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NASA Technical Memorandum 104633

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TGA and/or Microbalances**

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Methods of Measuring Vapor Pressures of Lubricants With Their Additives Using TGA and/or Microbalances

ABSTRACT

The life of a space system may be critically dependent on the lubrication of some of its moving parts. The vapor pressure, the quantity of the available lubricant, the temperature and the exhaust venting conductance passage are important considerations in the selection and application of a lubricant. In addition, the oil additives employed to provide certain properties of low friction, surface tension, antioxidant and load bearing characteristics, are also very important and need to be known with regard to their amounts and vapor pressures. This paper reports on the measurements and analyses carried out to obtain those parameters for two often employed lubricants, the Apiezon[®]-C and the Krytox[®] AB. The measurements were made employing an electronic microbalance and a Thermogravimetric Analyzer (TGA) modified to operate in a vacuum. The results have been compared to other data on these oils when available. The identification of the mass fractions of the additives in the oil and their vapor pressures as a function of the temperature were carried out. These may be used to estimate the lubricant life given its quantity and the system vent exhaust conductance. It was found that the Apiezon[®]-C has three main components with different rates of evaporation while the Krytox[®] did not indicate any measurable additive.

Introduction

Future space missions will employ systems and mechanisms which need to last for many years without maintenance. They will have to survive in an environment of very low ambient pressure, high radiation, energetic particles, meteoroids, absence of gravity, exposure to contaminant gases and particles and be limited in their weight and sizes. One of the important limiting features of these systems is the lubrication of moving parts which requires critical attention. The life of the lubricant is predicated on its vapor pressures at the operating conditions, and on its chemical additives, which are employed to produce certain characteristics of friction, surface tension, and load. The vapor pressures affected exponentially by the operating temperatures, the lubrication regimes, the amount of lubricant, and the ambient pressure dictate with the conductance of the vent passage, the rate of lube loss, and the eventual lubricated system failure. Another important consideration of a lubricated system, is the migration of the lubricant in liquid or molecular form on critical nearby surfaces. The migration and resultant de-

posits can cause thermo-optical degradation of those surfaces especially when the deposit is exposed to high radiations. These are some of the reasons to know the lube vapor pressures as characterized by the presence of oil additives. This paper reports the measurements of the vapor pressure of two commonly employed lubricants, the Apiezon[®]-C and the Krytox[®]AB. The measurements were made using a modified Thermogravimetric Analyzer (TGA), and an electronic microbalance. The results have been compared to data from manufacturers and from other sources of measurements.

Experimental

The Oils

As indicated, the two lubricants tested are the Apiezon[®] C and the Krytox[®] 143 AB. The Apiezon[®] C (M=479 g/mole) is a stable oil with a low vapor pressure (V.P.) designed for vacuum use. It includes esters and specially selected hydrocarbons. According to the manufacturer, it is unaffected by traces of water and other

Apiezon[®] is a product of Biddle Instruments, Blue Bell, PA.

Krytox[®] is a DuPont De Nemours and Company (Inc.) product.

vapors and does not liberate corrosive acids. Its physical properties are reported in reference 1. The reference includes the vapor pressures versus temperatures obtained using the Knudsen method. The manufacturer indicates that the oil can be treated with antioxidant to allow a large number of atmospheric exposures and can include inhibitors and passivators as additives. The Apiezon® C tested in this report contained a 5% lead naphthanate (Pb-N) additive which had been added by Ball Bros. for space applications and reported by them to have been performed successfully for many years since the 1960s. The oil does not pass the outgassing material acceptance criteria ASTM-E595 (reference 2) and concerns about its use were raised. These resulted in this and other investigations on the oil mass losses versus temperatures and on the assessment of the contamination hazards which could result from the evaporation of the lead-naphthanate additive. The initial investigation (reference 3) about this oil indicated the following results:

1. The percentage of the Pb-N in the oil remained unchanged after oil degassing, as indicated by x-ray fluorescent spectroscopy and FTIR analyses.
2. The oil absorbs atmospheric gases as other hydrocarbon oils do. It forms visible bubbles after being exposed for about 20 days to normal environment. Those entrapped gases are released in a vacuum and they may splash oil on nearby surfaces if the oil is not degassed for 30-40 minutes in a low vacuum at normal temperature.
3. The oil vapor pressures obtained from mass rate losses at 3 temperatures recorded by a Cahn analytical microbalance for a period of 48 hours, varied from 2×10^{-8} torr at 10 °C to 1.2×10^{-6} @ 70 °C. Those pressures are shown for comparison in a plot of pressures, obtained from other methods, which will be discussed later.

The Krytox® 143 AB oil is a Perfluorinated Alkyl Polyether designed to be used in vacuum pumps handling reactive chemicals. According to the manufacturer it has excellent oxidative and thermal sta-

bility, chemical inertness, low vapor pressure, excellent lubricity and is compatible with metal plastics and elastomers. These properties and plots of the vapor pressures obtained using the Knudsen effusion method are included in reference 4. The oil with a mole mass of 3500 g/mole consists of a series of fluorine end-capped linear homopolymers. The polymer chain is completely saturated and includes C, O and F with no H or additives. The vapor pressures indicated in the reference are reported here with the present results. In addition to those vapor pressures, values obtained using an equation developed in reference 5 from an isoteniscope measurements are also shown. Also reported, are the vapor pressures of the oil obtained from the rate of accumulation of condensed oil on a Thermal Quartz Crystal Microbalance (TQCM) located on the wall of a box containing a motor lubricated with this oil (reference 6).

Test Data

The two oils were tested in a TA Instruments 951 TGA which was modified to accept a vacuum of less than 10^{-4} torr in the volume where the oil to be analyzed is contained. The electronic balance of the TGA measures continuously the mass loss of the oil which is held in a basket at a preset temperature. The mass and the temperature are continuously monitored and computer recorded. The mass loss and the rate of mass loss for the oils held at constant temperatures were utilized to calculate the vapor pressures of the oil and its components. The percentage of those components in the oil were obtained from changes in mass loss rates occurring during the tests and the duration of each of those rates. Apiezon® mass losses were carried out at temperatures of 37.51, 37.17, 45, 53 and 70 °C as shown in (figures 1, 2, 3, 4 and 5). The Krytox® tests were carried at several temperatures as indicated on the plot of its vapor pressures. Individual plots of mass

loss for the Krytox® are not included since the pressures were obtained from the mass loss rates directly, with no concern for components since they are known to be absent in this oil.

Analysis

Figures 1, 2, 3 and 4 show the percent mass loss of the Apiezon® oil versus time at 4 different temperatures. Along the mass loss curves at those temperatures, the changes in loss rates occur and are well distinguishable. The location of the changes are also reflected in the plot of the temperatures. Those changes are produced by the components of the oil and have been interpreted to reflect the presence or the depletion of oil components. The temporary changes in temperature reflect the depletion of one of the components of the oil. During the evaporation of that component, the temperature of the oil is constant and the supplied evaporation energy is constant. However, when the component is depleted, the supplied energy exceeds the requirements and the oil temperature increases. The instrument then adjusts the amount of energy being supplied and the temperature returns to the set value. The four figures indicate that Apiezon has 3 major different rates of evaporation. These 3 rates have been employed to obtain the corresponding vapor pressures of 3 stages of the oil evaporation and they have been taken to reflect the presence of 3 components in the oil. Figure 5 shows the mass loss of the oil at 70 °C. At that temperature, the higher volatile components of the oil are rapidly being exhausted and it is more difficult to obtain the loss rates versus time of the oil components.

The vapor pressures were obtained from the rate of mass loss w (g/s) at the various test temperatures utilizing the Langmuir's relation $w = PA \sqrt{T/M} / 17.14$ (g/s) where P (torr) is the pressure, T (K) the temperature, M (g/mole) the mole mass and A (cm²) is the exposed surface area of the oil. The various oil

components were identified by the different mass loss rates shown by the record of the mass loss versus time. The mole mass M for the components utilized in the above equation were estimated by comparing the ratios of the loss rates of the components to that of the long term rates which reflect the known mole mass of the oil ($M=479$ g/mole). For example, the loss rate of the long term oil component at 45 °C (figure 3) was 9.56×10^{-6} %/min while the rate of the second component was 2.99×10^{-5} %/min, i.e., 3.1 times greater than the long term rate. The mole mass of the second component was then assumed to be 3.1 times smaller than that of the final component. The method was carried out for the data of each isothermal test and the results were then averaged. The average ratio for the second component was found to be 3.06 and for the first component 8.95 so that the first component may have a $M=479/8.95=54$ g/mole and the second $M=479/3.06=156$ g/mole.

The vapor pressures (V.P.) and the fractions of the various components in the oil have been obtained from the isothermal evaporation rates shown in figures 1, 2, 3, 4. The values of the rates and the periods of time during which those rates existed are indicated. Those rates have been identified as rate R_1 , R_2 and R_3 where R_1 identifies the initial evaporation rate of the oil. The V.P. for each of those regions of the evaporation were calculated using the indicated equation applied for the 4 tested temperatures and using the estimated mole masses. Figure 6 shows those V.P. The process was carried out for each of the 3 recognized components.

Component 1 has a V.P. about 7 times higher than that of component 2, about 30 times higher than that of the component 3 which is the long term and the major component of the oil. The V.P. of the same oil as reported by the manufacturer (reference 1) and as calculated from measurements using a vacuum Cahn micobalance (reference 3) are shown. The Cahn measurements recorded the integrated evaporation

Sample: Apiezon C 44.6g
 Size: 44.7500 mg
 Methods: Ramp to 30C
 Comment: Vacuum

TGA

File: Apiez.08
 Operator: MKM
 Run Date: 26-Dec-95 09:08

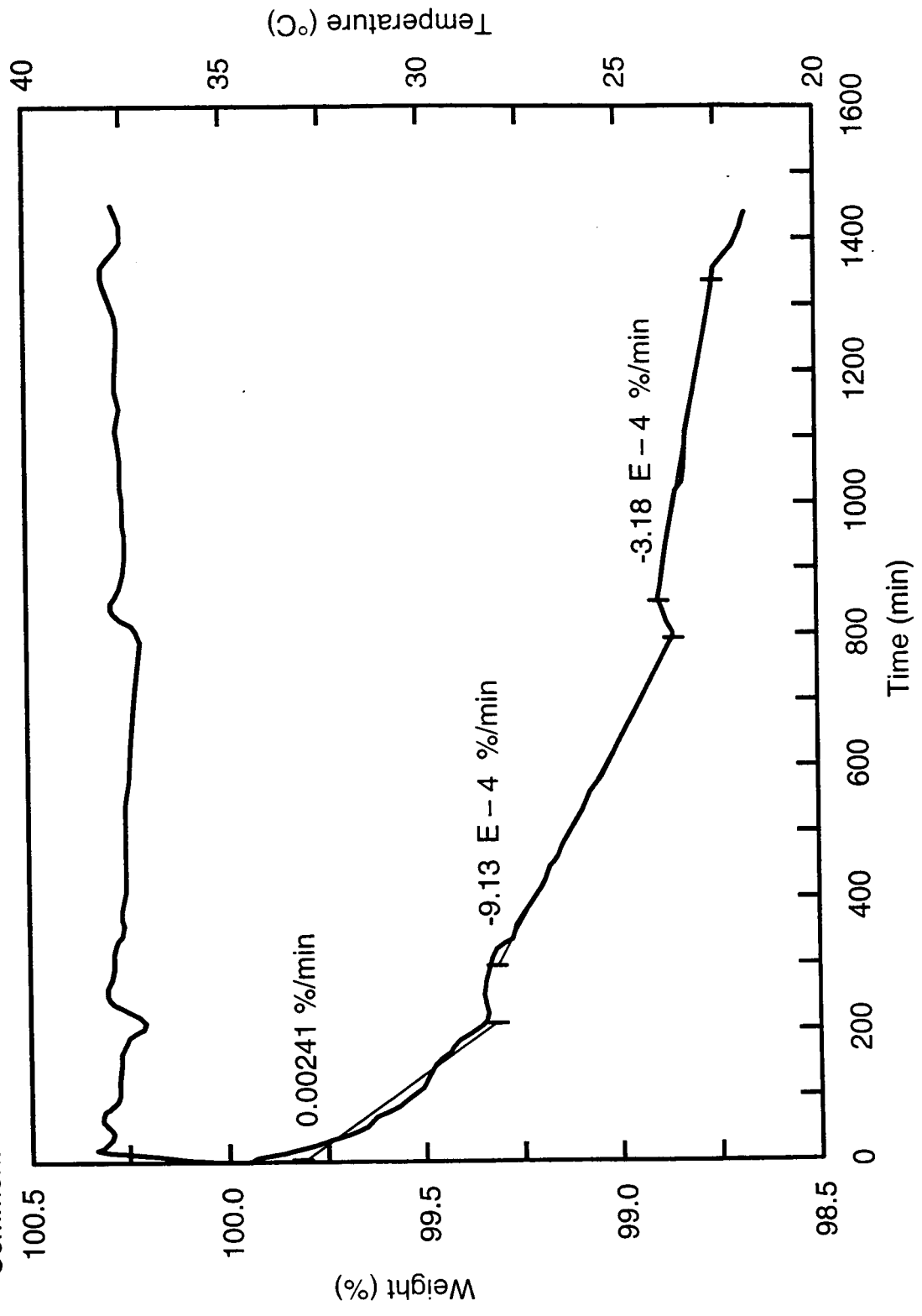


Fig 1 Apiezon C Weight loss vs. Time at 37°C

Sample: Apiezon C 33.1mg
 Size: 32.5690 mg
 Method: Ramp to 40C
 Comment: Vacuum
 File: Apiez.15
 Operator: MKM
 Run Date: 23-May-95 14: 55

TGA

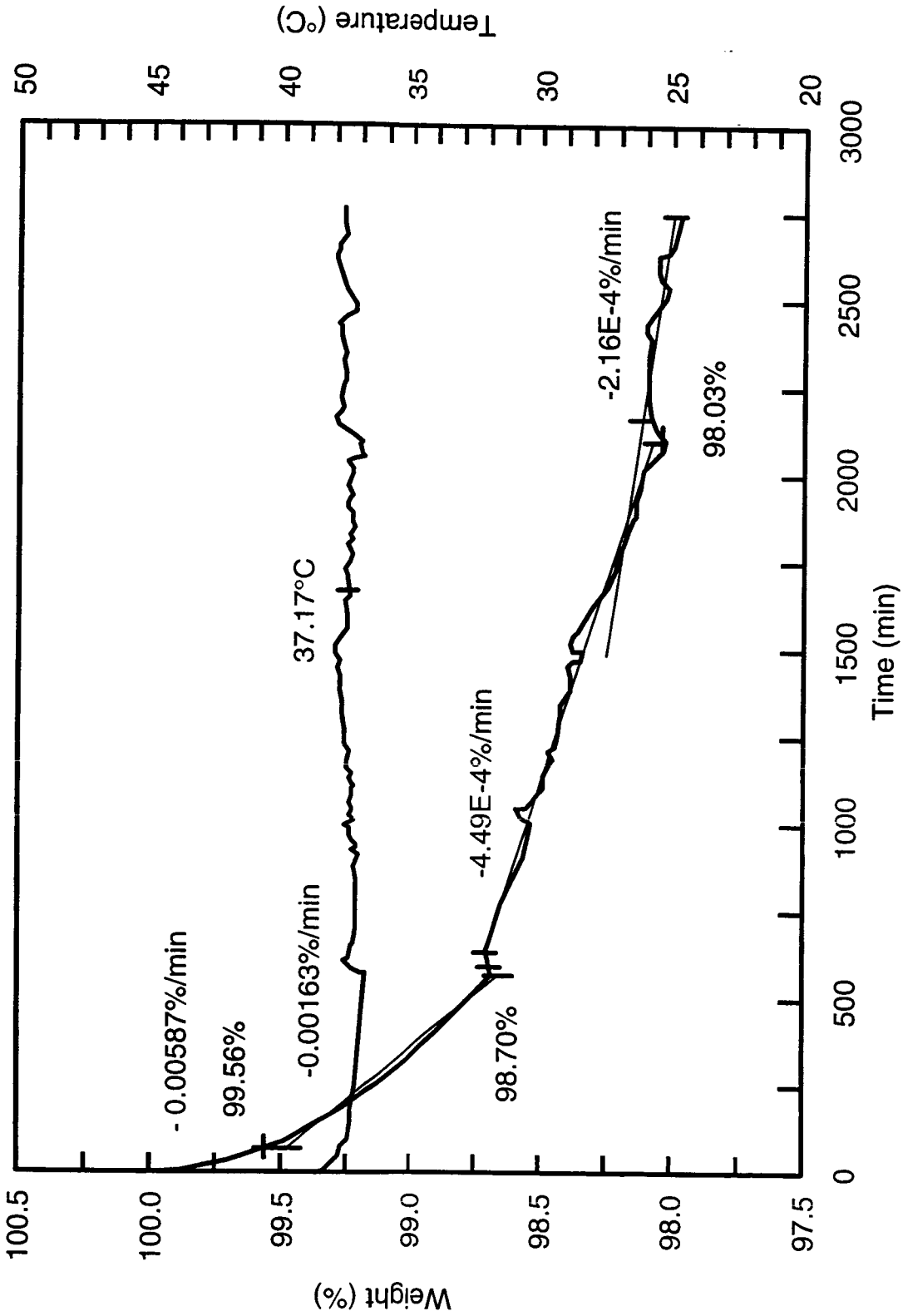


Fig 2 Apiezon C Weight loss vs. Time at 37.17°C

Sample: Apiezon C 36.0mg
Size: 36.0860 mg
Method: Ramp to 40C
Comment: Vacuum

TGA

File: Apiez.12
Operator: MKM
Run Date: 7-Jan-95 11: 20

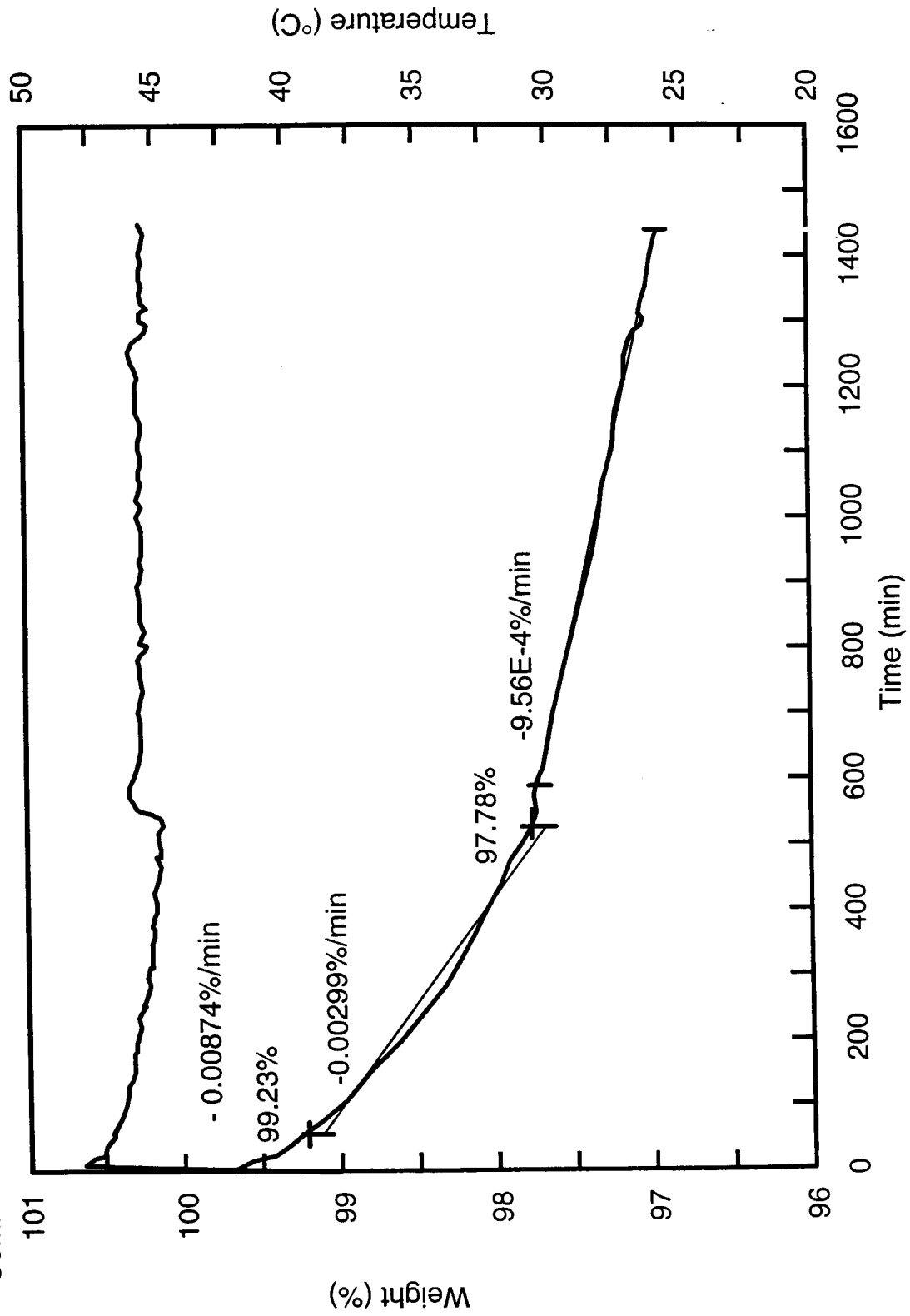


Fig 3 Apiezon C Weight loss vs. Time at 45°C

Sample: Apiezon C 44.9mg
Size: 44.8960 mg
Method: Ramp to 50C
Comment: Vacuum

TGA

File: Apiez.10
Operator: MKM
Run Date: 28-Dec-95 08: 56

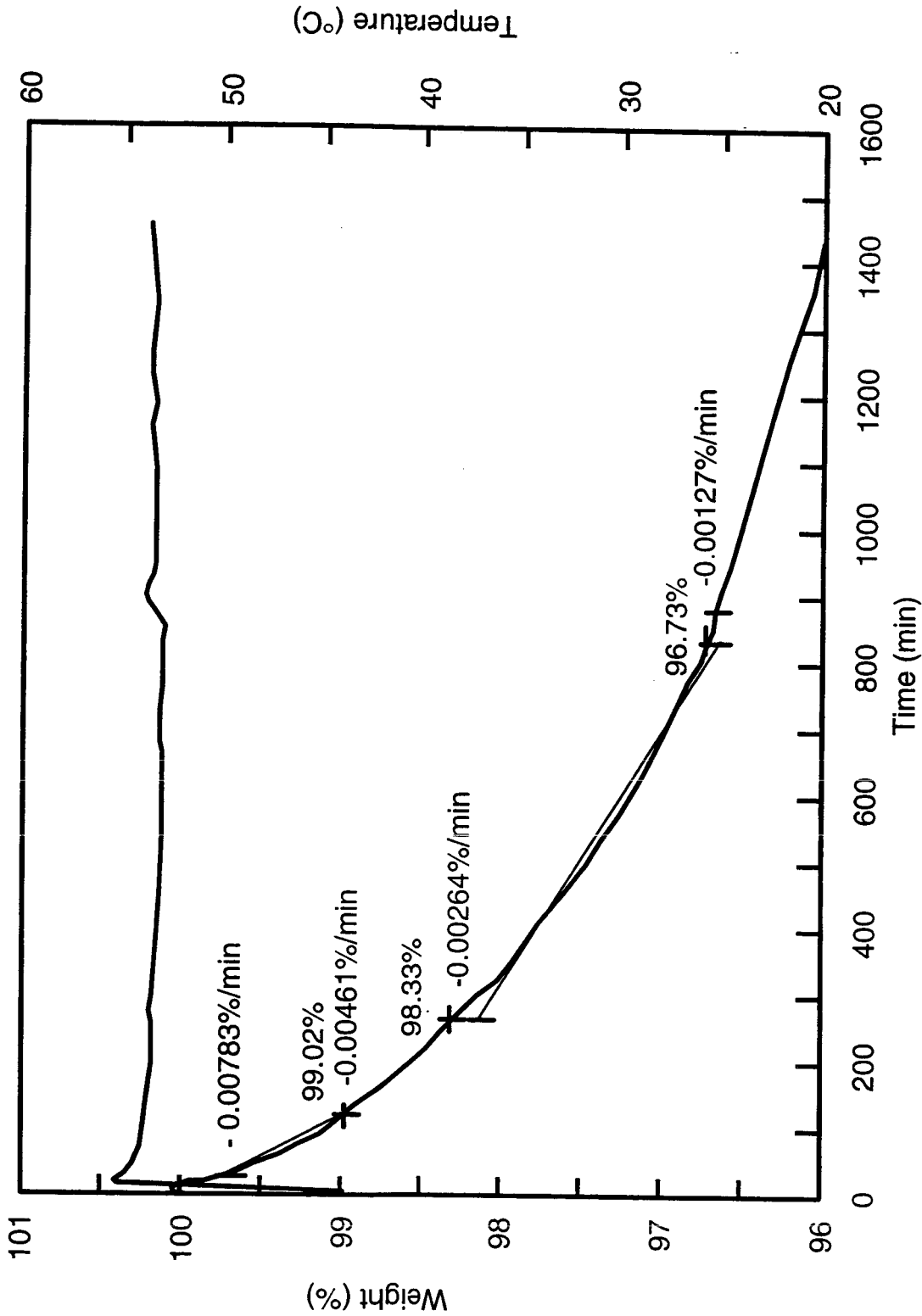


Fig 4 Apiezon C Weight loss vs. Time at 53°C

Sample: Apiezon C 58.4mg
 Size: 58.3370 mg
 Method: Ramp to 70C
 Comment: Vacuum

TGA

File: Apiez.11
 Operator: MKM
 Run Date: 31-Dec-95 10: 15

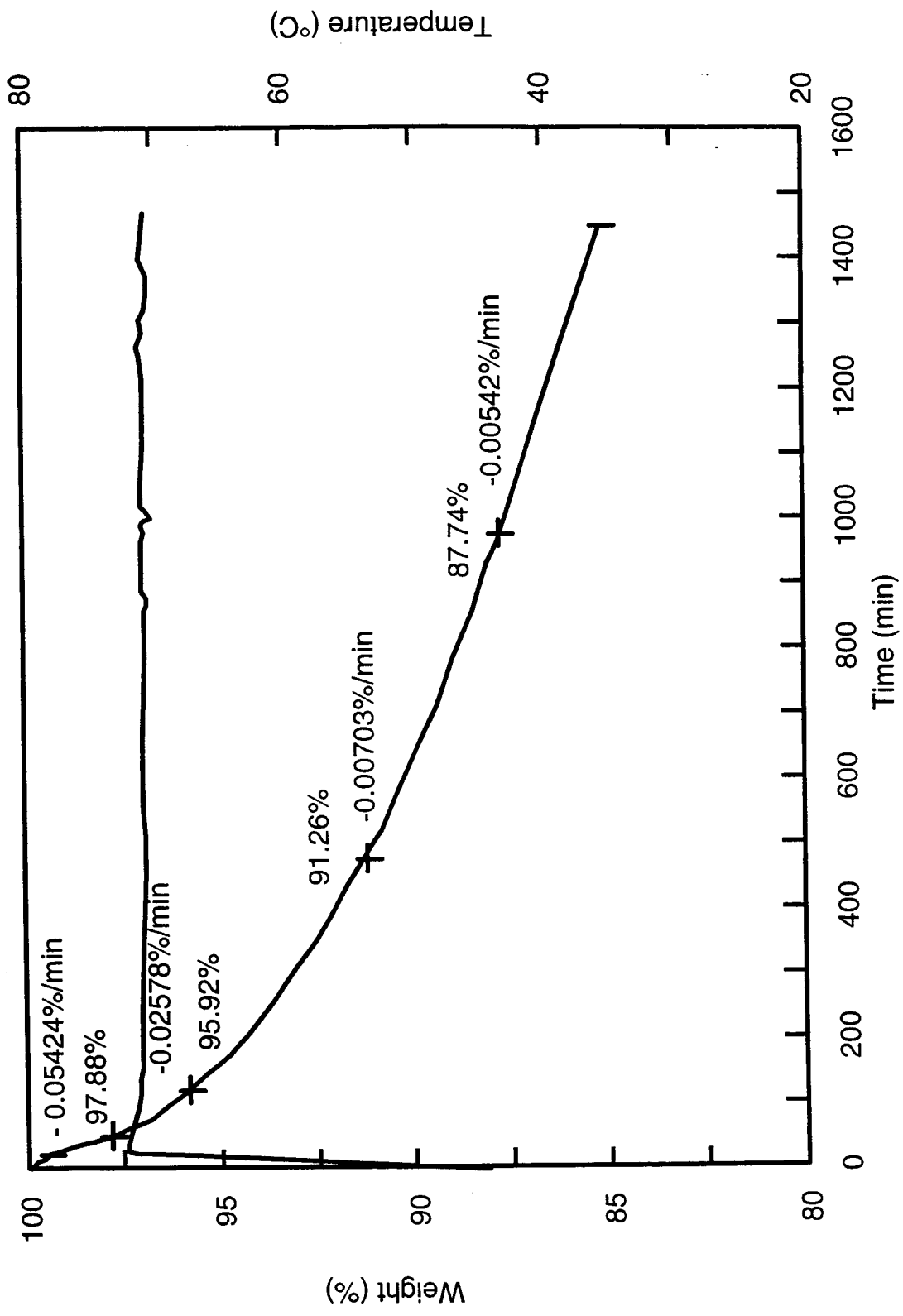


Fig 5 Apiezon C Weight loss vs. Time at 70°C

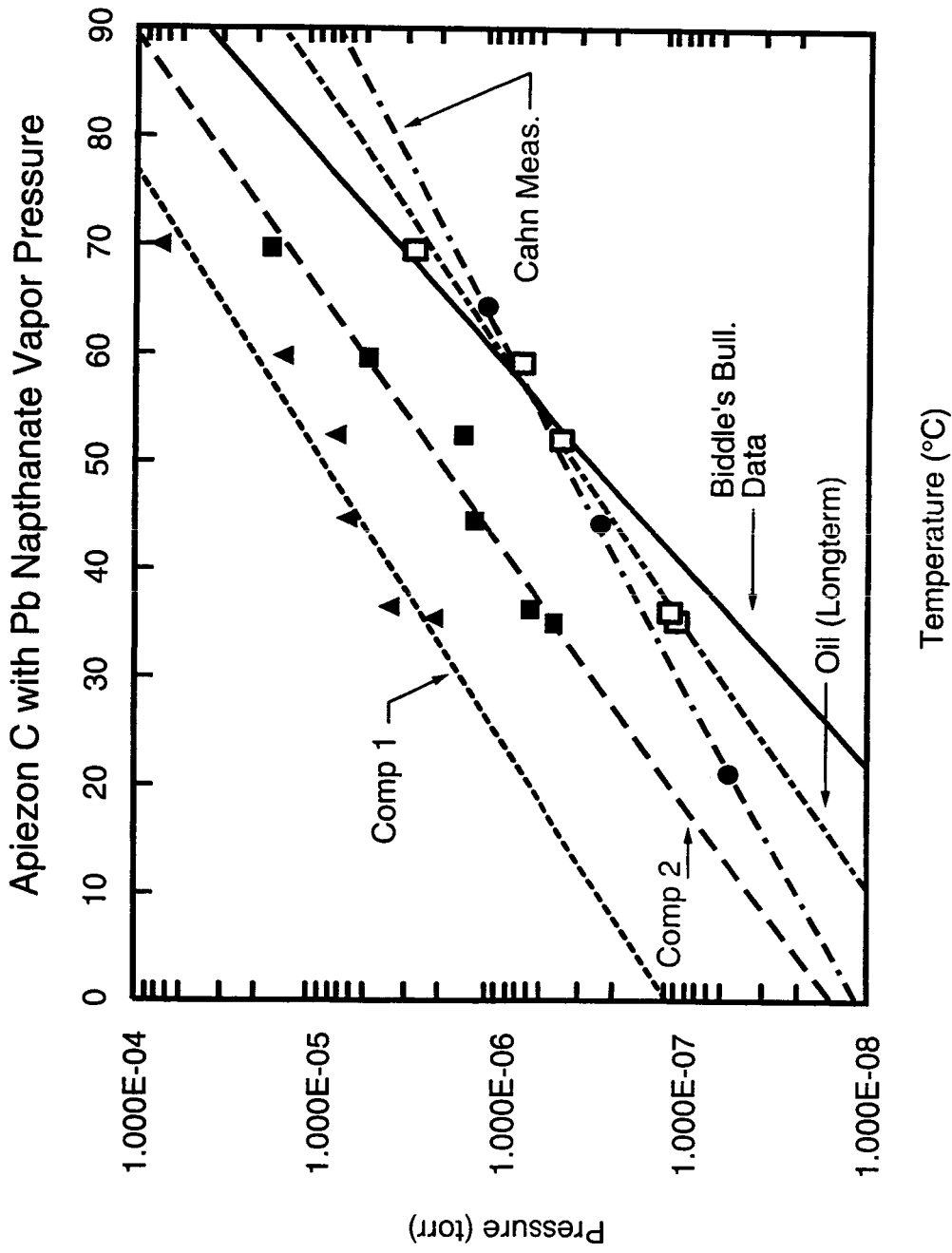


Fig 6 Apiezon C Vapor Pressure

loss of the oil during 48 hours of tests carried at several temperatures. No differentiation of the component's rates was possible with the Cahn balance. The V.P. from those two sources appear to match those of the TGA long term component at a temperature of 60 °C.

The actual V.P. of the oil characterized by the 3 stages of evaporation and the components fractions in the oil were obtained as follows. The measured evaporation rate R_1 includes the evaporation of component 2 and 3 while the rate R_2 includes that of component 3, R_3 . The rate R_3 is the long term evaporation of the lube and does not contain other components. The actual evaporation of the component 1 is then $r_1=R_1-(r_2+r_3)$, for a component 2 is $r_2=R_2-r_3$ and for a component 3 is $r_3=R_3$. These relations were applied and solved for the four tested temperatures and eventually the results averaged as shown in Table 1. For example, for the test at 45 °C, the results using the rates shown in figure 3 were $r_1=5.75 \times 10^{-3} \%$ /min, $r_2=2.034 \times 10^{-3} \%$ /min and $r_3=9.56 \times 10^{-4} \%$ /min. The percentage refers to the original amount of the oil used in the test as indicated in the figure (36.08 mg for the 45 °C test).

The percentage of those components in the oil were obtained using the above rates r_i (%/min) and the length of time t_i each of those rates (R_i) existed as indicated by the curves for mass losses versus time. For example for the 45 °C test, the amount of component one is $M_1=r_1 t_1=5.75 \times 10^{-3} \%$ /min \times 60 min=0.345%, for component two $m_2=r_2 t_2=2.034 \times 10^{-4} \%$ /min \times 540 min=1.098% and for component three $m_3=100\%-(m_1+m_2)\%=98.5\%$. The average for the 4 tested temperatures, as shown in Table 1, are: 0.371% for component one, 0.746% for component two and 98.85% for the long term component three. The percentages for components one and two are quite small and could reflect the molecular distribution of the oil with component one being the fraction of molecules with the lowest molecular mass and component three the highest and largest frac-

tion of the oil. This may indicate that no other additive is included in the oil other than the 5% lead-naphthanate which as indicated from other analyses remains unchanged at least at these temperatures.

The V.P. of the Krytox® 143 AB as shown in figure 7 was obtained from isothermal tests at temperatures shown by data points and varying from 22 to 84 °C. The figure shows also the V.P. obtained from other sources. The Vacuum TGA results, reported here, are about 5% of those reported in the Dupont bulletin for this oil and about 10 times higher than the values measured in a system utilizing oil condensation on a TQCM mounted on the surface of a box which contained a motor lubricated with this oil (reference 6). Another comparison is with values reported in reference 7 obtained with a isoteniscope at high temperatures (>100 °C) and extrapolated to lower temperatures. These values are 2-3 orders of magnitude lower than those found here. The oil has no additives and no differentiation of rates of losses were noted during TGA testing.

Conclusions

The vapor pressures as a function of temperature of the components of two lubes, the Hydrocarbon based Apiezon® and the perfluorinated Alkyl Polyether Krytox® were obtained experimentally using a TGA instrument modified to work in vacuum. These oils are frequently employed to lubricate space mechanisms. An important result of the tests and their interpretations has been the identification of the fraction of additives in the oil and their respective rates of evaporation as a function of temperatures. Using the method developed here in conjunction with TGA measurements, the life of the lubricant which depends on the rates of evaporation of the oil components and the amount of those components in the oil, can be estimated when the lube exhaust conductance is known.

Table 1
 Components of Apiezon C Oil
 Their evaporation rates and masses

Test Temp °C	Component 1		Component 2		Component 3	
	r_1 (%/min)	m_1 (%)	r_2 (%/min)	m_2 (%)	r_3 (%/min)	m_3 (%)
53	3.22×10^{-3}	.418	2.665×10^{-3}	.703	1.955×10^{-3}	98.85
45	5.75×10^{-3}	.345	2.034×10^{-3}	1.978	9.56×10^{-4}	98.5
37.17	4.24×10^{-3}	.424	1.181×10^{-3}	.7086	$.44 \times 10^{-3}$	98.86
37	1.497×10^{-3}	.299	5.95×10^{-4}	.476	3.18×10^{-4}	99.22
Average		.371%		.746%		98.85%

r_i (%/min), evaporation rate of the component

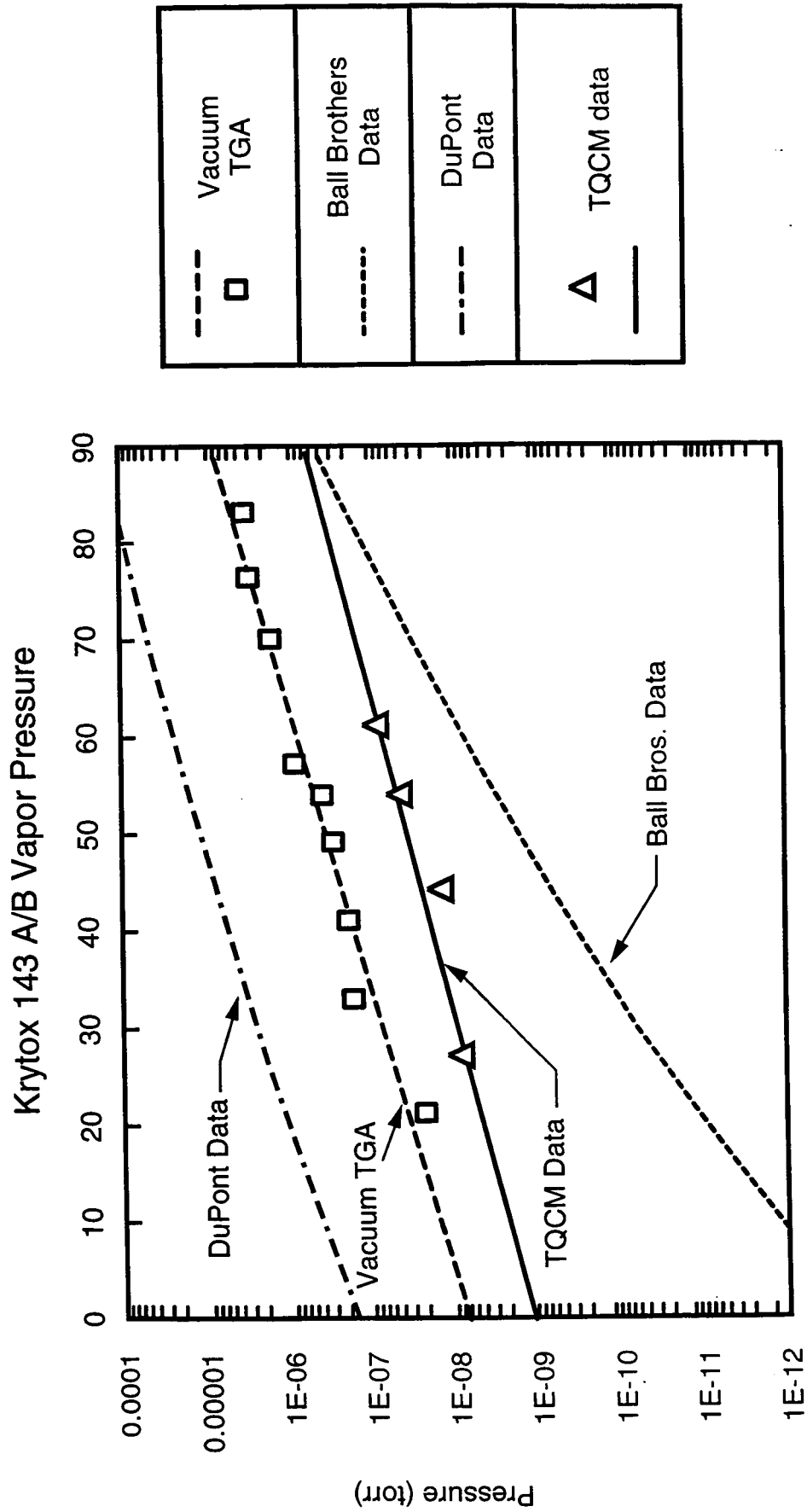
m_i (%) = $r_i t_i$, percentage of component in the oil, t_i (min) is duration of the evaporation of stage i

A method to obtain length of time, a specific rate of evaporation and mass would last $t = \frac{\text{component mass}}{\text{rate of oil loss for component}} = \frac{m_i W}{C P_i} \left(\frac{g}{g/s} \right)$

Where W (g), total mass of lube

P_i (torr) vapor pressure at T_i from evaporation stages

C (g/s/torr) conductance of ventioio passage, evaluated for T (°K) and M (g/mole)



--- □	Vacuum TGA
.....	Ball Brothers Data
--- △	DuPont Data
—	TQCM data

Temperature (°C)

Fig 7 Krytox 143 A/B Vapor Pressure

For the oil analyzed here, it was found that the Apiezon® C lube includes 3 components with different rates of evaporation. It has an initial high evaporation rate followed by a second and eventually a lower long term rate. In fact, the initial rate applies to 0.37% of the oil mass and has a rate about 7 times higher than that of the second evaporation rate which applies to 0.75% of the oil. The initial rate is also about 30 times higher than the rate of the long term fraction of the oil which is 98.85% of the lube. The vapor pressure of this oil at 20 °C has an initial value of 6×10^{-7} torr and a final long term pressure of 2×10^{-8} torr. The time for the change from one pressure to the other depends on the amount of the components in the oil. Those pressures and the evaporation rates are of course exponential functions of the temperatures and equations of pressures versus temperature could be derived from the plots shown here.

The results of the tests for the Krytox® AB show as expected the absence of additives and that its vapor pressure as shown in the plot of V.P. versus temperature is about 5×10^{-8} torr at 20 °C and 2×10^{-6} torr at 70 °C. These pressures are about one order of magnitude lower than those given by the manufacturer but higher than those provided by the use of a TQCM in a special test set-up. Comparison with other measurements of vapor pressure have been included in the presentation of the V.P. for both oils.

Acknowledgement

One of the authors, M.K. Miller, wishes to thank Dr. P. Chen for his guidance and advice while he was at GSFC as a PREST (Program for Research and Education for Space Technology) graduate student of the Air Force Academy.

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