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A Model to Describe Oil Loss Under Vacuum Conditions

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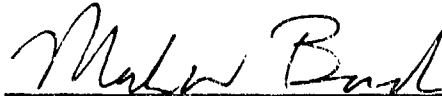
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) A computer model of oil loss under vacuum conditions has been generated. The model is based on empirically determined vapor pressures and, thus, loss rates of a homologous series of straight-chain hydrocarbons. Several hypothetical oil distributions, i.e., component percentages vs molecular weights, are discussed in terms of bulk vapor pressure and oil loss. The use of the vapor pressure of unused oil to calculate oil loss rates is shown to be inappropriate.						
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I. INTRODUCTION

Satellite orbital lifetimes are expected to increase with future generations of spacecraft. Increased lifetime implies increased systems reliability. As a result, the lubricants used in moving mechanical assemblies must provide adequate lubrication for longer periods of time. Loss of lubricant through evaporative transport under the low pressures of the orbital environment is a process that must be understood. Evaporative transport is generally modeled by choosing a vapor pressure for the lubricant based on manufacturer's data, without the benefit of measurement of vapor pressure as a function of lubricant loss. It is well known that, within a homologous series of compounds, vapor pressure decreases with increasing molecular weight. However, the effect of the loss of the more volatile oil components on the vapor pressures of complex mixtures, like petroleum-based oils, is not well known and is not appreciated by designers. In this report, a model is presented, based on empirical vapor pressure data, that demonstrates the dependence of vapor pressure and oil loss on the molecular weight distributions of several hypothetical oil mixtures.

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II. THE MODEL

A blend of straight-chain hydrocarbons, paraffins, was chosen as a starting point for the model lubricants. The choice was due to the availability of vapor pressure data for paraffins of appropriate molecular weight [i.e., data existed for each member of the homologous series from 21 to 29 carbon atoms¹] and the paucity of data for branched compounds. (The number of possible isomers for a 30-carbon hydrocarbon is 4×10^9 . All of these isomers are possible in petroleum-based oil mixtures. Thus, it is not unreasonable to be unable to locate vapor pressure data on all possible isomers for C21 through C29 hydrocarbons.) The vapor pressure data for the paraffin series are shown in Figure 1. (In Figure 1, the data for C22 yield a slope that is less than the slope for C21, resulting in the slopes crossing. The C22 data appear to be out-of-family. Since the origin of this anomalous behavior is not known, the C22 data were used for the model with the understanding that the deviations would not result in significant adverse consequences in the model.) The data were taken at high temperatures and were extrapolated to 50°C, the temperature chosen for the model. (It is assumed that the log vapor pressure is correlated linearly with inverse temperature as given by the Clausius-Clapeyron relationship over the temperature range of the extrapolation.)

From the extrapolated vapor pressure data, the loss rates can be calculated using the Langmuir equation, as follows²:

$$P_{mm} = 17.14G(T/M)^{1/2}$$

where G is the loss rate in $g/cm^2/sec$, P_{mm} is the vapor pressure in mm of mercury (torr), M is the molecular weight of the evaporating species in g , and T is the absolute temperature in K .

Loss rates for the hydrocarbons were calculated for the hydrocarbon series from vapor pressure data at 50°C. These data are shown as a semilog plot in Figure 2. The data were least-squares fitted to a straight line. The slope of the line was extrapolated to obtain loss rates outside of the molecular weight range of the original data. (The same treatment was applied to the vapor pressure data to estimate vapor pressures over an extended molecular weight range.)

Gas chromatography (GC) data indicate that, in typical petroleum oils, there are so many separate components that a chromatogram (showing component quantity as a function of retention time, which is proportional to boiling point for the GC columns we used) resembles a relatively smooth distribution function.³ Figure 3 exhibits the chromatogram (boiling point

¹Handbook of Chemistry and Physics, 49th ed., R. C. Weast, ed., The Chemical Rubber Co., Cleveland, Ohio (1968), p. D-135.

²S. Dushman, Scientific Foundations of Vacuum Technique, 2nd ed., J. M. Lafferty, ed., John Wiley & Sons, New York, NY (1962), p. 19.

³D. J. Carré, R. Bauer, and P. D. Fleischauer, "Chemical Analysis of Hydrocarbon Grease from Spin Bearing Tests," ASLE Trans. 26(4), 475 (1983).

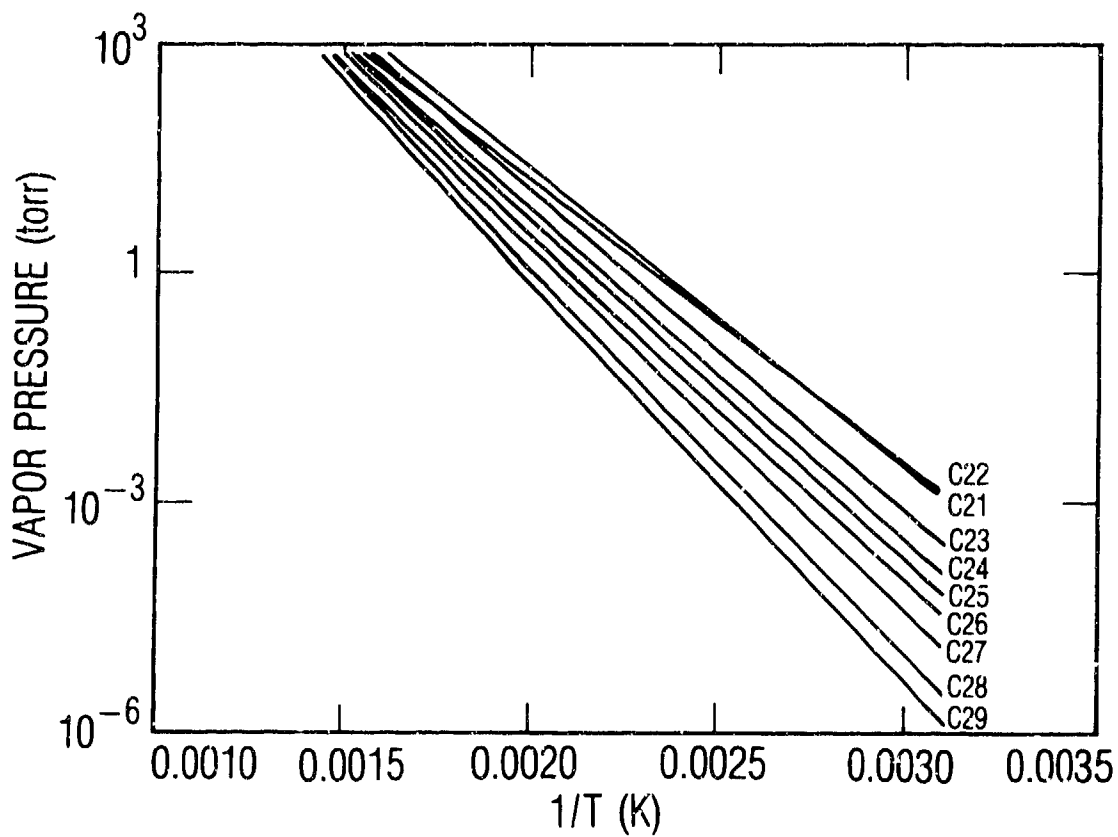


Figure 1. Log vapor pressure vs reciprocal temperature for the homologous series of paraffinic hydrocarbons from C21 to C29. [C22 exhibits anomalous behavior (see text).]

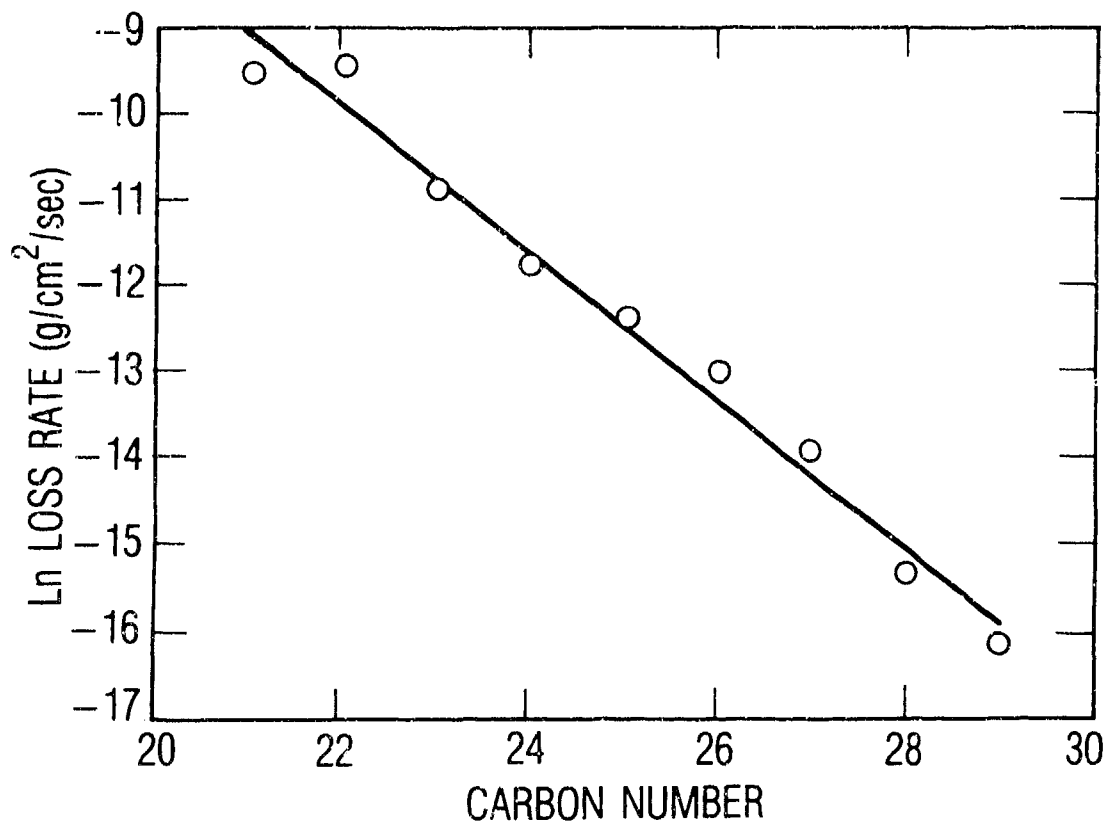


Figure 2. Ln loss rate vs carbon number for paraffins at 50°C. Solid line represents least-squares fit to the data.

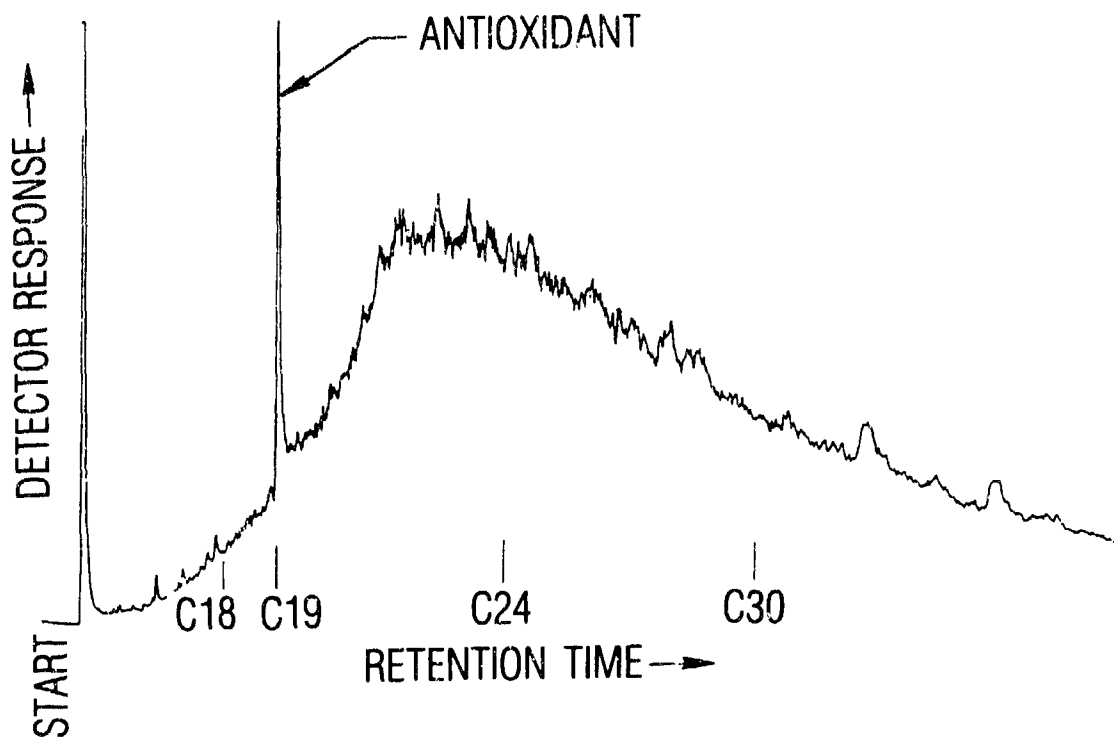


Figure 3. Gas chromatogram of typical petroleum-based oil.

and molecular weight distribution) for a typical petroleum-based hydrocarbon oil. Positions of paraffins on the chromatogram are also indicated. The shape of this oil distribution was used as a starting point for the model.

The molecular weight distributions of the various hypothetical oils were created by summing overlapping Gaussian functions of the following form:

$$y = A \exp[-a(x-a')^2]$$

where the constants A , a , and a' were adjusted for each function to achieve the desired distribution shape. The distributions are composed of 500 equally spaced "species." The paraffin vapor pressure and loss rate data were used for the integer carbon numbers. The remaining points (species) in the distributions that appear to be associated with noninteger carbon numbers are used to simulate the many branched isomeric hydrocarbons that exist in real oil blends. (The vapor pressures of these branched components are dependent upon both molecular weight and structure, so that structural isomers will exhibit a range of vapor pressures.) Oil vapor pressures and loss rates were interpolated from the paraffin data to account for these branched species.

To determine the loss rates as a function of time, an arbitrary "time interval" was chosen for each different oil distribution. (Since loss rate is a function of area, the "evaporation area" was incorporated into the "time interval," i.e., the "time interval" corresponds to time \times area.) The magnitude of the time interval was adjusted so that the percentage oil loss and vapor pressure change would be significant. Due to the differences in molecular weight distributions, different "time intervals" were used for each distribution.

The computer program consisted of 500 iterations. The initial 500-point oil distribution was normalized to an area of 100%. The mole fraction of each component was multiplied by its vapor pressure to give 500 partial pressures. These partial pressures were summed to give the total vapor pressure for the distribution. The mole fraction of each component was multiplied by its loss rate, and the resulting component oil losses were subtracted from the previous distribution to give a new distribution. The components were summed to give a total oil quantity relative to the initial oil quantity. The new distribution was again normalized to 100%, and the vapor pressure calculated. (The reason for the renormalization at each time interval calculation is that the component mole fractions need to be determined so that the component vapor pressures can be calculated in accordance with Raoult's law.) The process is repeated 500 times (500 time intervals), resulting in three matrices: a 500 \times 500 matrix of oil distributions and two 1 \times 500 matrices of total oil quantities and vapor pressures. As a result, oil loss vs time interval and vapor pressure vs time interval can be plotted readily. Oil distribution as a function of time interval can also be plotted. (However, in order to keep the plots relatively uncluttered, only the distributions at every 25th interval were plotted.)

III. RESULTS AND DISCUSSION

A. OIL DISTRIBUTION CASE 1

Figure 4 displays the oil distribution for "case 1." (The distribution with the largest envelope corresponds to the initial oil distribution at time zero.) This distribution is nearly symmetrical but is skewed toward higher molecular weights to resemble the shape of the distribution shown in Figure 3. Figure 5 exhibits the change in total oil amount and vapor pressure as a function of time interval. As can be seen in Figure 4, after 25 time intervals (the distribution with the next largest area), the lower molecular weight components have been stripped, and the distribution essentially starts at C22. Approximately 23% of the original oil amount has been lost. The vapor pressure of the remaining oil is more than an order of magnitude lower than that of the initial oil mixture. After the initial steep drop in the oil amount and vapor pressure, the slopes of the oil percent and vapor pressure curves decrease significantly. After approximately 130 time intervals, 50% of the oil has been lost and the vapor pressure of the remaining oil has dropped another decade. At 500 time intervals, the remaining oil corresponds to 30% of the original amount, while the vapor pressure has only decreased slightly from the value at 130 time intervals. The reduction in the rate of oil loss and the rate of decrease in vapor pressure reflects the fact that the lower molecular weight components (light ends) have been lost and the mixture has been enriched in the higher molecular weight components.

B. OIL DISTRIBUTION CASE 2

Figure 6 displays the oil distribution for "case 2." The initial distribution covers the same molecular weight range as that in Figure 4. However, the shape is considerably different, i.e., the shape is bimodal with a significant amount of lower molecular weight components. (This type of distribution may occur in blends in which a large fraction of light ends has been used for viscosity considerations or if a significant quantity of a volatile additive is used.) After 25 time intervals, the distribution (the second curve in Figure 6) has changed significantly with loss of nearly all the components below C24. The loss percentage (Figure 7) is essentially the same as that for case 1 after 25 time intervals, approximately 23% oil loss. The vapor pressure (Figure 7) is approximately one decade lower than that for case 1. This reflects the fact that the average molecular weight for the distribution in case 2 is larger than that for case 1 by two carbons at 23% oil loss.

C. OIL DISTRIBUTION CASE 3

Figure 8 displays the oil distribution for "case 3." As opposed to the oils in cases 1 and 2, which had distributions similar to what would be expected for petroleum-based oils, the distribution of the oil in case 3 represents what might be expected for a poly- α -olefin, synthetic oil. Since these oils are synthesized using 1-decene as the monomer, there should be

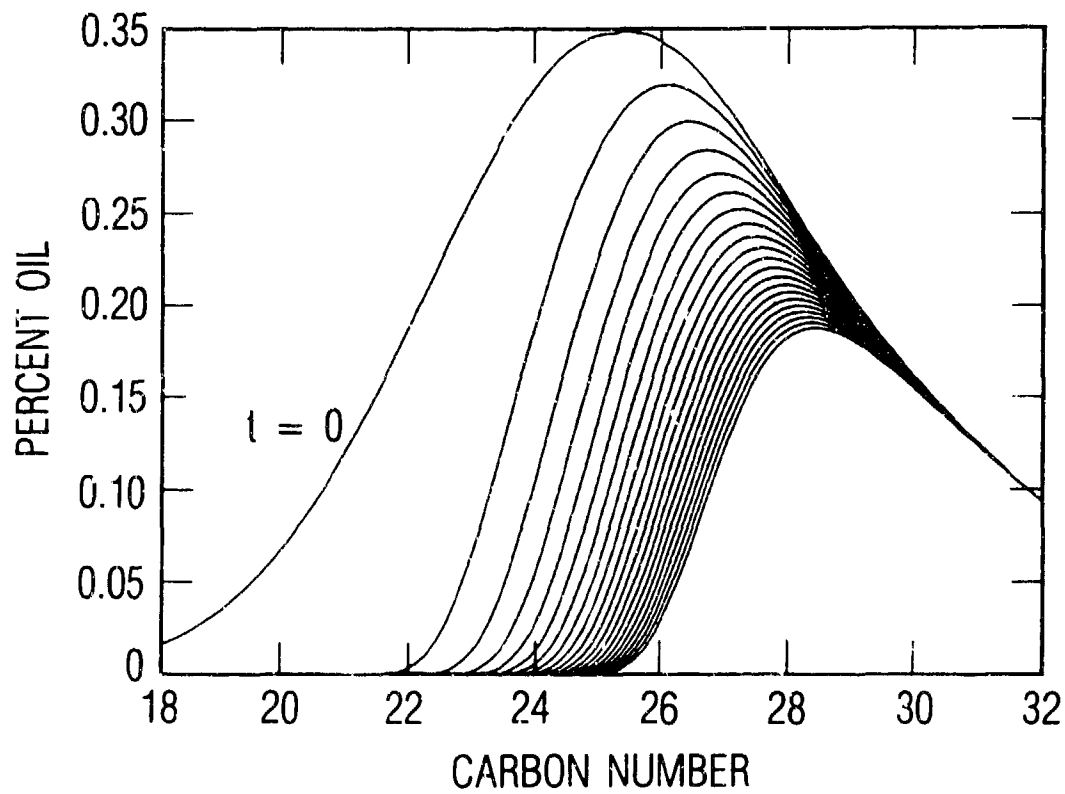


Figure 4. Oil distribution as a function of carbon number for case 1 oil. Curves every 25th time interval (see text). Distribution at $t = 0$ corresponds to unused oil.

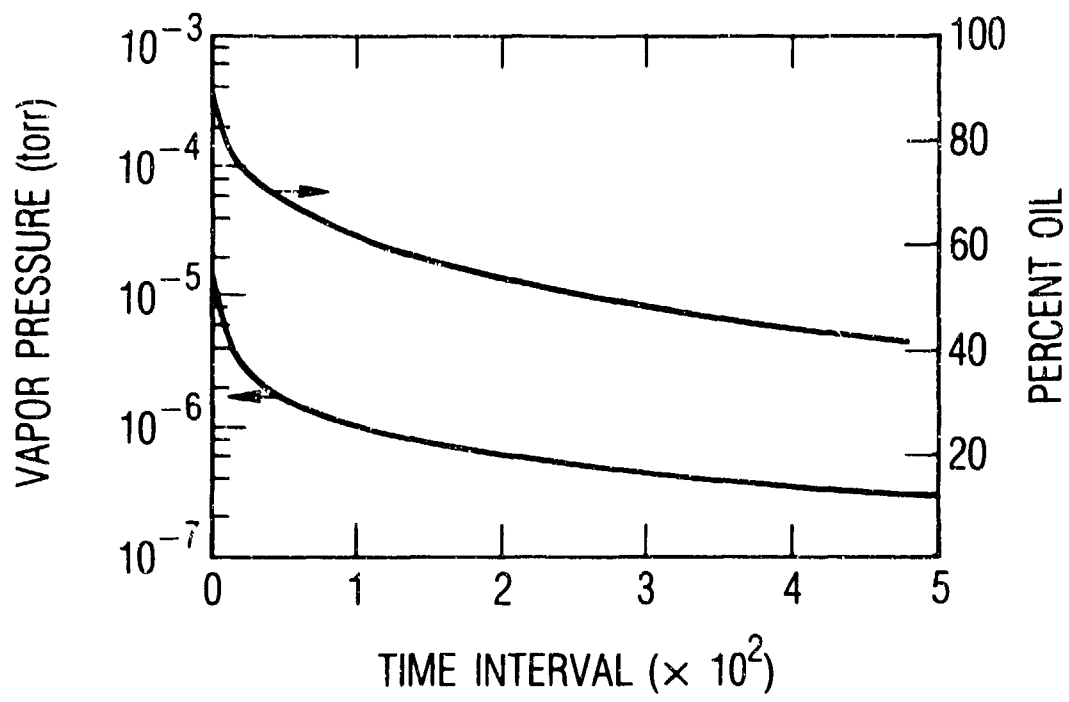


Figure 5. Percent remaining oil and vapor pressure vs time interval for case 1 oil.

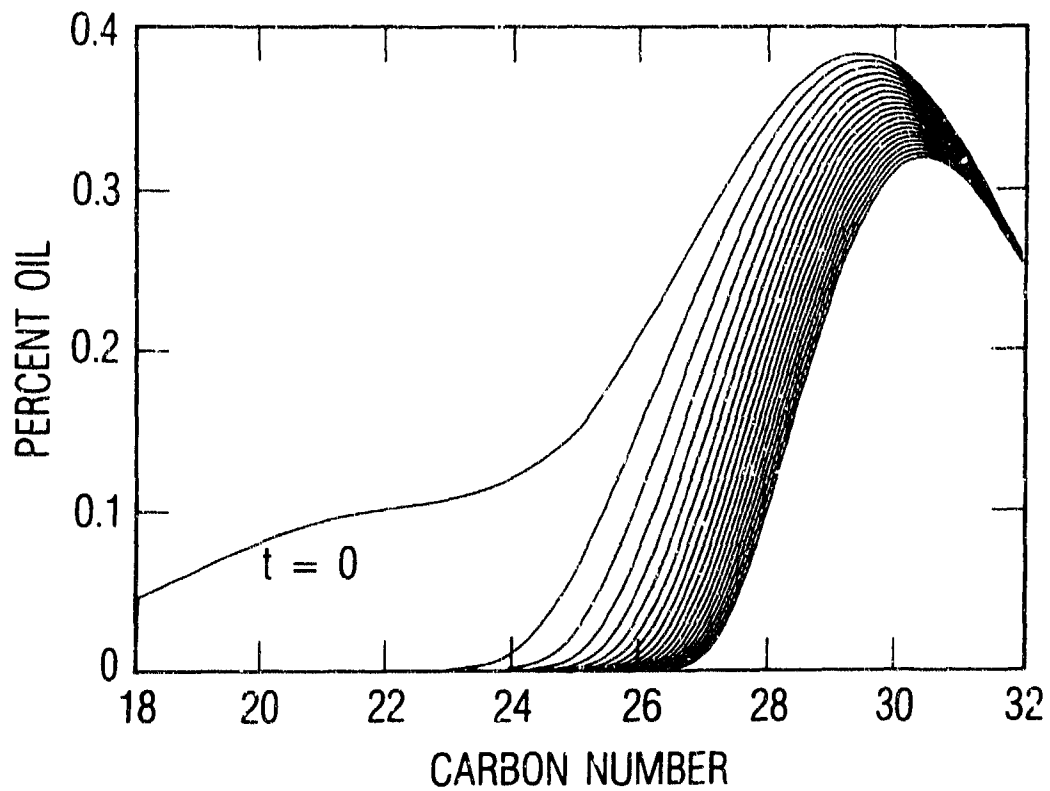


Figure 6. Oil distribution as a function of carbon number for case 2 oil. Curves every 25 h time interval (see text). Distribution at $t = 0$ corresponds to unused oil.

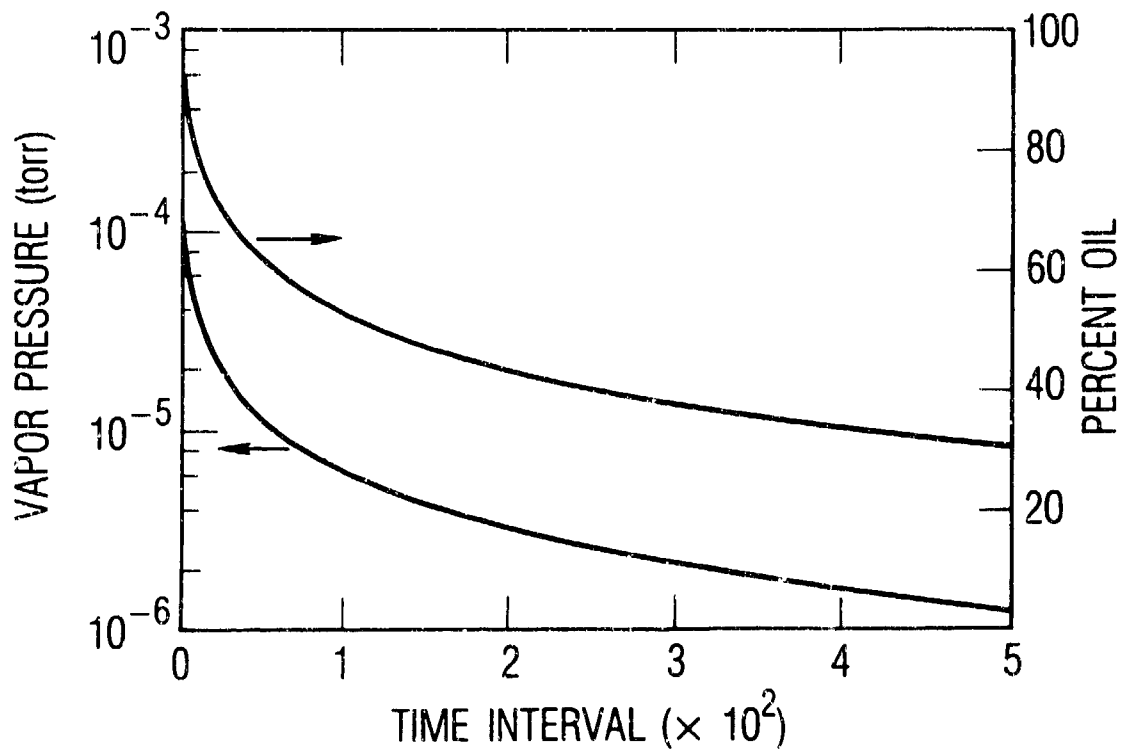


Figure 7. Percent remaining oil and vapor pressure vs time interval for case 2 oil.

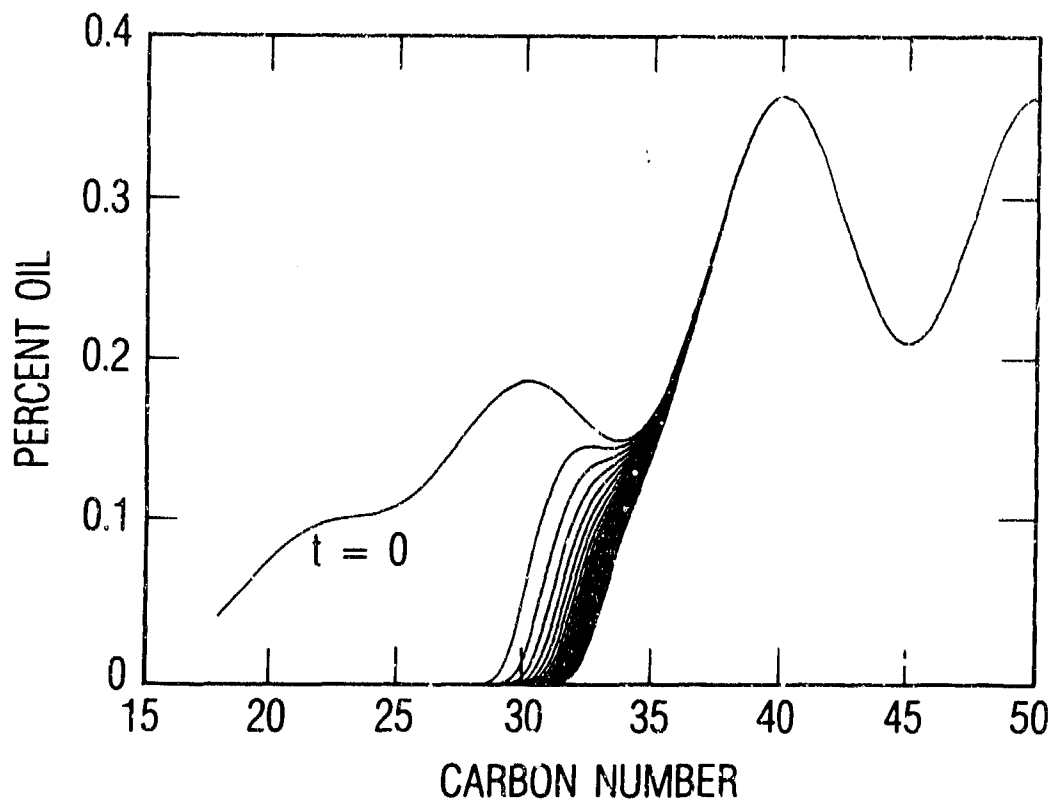


Figure 8. Oil distribution as a function of carbon number for case 3 oil. Curves every 25th time interval (see text). Distribution at $t=0$ corresponds to unused oil.

a preference for components that are multiples of C10. Because the synthetic oils generally have a larger percentage of higher molecular weight components than do the petroleum-based oils, the distribution in the model for case 3 has been extended to C50. The initial distribution shows the preponderance of the expected species at 10 carbon intervals. Figure 9 exhibits the percent oil and vapor pressure vs time interval data for the case 3 oil. At 25 time intervals, the oil has lost approximately 23%, similar to cases 1 and 2. However, the vapor pressure of the residual oil is three and four orders of magnitude less than the vapor pressures in cases 2 and 1, respectively, for equivalent amounts of oil lost. This results directly from the much higher average molecular weight of the residual oil in case 3 than that of the oils in cases 1 and 2. (This vapor pressure behavior demonstrates one of the pitfalls of using the initial vapor pressure of an oil as representative of its bulk vapor pressure behavior. The vapor pressure drops substantially with relatively small loss of oil.) At 500 time intervals, the case 3 oil has only lost approximately 32%, and the vapor pressure has dropped another decade. The vapor pressure of the residual oil has become so low that the loss rate, which is proportional to vapor pressure, has become insignificant, within the bounds of the time interval range that was chosen. (The time interval for case 3 is considerably larger than that for cases 1 and 2, so that the actual time elapsed per time interval is much longer for case 3.)

D. MODEL VS REALITY

The best test of a model is how well it describes the actual behavior. Unfortunately, there are limited data on oil vapor pressure behavior. Figure 10 exhibits a plot of vapor pressure vs oil loss for three oils. The vapor pressures were measured in our laboratory under equilibrium conditions using an ion gauge that was calibrated with a hydrocarbon with known vapor pressure vs temperature behavior. The oils correspond to commercial products. Oil 1 is a highly refined mineral oil with a distribution similar to, but slightly lighter than, that in case 1; oil 2 is a poly- α -olefin (PAO); and oil 3 is a neopentyl ester. The change in vapor pressure with 15% oil loss for oil 1 is very close to what the model predicts for the case 1 distribution. (The similarity in behavior is somewhat serendipitous. The data in Figure 10 are for 40°C, whereas the model is for 50°C. The difference in molecular weight distribution is compensated somewhat by the difference in temperature.) Oils 2 and 3 exhibit a vapor pressure decrease that is similar to the vapor pressure decrease for oil 1, but with much less oil loss, as shown for the simulated PAO oil in case 3.

The absolute values of the vapor pressures for the various oil distributions are not as important as the relative behaviors of the oils evaporatively, i.e., vapor pressures as a function of oil loss. Vapor pressure data based on equilibrium measurements on an unused oil do not reflect behavior under spacecraft orbital conditions.

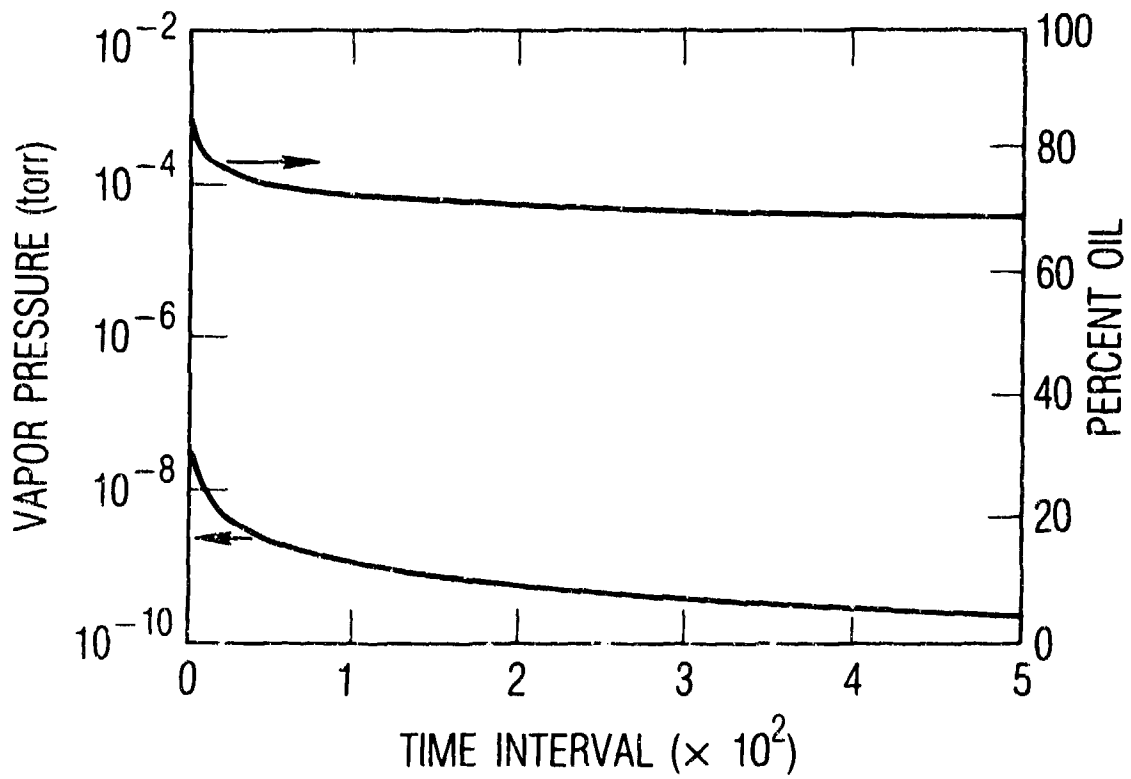


Figure 9. Percent remaining oil and vapor pressure vs time interval for case 3 oil.

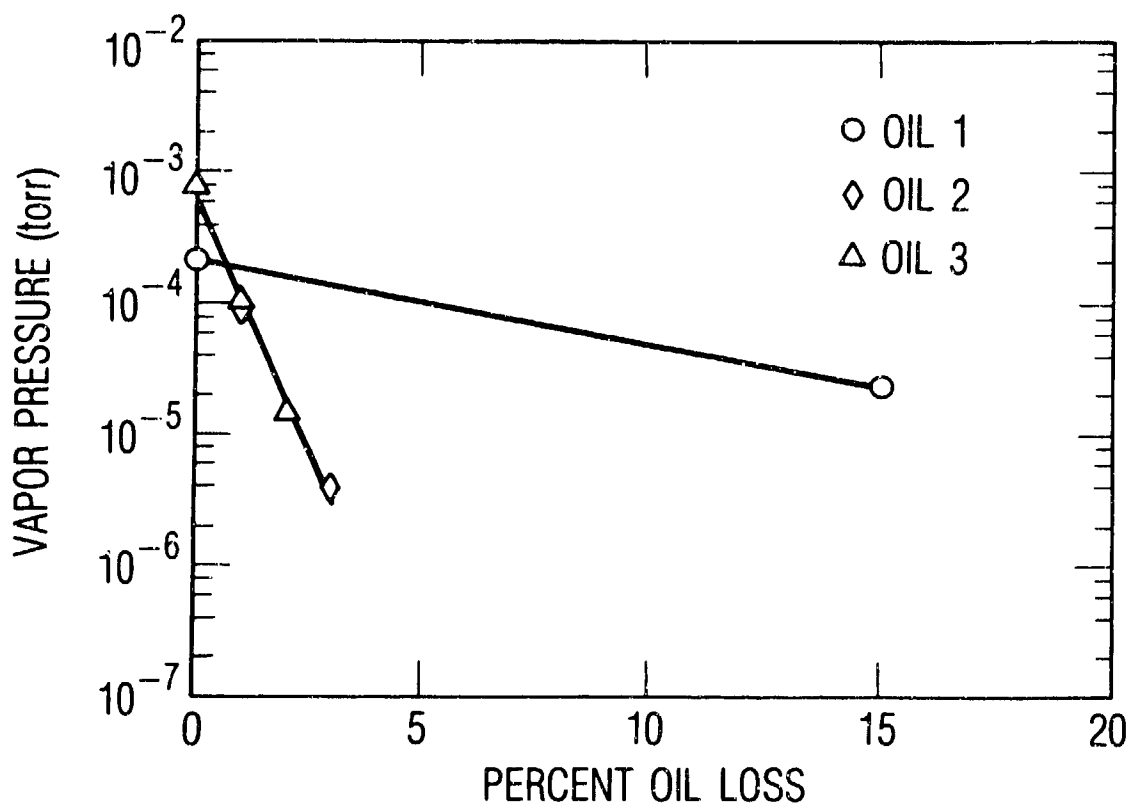


Figure 10. Vapor pressure vs percent oil loss for a petroleum-based, hydrocarbon oil (oil 1), a poly- α -olefin synthetic hydrocarbon (oil 2), and a synthetic neopentyl ester oil (oil 3).

IV. CONCLUSIONS

The model presented in this report demonstrates that it is important to understand the molecular weight distribution of an oil before reasonable estimates of the oil vapor pressure as a function of oil loss can be achieved. It is also important to recognize that the vapor pressure of the unused oil is representative of the vapor pressure prior to use but cannot be used to calculate oil loss after the more volatile components have evaporated from the oil.

It is apparent that oils for space mechanisms would suffer less relative loss during lifetime if they were vacuum stripped prior to use. If it can be established that vacuum stripping will have little effect on oil viscosity and performance, then such a processing step should be made a part of the routine practice in the lubrication of spacecraft mechanisms.