C12.H26.O	186	41	807	957	834

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Figure 1. Contaminant Dispersion on Test Bearing x 125

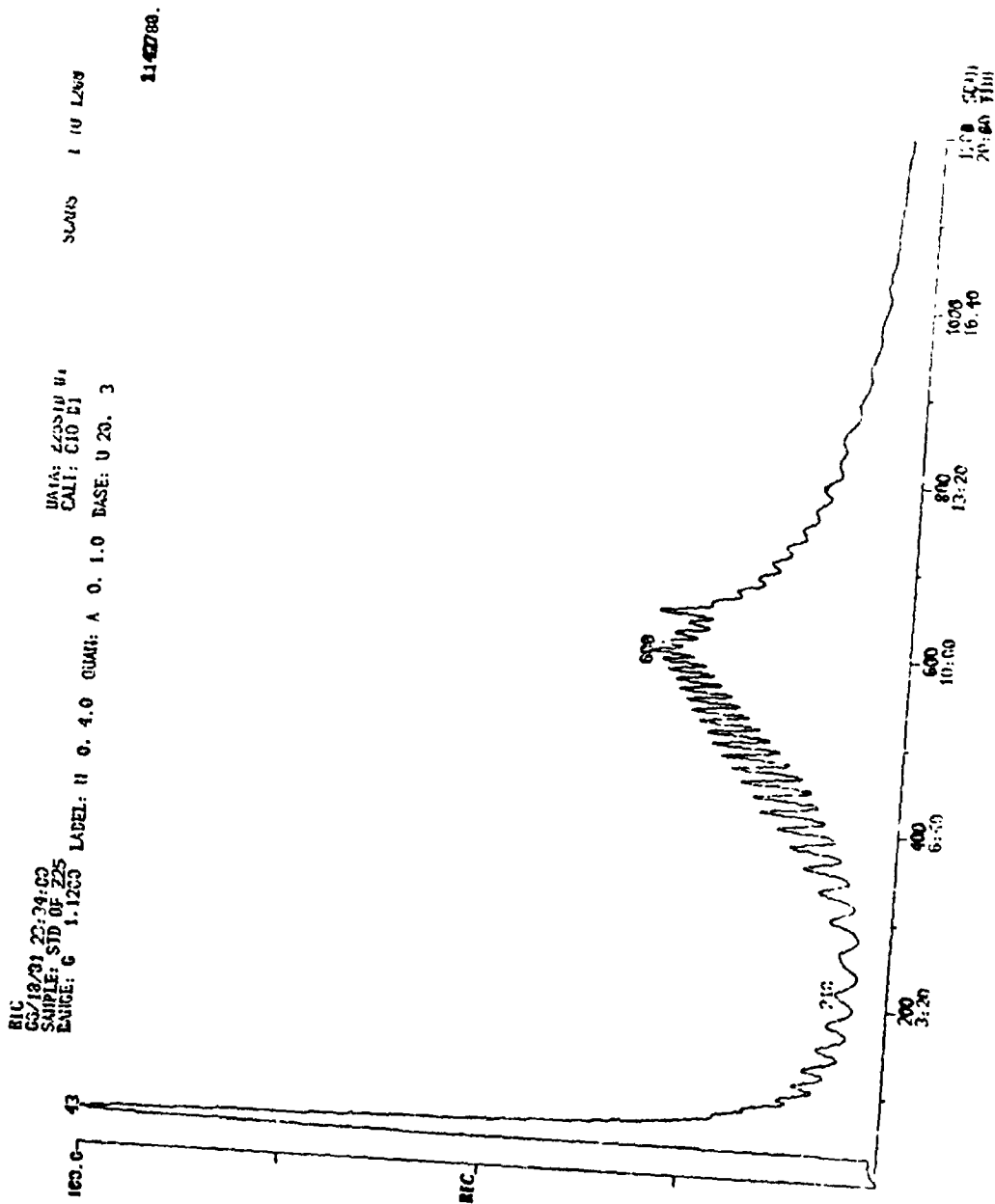


Figure 2. PGC MS of Fresh Z25

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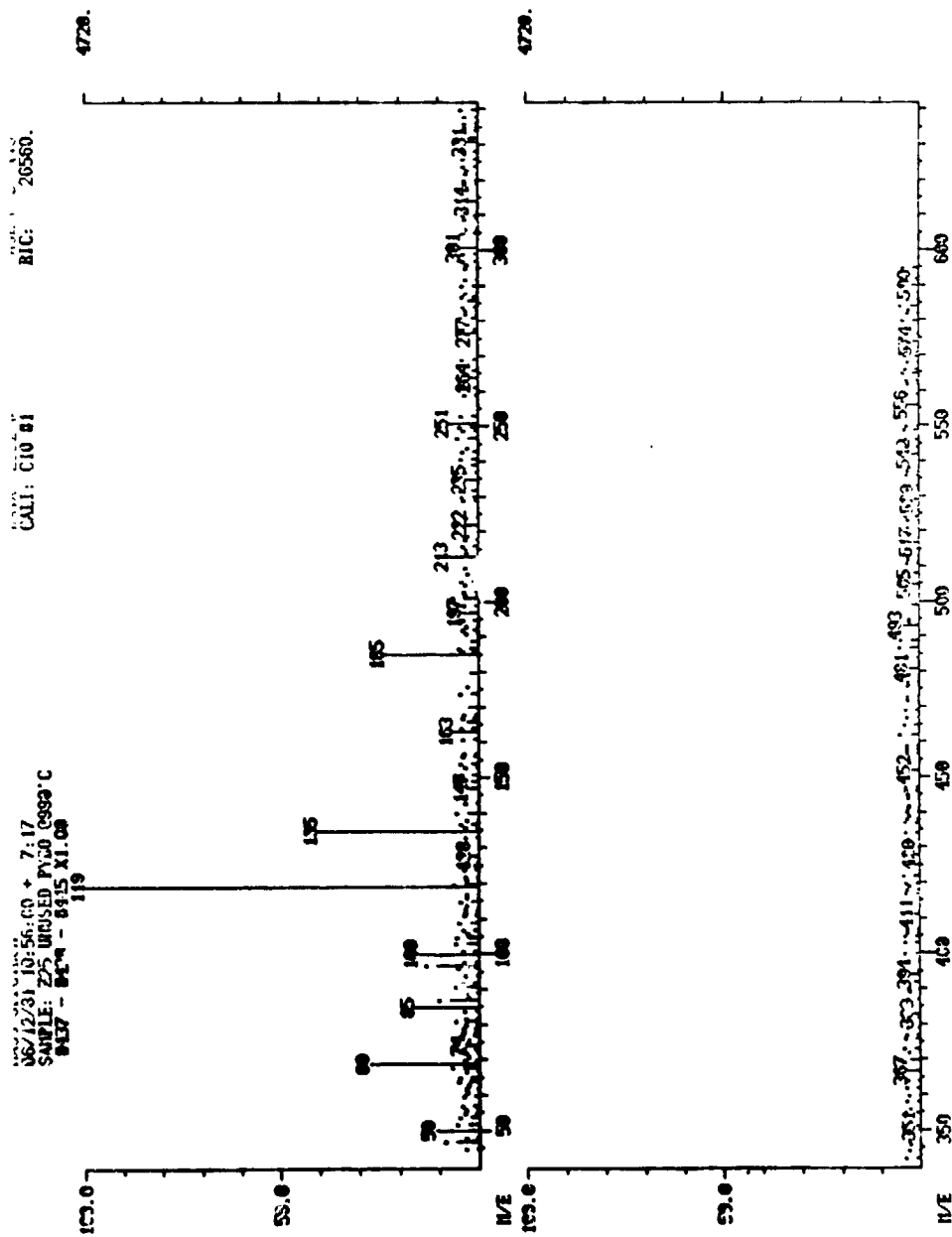


Figure 3. Mass Spectrum of Pyrolytic Fragment (Z25)

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11/11/91 11:25:01
SAMPLE: 11661.P (3) SEVERAL TIMES IN FRONT OF (5) 11661.P
RUNNING: 11661.P (3) 4 6 00:00 7 0 1.9 1.52 0.20 3

546816.

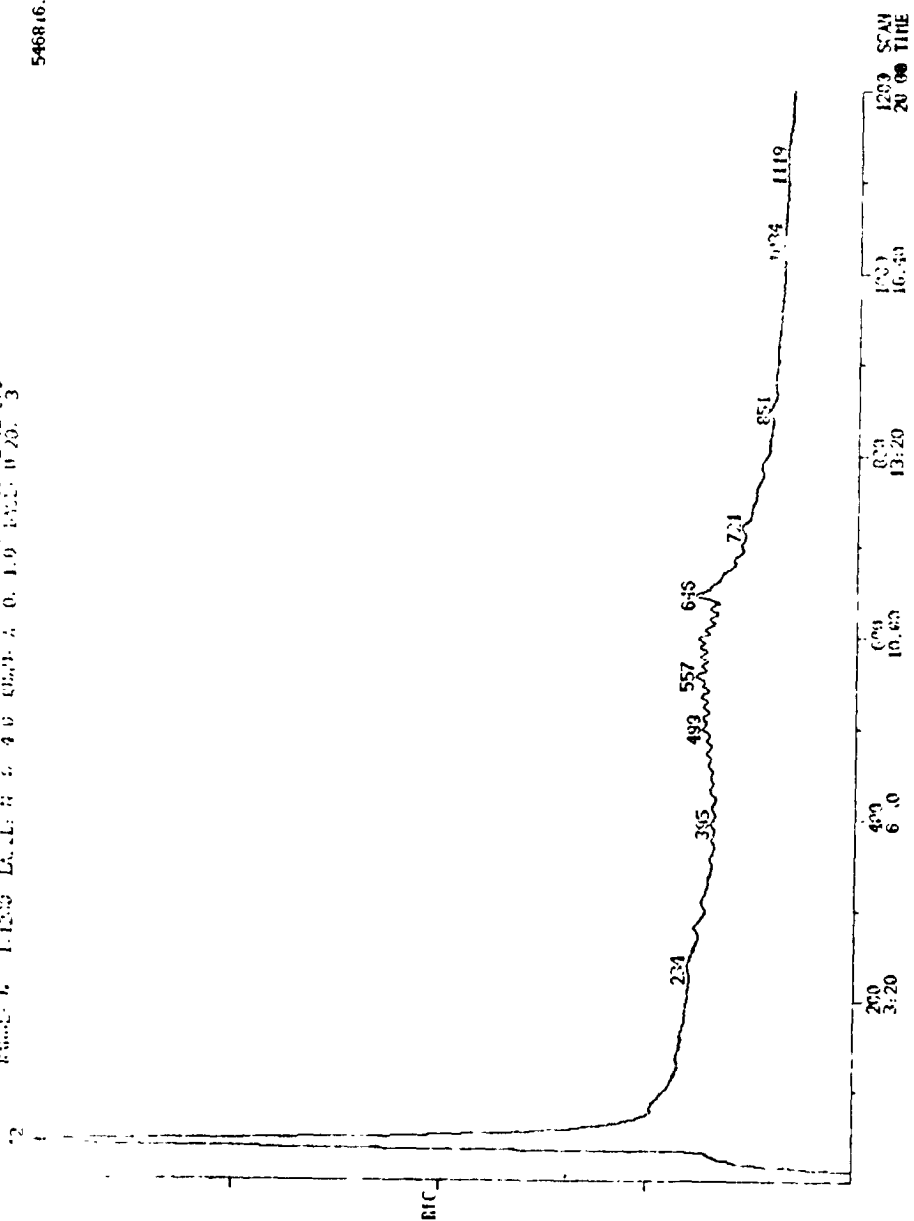


Figure 4. PGC MS of Freon Insoluble Contaminant

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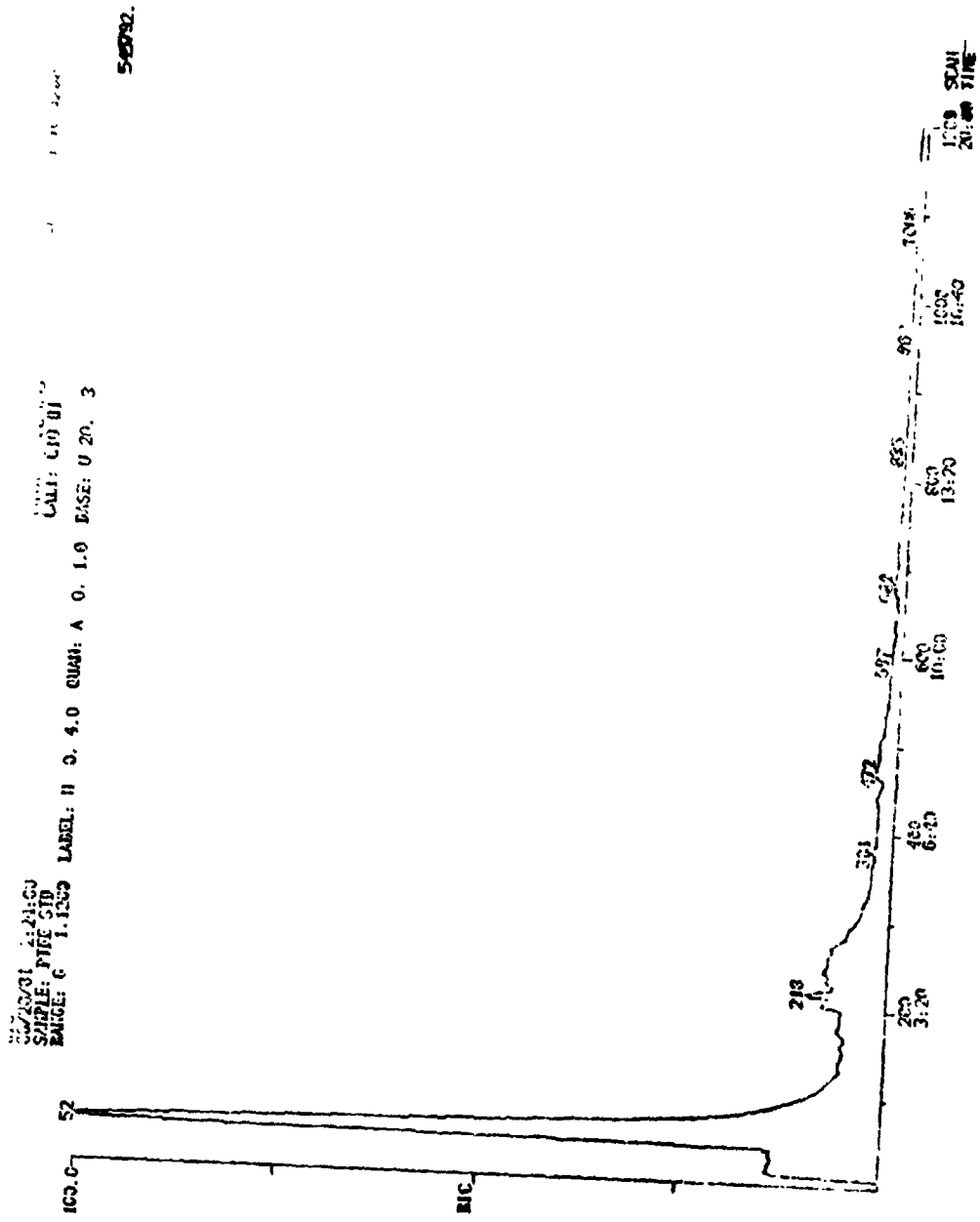


Figure 5. PGC MS of PTFE

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Twist Page Figure

Figure 6. Cloudy Oil Film; Re-run Test Bearing x 50

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Figure 7. High Magnification Micrograph of Re-run Test Bearing x 125

LIC
 09/07/02 P. 25.89
 SAHLE PISLE A QUER LUB RESINUE
 BOME C 1.2000 LABEL N 0.4.0 QUAM: A 0.1.0 PASE. U 29. 3
 DATA: PISLE 2 1
 CALL: AG01 03
 SCANS 1 TO 1000
 77440

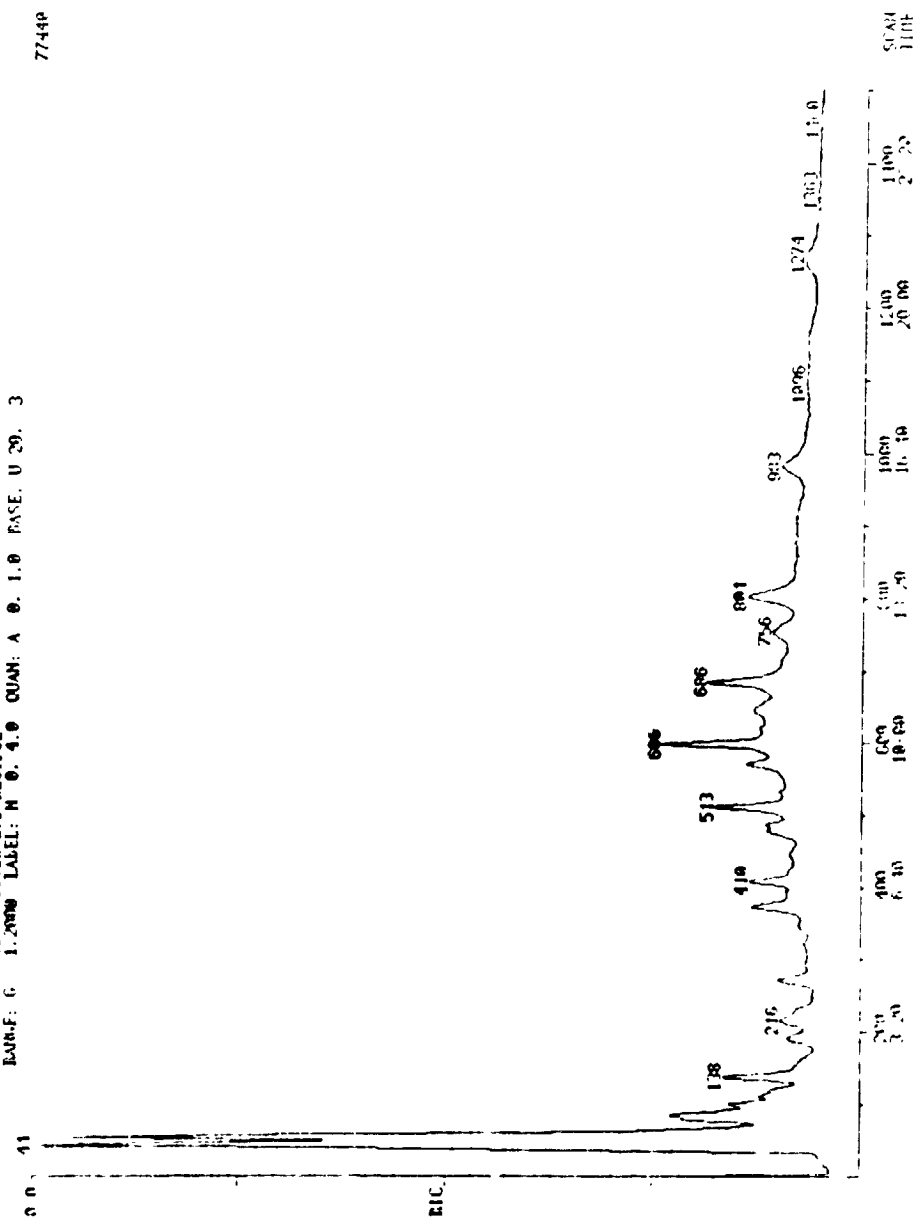


Figure 8. GC MS of Re-run Test Lubricant (Z25), Hydrocarbon Mix

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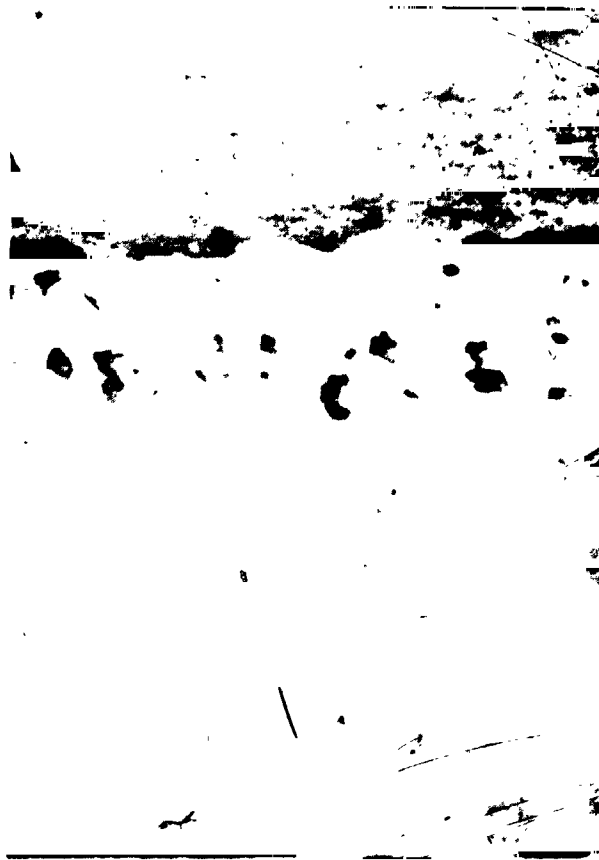


Figure 9. Coated Bearing Surface x 125

427 0022 01 000 SCANS
 7652

DATA: OUTNUMBER2 0445
 CALL: 124 83

BIC
 05/04/04 11:00:00
 SAMPLE: FROEN INSOLUBLE RESIDUE FROM RISLEY BEARINGS (ZFS UNDEGRADED)
 RANGE: C 1.3000 LABEL: M 0. 4. 0 (SCAN: A C. 1. 0 BASE: U 20. 3

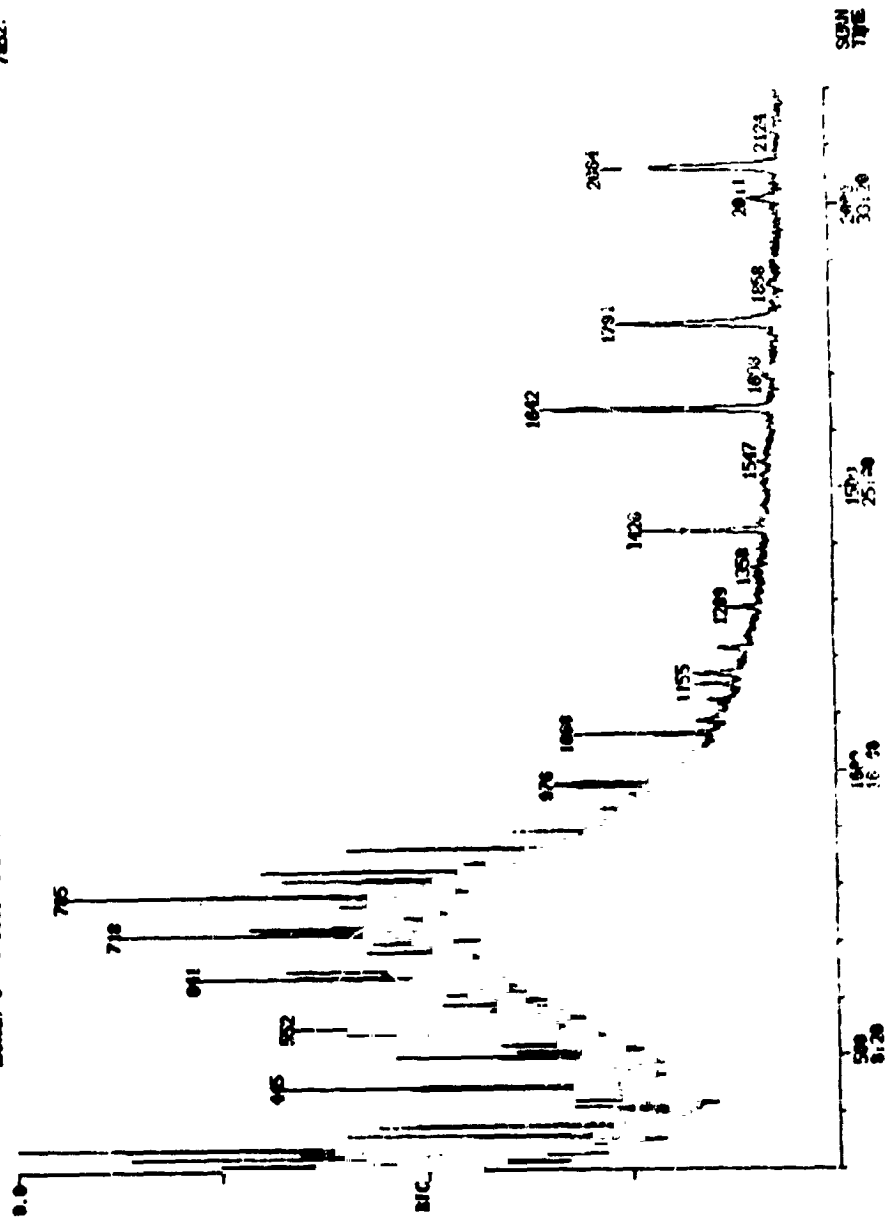


Figure 10. GC-MS of Freon Insoluble Residue, Coated Bearing Test x 125

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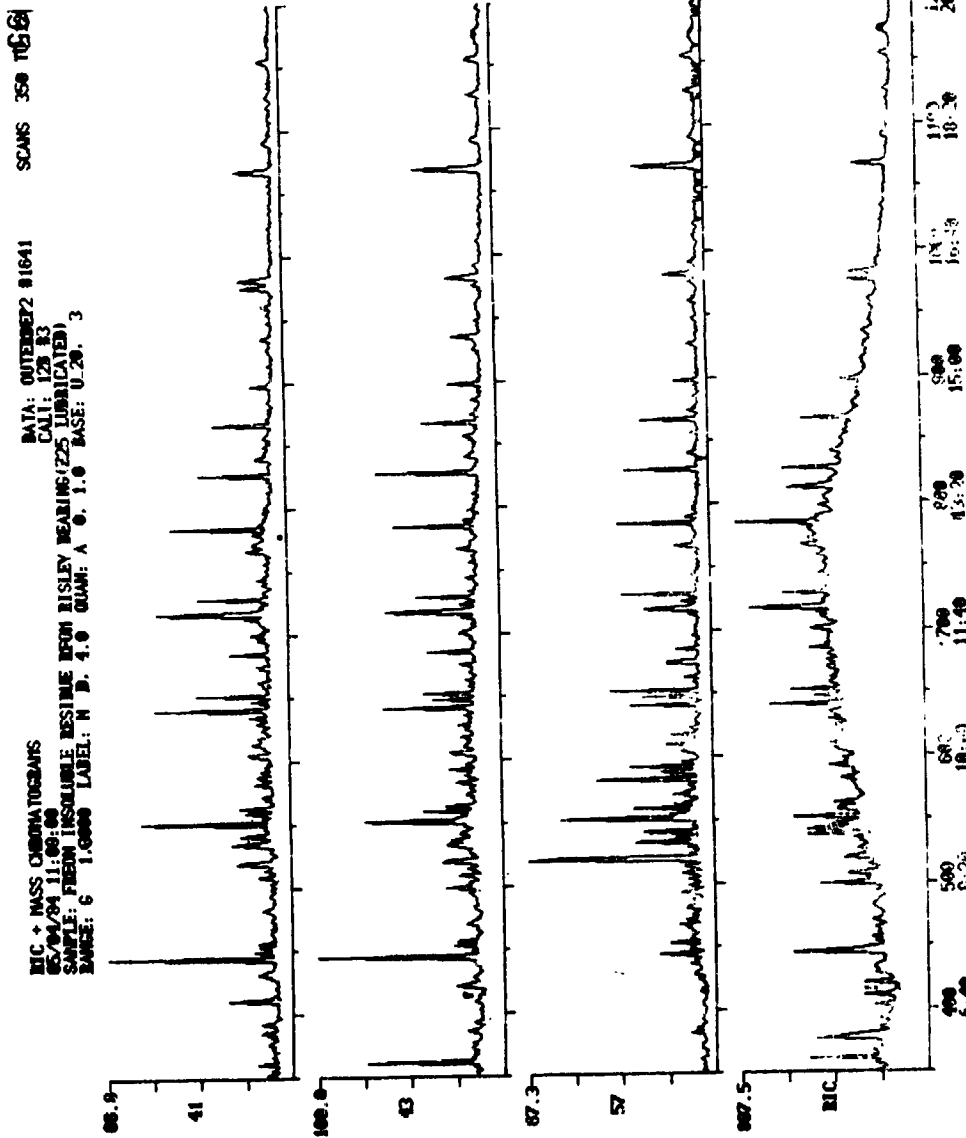


Figure 11. Ion Selective Search, Figure 10 Output (Hydrocarbon)

TIC + MASS CHROMATOGRAMS
 05/04/84 11:09:00
 SAMPLE: FROM INSOLUBLE RESIDUE FROM RISLEY BEARING'S LUBRICANT (J.D)
 RANGE: C 1.0000 LABEL: N O. 4.0 QUAN: A O. 1.0 BASE: U 4. 3
 DATA: OUTERDET 01641
 CALL: 128 43
 SCANS 350 TO 5

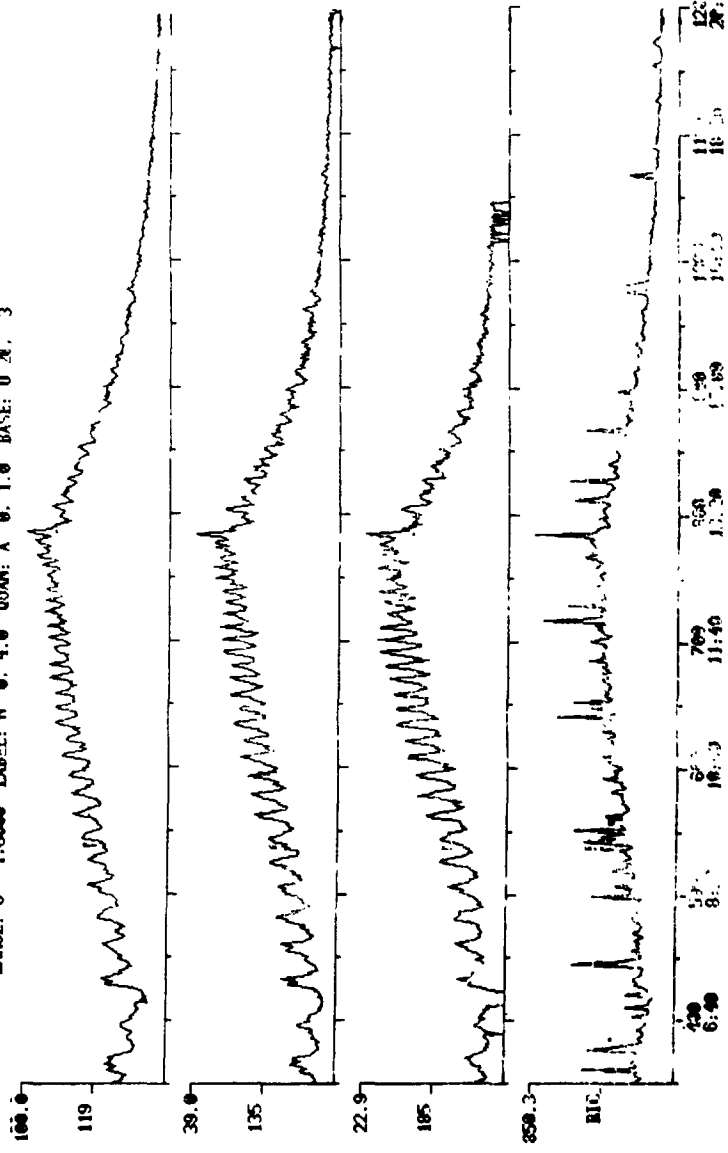


Figure 12. Ion Selective Search, Figure 10 Output (Fluoroether)

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Figure 13. YVAC 40/11; Test Bearing Surface x 125

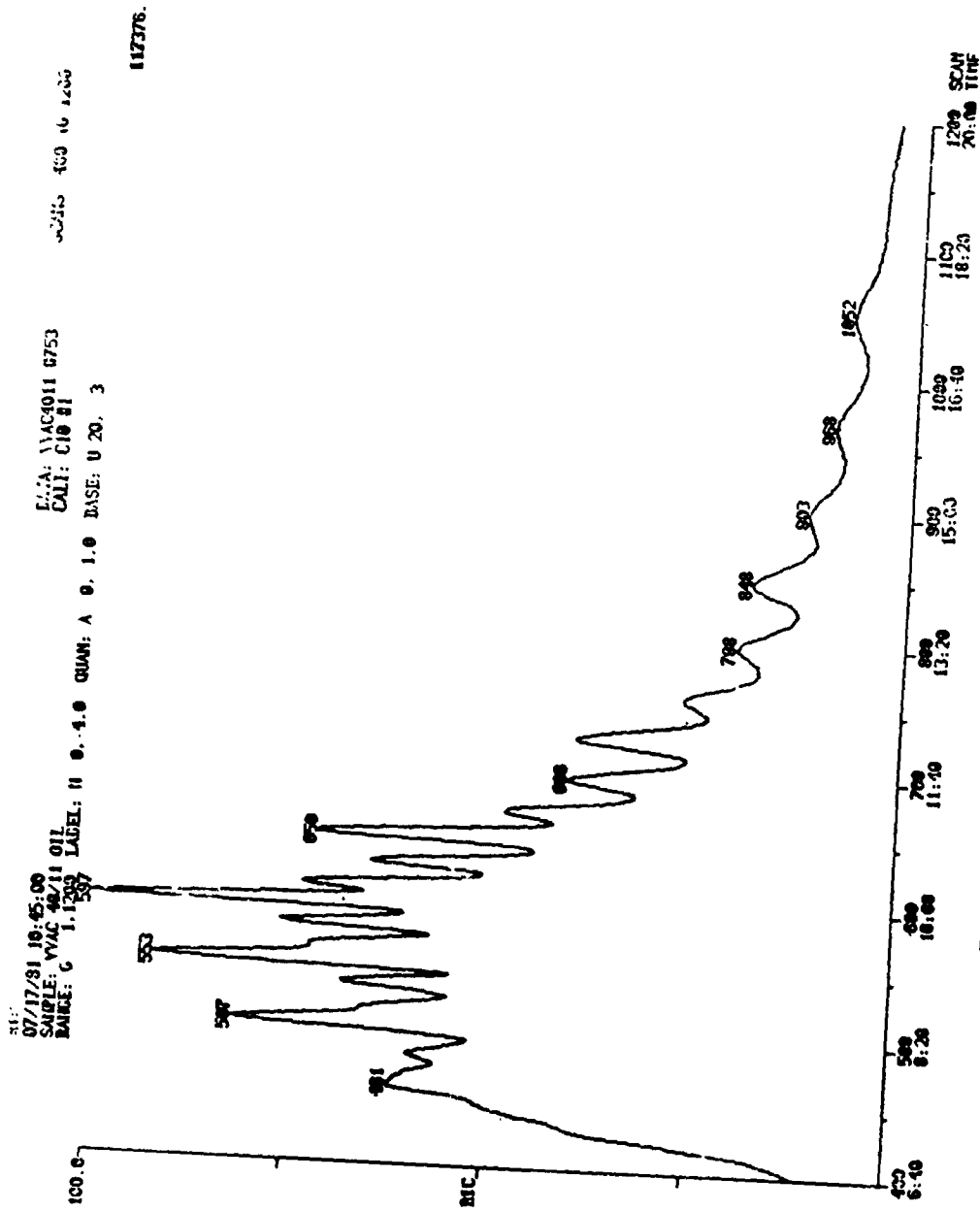


Figure 14. PGC MS YVAC 40/11 (Unrun)

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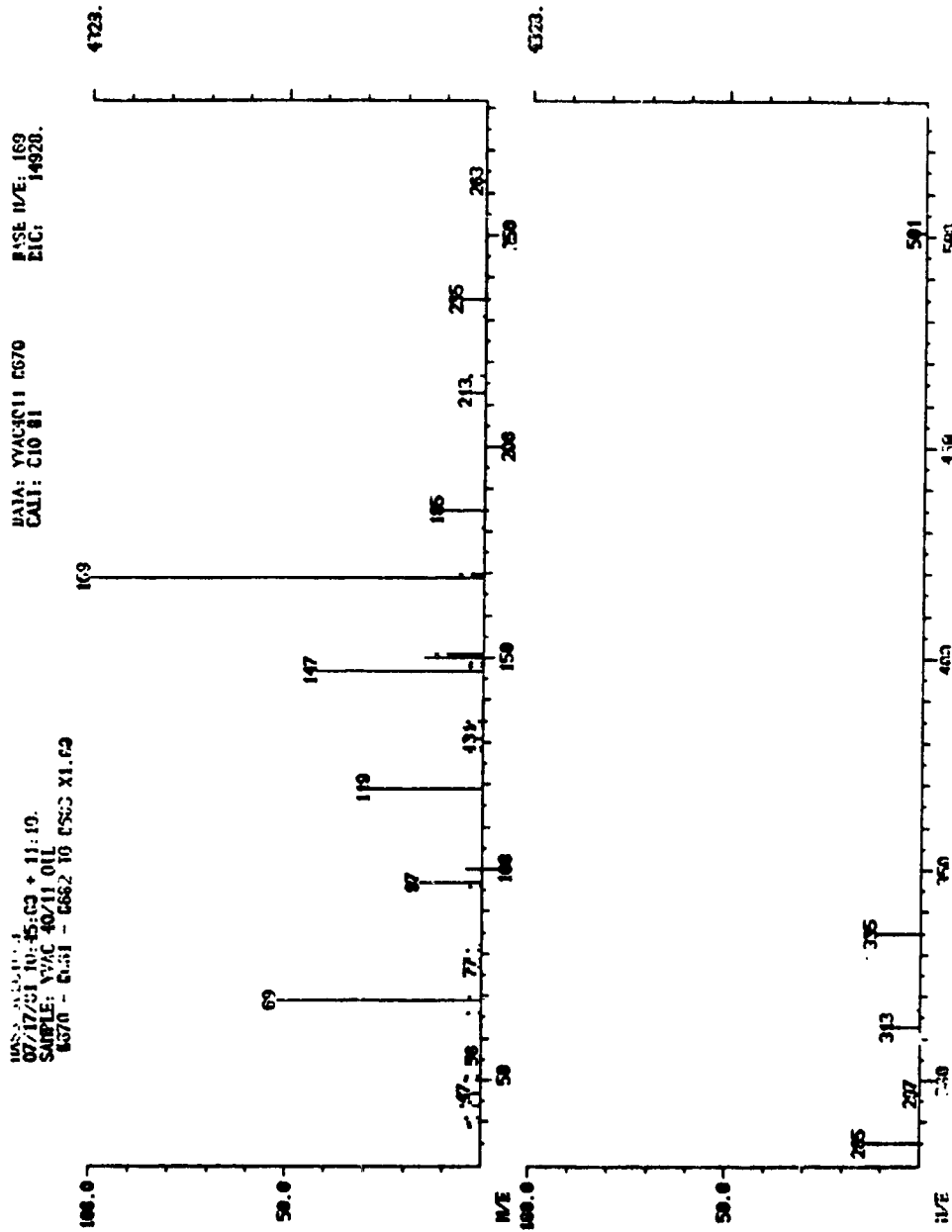


Figure 15. Mass Spectrum of Pyrolytic Fragment (YVAC 40/11)