Nylon Pore System

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Porous nylon blocks are currently used as lubricant replenishment reservoirs in moving mechanical assemblies within communication satellites and other spacecraft that must have long mission lifetimes. This report presents theoretical and experimental evidence that the reservoir function is not fulfilled under isothermal conditions because of capillary effects. The LaPlace equation is used to indicate that the direction of lubricant flow is from flat surfaces, toward and into the narrow pore system of the reservoir. The Kelvin equation predicts when this process reaches equilibrium. The Washburn equation is used to indicate that the capillary driven flow is much faster than mass transfer through the vapor phase.

Nomenclature

f = frequency
G = free energy
g = gravity, Eq. (2)
h = height above free surface of reservoir, Eq. (2)
ℓ = length of capillary
P_c = pressure difference across a liquid interface, Eq. (1)
p = gas phase pressure
p_0 = vapor pressure of liquid
R = universal gas constant
r_1, r_2 = radii of curvature, Eq. (1)
r_c = radius of capillary, Eq. (2)
r_p = radius of pore, Eq. (7)
r' = radius of mechanical assembly
r_e = radius of curvature at edges
T = absolute temperature
t = time
V = molar volume, V = mol wt/ρ
η = fluid viscosity
γ = surface tension
ρ = liquid density, Eq. (2)

Subscripts

sv = solid/vapor
lv = liquid/vapor
sl = solid/liquid

I. Introduction

IN communication satellites, oil lubrication of bearings is still the most accepted method for providing satisfactory performance of a moving mechanical assembly for long-term, i.e., 5- to 10-yr, mission lifetimes. At present, there is no reliable short-term testing technique to determine whether or not a specific oil/additive system will be efficient over long periods. As a result, current lubricant system designs are usually based on those systems that have previously exhibited satisfactory performance in actual spacecraft operation. Low vapor pressure oils are required because of evaporative loss to the space vacuum environment. In order to replenish lost lubricant, reservoirs consisting of porous nylon blocks (PNB) (called Nylasint by manufacturer)[1] impregnated with oil are placed near the bearings. The total amount of available oil in the spacecraft assembly is thus typically increased by a factor of 2 to 20 times that calculated lost through evaporation. A major assumption, of course, is that the PNB release oil by evaporation at a rate nearly equal to the rate of oil loss from the bearings. By necessity, a controlled replenishment rate is required to prevent an undesirable condition in which the bearings become either dry or flooded.

This investigation addresses itself to the validity of the assumption that the PNB will release oil to nearby surfaces. We will show evidence, both theoretical and experimental, that under isothermal conditions, when the nearby surfaces are lubricated, narrow pore systems such as PNB will, if not completely full, seek to imbibe oil through a capillary effect. Thus, it appears that PNB can, under certain circumstances, impede the long term effectiveness of the lubricant supply systems in spacecraft moving mechanical assemblies.

Quite pertinent to this subject is some recent work by W. Wilkens.[2] While attempting to compare the rate of spreading of the high vacuum pumping fluid bis (2-ethylhexyl) sebacate on glass, TiO_2, and ZnO surfaces, Wilkens found measurable rates, but more importantly, no oil flow when the oil was kept in a PNB. Wilkens made no attempt to interpret this phenomenon. The present paper provides explanation through the correct interpretation of capillarity effects.

II. Background

Lubricant flow within a porous medium may be approached thermodynamically by consideration of the manner in which equilibrium can be reached.[3] When the displacement involves a change in the areas or curvature of the various interfaces, the hydrostatic equilibrium thus reached is called a LaPlace equilibrium. When the displacement tends to reach a chemical potential equilibrium by evaporation and condensation, it is called a Kelvin equilibrium. Both of these processes are important to the transfer of lubricants within a spacecraft.

A. LaPlace Equilibrium

The Young and LaPlace equation

$$P_c = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{1}$$

describes the shape of liquid surfaces. If one visualizes a soap bubble, it is easy to keep in mind that the pressure under the convex side of the meniscus is less than that along the opposite side of the interface. When applied to a cylindrical capillary, the equation becomes $P_c = 2\gamma/r_c$. When the capillary force opposes gravity,

$$P_c = \rho g h = \frac{2\gamma}{r} \tag{2}$$

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In space, the gravity field is negligible, and the pores should completely fill at the expense of any nearby liquid. The effects of a gravity force of very small magnitude opposing the capillary force are not typically taken into consideration. Figure 1 typifies a system in which gravity effects can be analyzed in fundamental terms. The pressure differential P_c across any flat interface, such as indicated by point A, is zero because the radii of curvature are both infinite; thus, $P_1 = P_2$. However, the pressure differential near any edge, such as indicated by point B, is γ/r and is equal to P_1-P_3. The pressure difference P_1-P_3 is a force that can cause the liquid to flow. In this example, flow will occur by withdrawing liquid from the nearby flat surface, thereby reducing the thickness of the liquid film. When referring to liquid flow of a soap film in a wire frame (or in a foam), this liquid transfer, caused by pressure differentials, is called the Plateaux effect. Flow of liquid from the flat regions into the curved boundaries continues until the film either bursts or becomes essentially bimolecular in thickness.

The same type of argument may be applied to the curved interface in the capillary. In this case, however, the curvature cannot decrease as it is equal to the radius of the capillary. Thus, the liquid rises keeping a constant curvature. It stops rising only if there is an opposing force such as gravity; the extent to which it rises is again given by Eq. (2).

Schwartz and Minor[4] have shown a particularly simple and essentially thermodynamic approach to the calculation of the direction of flow caused by LaPlace instability. Considering the free energy differential δF of a constant volume of liquid in terms of the interfacial tensions and areas of the solid/vapor, liquid/vapor, and solid/liquid, we have

$$\delta F = \gamma_{sv}\delta A_{sv} + \gamma_{lv}\delta A_{lv} + \gamma_{sl}\delta A_{sl} \tag{3}$$

This expression can be simplified by using the Young-Dupres relation in terms of the contact angle θ at the three-phase boundary

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \tag{4}$$

and recognizing that, for any change in areas $\delta A_{sv} = -\delta A_{sl}$, Eq. (3) becomes

$$\delta F = \gamma_{lv}\left[\delta A_{lv} - \cos\theta\delta A_{sl}\right] \tag{5}$$

A process can occur spontaneously when the free energy change is negative or, as below, when the time derivative of the free energy is negative:

$$\frac{\mathrm{d}F}{\mathrm{d}t} = \gamma_{lv}\left[\frac{\mathrm{d}}{\mathrm{d}t}A_{lv} - \cos\theta\frac{\mathrm{d}}{\mathrm{d}t}A_{sl}\right] \tag{6}$$

For the example shown in Fig. 1, A_{lv} does not change as flow occurs; therefore, the first term is zero. As long as the contact angle is less than 90 deg, $\cos\theta$ will be positive, and the condition for flow is that A_{sl} increase. The geometric arguments, which are not presented here, show that δA_{sl} will be positive whenever the dimension z (as defined by Fig. 1) is greater than $2r$. The useful rule derived from this is that whenever the diameter of a capillary is smaller than the dimension of the free space outside of the capillary, the direction of flow will be into the capillary.

In a satellite spinning at frequency, the centripetal acceleration term $2\pi^2 f^2 r'$ replaces the gravitational term of Eq. (2). As an example, the force retarding inward fluid flow 10 cm away from the center of a satellite spinning at 60 rpm is fifty times smaller than earth's gravitational field. For a typical lubricant oil with a surface tension of 30 dynes/cm^2 and typical reservoir pore diameter of 3μm,[5] Eq. (2) implies a possible rise of 2 m (6.6ft) in the earth's gravitational field and 100 m (330 ft) in the satellite. In effect, this retarding force is negligible, and the pores should fill completely.

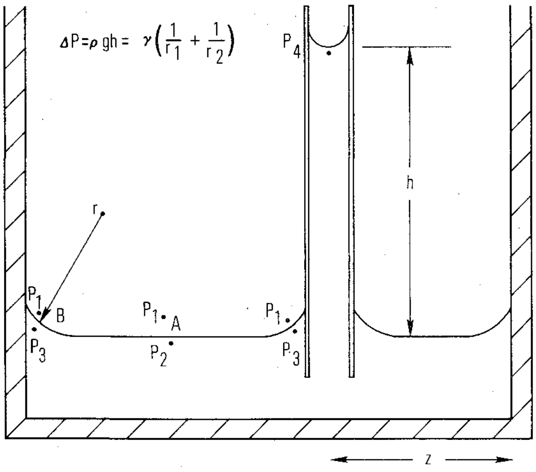

Fig. 1 Explanation of capillary effects in terms of the Young-LaPlace equation.

During the establishment of LaPlace equilibrium, edges, corners, and crevices will compete with the pores for the available oil, at least until their radii of curvature are equal to one half of the radius of curvature within the pore system. For each centimeter of inside edge, there will be 1/4 $(4r^2 - \pi r^2)$ cm^3 or 1.2x10^{-9} cm^3 (1.1 x10^{-9}g) of oil when these are in equilibrium with e 3μm pores (where r is the radius of curvature at the edges).

Kelvin Equilibrium

Processes that do not involve any mechanical aspects but are centered instead about the chemical potential equilibrium within phases are treated here in terms of the Kelvin equation. One important prediction from setting up this equation is that, when equilibrium occurs through the vapor phase, the mechanism is no longer important. This is, of course, only an approximation, albeit a close one, because condensation within porous systems is not reversible (i.e., an entropy producing process). This irreversibility is not important in a satellite system, which is in effect an open system as it is continuously being heated and cooled and is evaporating to a vacuum.

Over a long time period this small irreversibility need not be considered, but only that the pores fill as long as there exists bulk liquid within the system. The competition is among the fraction of molecules in the vapor phase, the fraction as a liquid with a nearly flat interface, and the fraction within the pore system. Since the final equilibrium will be (at least approximately) the same, it could be assumed an ideal gas phase, and only how much liquid can be withdrawn from the flat areas into the edges and pores need be considered. In the case of soap solutions, the natural termination point (unless the film breaks) is a bilayer on the order of 5.0-10.0 nm thick. For an oil/additive on a metal, the amount should not differ appreciably. The exact amount could be calculated if the adsorption isotherm were measured, as this is a graphical or analytical relation between the free energy with reference to the gas phase $G = RTln\ p/p_o$ as a function of the amount (or the thickness) adsorbed. This free energy is equal to that of the liquid in the pores, as given by the Kelvin equation

$$RT\ln p/p_o = 2\gamma V/r_p \tag{7}$$

Although the isotherm has not been studied, reasonable estimates can be made from the literature on similar systems. The maximum amount adsorbed (as p approaches p_o) is typically between one and five monolayers, although Wilkens[2] found less than 0.1 monolayer. This implies that, for more oil to be present on the surface, the pressure would have to be exactly p_0, the saturation pressure at that temperature. Bulk oil could then be present in puddles anywhere in the system.

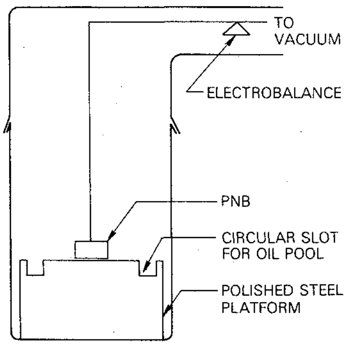

Fig.2 Experimental assembly.

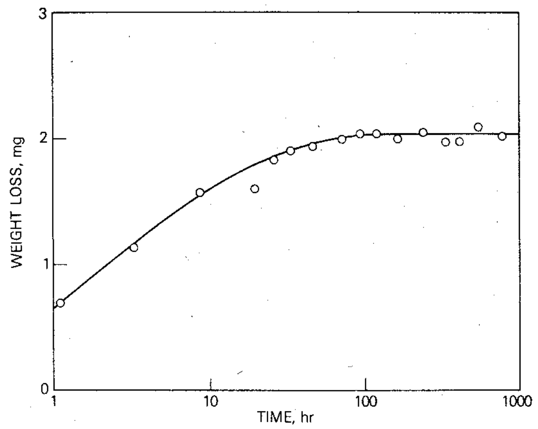

Fig.3 Weight loss of PNB filled with 127 mg of oil.

The previous considerations of the direction of flow to achieve thermodynamic equilibrium were based only on the first two laws of thermodynamics and a knowledge of the typical shapes of adsorption isotherms. The effects of temperature gradients are not considered at this time. In order to verify these findings, the direction of flow in three cases has been studied experimentally under isothermal conditions.

III. Experimental Procedure and Results

Type 64 HV Nylasint was obtained from the Polymer Corp.[1] Reservoir specimens prepared from the material were dry machined to a size slightly larger than the dimensions required for the experiments. Several techniques, including the utilization of various speeds of a microtome device, were then tried to open the surface pores, since normal machining is reputed to close them. Some microtome speeds provided acceptable surfaces; however, it was found that the simplest, most effective technique for final machining was the removal of the last few tenths of a millimeter with a razor blade. The adequacy of the razor blade technique to open the pores was verified by microscopic observation. The verification porcedure involved absorbing an oil (which contained a dye) into the reservoir after final machining. The amount and distribution of oil that was taken up by the pores could then be checked by microtoming the piece $20\mu m$ at a time.

The weight gain and loss were measured with a Cahn RH vacuum electrobalance that was equipped with a lowering and raising mechanism. The pressure was $\sim 5\times10^{-6}$ Torr except for periods during the experiment when the apparatus was backfilled with nitrogen. Difficulties encountered with electrostatic charging were remedied with commercial polonium sources.

The reservoir liquid was a high boiling point mineral oil, Apiezon C. The observed effective oil evaporation rate for this apparatus was 5×10^{-11} g-cm^{2}-sec^{-1}.

The apparatus is shown in Fig. 2. The PNB is placed concentrically on the steel table during the equilibration period and can be lifted electronically during the time required to make measurements.

A. Experiment 1

This phase of investigation was designed to determine whether or not the empty PNB takes up oil when the surface on which it rests is lubricated with a film in the range of 1 to 5 μm thick. This range is typical of lubricant film thicknesses in communication satellites. The slot, acting as a reservoir, was filled to 75% of its capacity with oil. In this experiment, the electrobalance could not rise far enough to break free of the oil meniscus, so the apparatus was backfilled with nitrogen to a pressure slightly greater than atmospheric pressure, and the seal was moved slightly whenever a data point was taken. Because of this procedure, kinetic data could not be taken. The filling did proceed smoothly until the PNB was completely filled. During this experiment, there were no indications that the PNB lost oil to the surroundings. The PNB plus oil were heavy enough (450 mg) that evaporation losses were essentially insignificant.

B. Experiment 2

In this case, the PNB reservoir was completely full, and the steel surfaces were initially clean. After the sides of the Nylasint were cleaned by wiping with a steel spatula, the weight of the oil in the 342.4 mg Nylasint reservoir was 126.7 mg.

As shown in Fig. 3, equilibrium essentially is reached after 30 hr. The scatter is due primarily to the inability to reproduce the breaking of the oil bridge that formed between the steel and the Nylasint . A considerable amount of the 2 mg of oil that was lost from the reservoir remained in the spot on which the Nylasint rested. Thus, while the weight loss was $2mg/126.7mg=0.0157=1.57\%$, this amount was not available to nearby bearing surfaces but remained in the meniscus near the edge formed by the Nylasint and the steel surface.

At the completion of the experiment, the amount of oil recovered from the 1 cm diam spot on the steel surface where the Nylasint rested was 1.3 ± 0.5mg. This implies that, over the range of 30 to 1000 hr, about 0.6% of the oil in the Nylasint escaped. We then concluded that, within the configuration of our experimental assembly, equilibrium had been reached.

C. Experiment 3

If PNB reservoirs functioned as intended, loss of lubricant would result after a given period of exposure. This experiment was designed to determine the direction of oil flow from and to partially filled PNB reservoirs. Experiment 1 had already shown that, when the nearby surfaces are lubricated, the flow is toward the empty PNB. This experiment was carried out with the PNB one quarter full and the nearby surfaces unlubricated.

The sample was prepared by completely filling a 345.3 mg Nylasint reservoir with 117.6 mg of oil. As a means of reducing the oil content with minimum contamination, the oil-filled PNB was rinsed for 5 min with hexane. After this treatment, 29.2 mg of oil (24.8% of the initial amount) remained. Because of the hexane treatment, no oil remained on the sides of the Nylasint; therefore, the uncertainties in the weighing were solely electronic, about ±0.02 mg. Within this uncertainty, *no oil was lost* to the system over a period of 300 hr.

IV. Conclusions

Although there are several statements in the literature to the effect that PNB are placed in satellites for the express purpose of achieving a slow release of lubricant, it has been shown herein that, under isothermal conditions, neither theoretical nor laboratory evidence substantiate this premise. The authors believe that the theoretical and experimental sections of this paper prove that the general assumption of PNB function is not warranted. Indeed, under isothermal conditions, the reverse process is true, i.e., any lubricant lost from the

PNB through evaporation will be replaced by lubricant from nearby surfaces. Thus, if the PNB is in intimate contact with a lubricated surface, there should be an uptake rather than a release of lubricant.

Thus far, the vapor phase has not been mentioned as a means of reaching equilibrium. One reason is that the rate of fluid flow is usually greater than flow in the extremely dilute vapor phase. A numerical example will be helpful: consider a 3.5 μm capillary 1 cm long. At 27°C, the rate of evaporation R_e of a typical high vacuum oil is 8×10^{-10} g-cm^2 -sec^{-1}. At this rate, evaporation would take $\rho/R_e = 0.874/8\times10^{-10}$ sec $= 1.1\times10^9$ sec. If this capillary is in contact with a reservoir of oil, the Washburn equation[6]

$$\frac{d\ell}{dt}=\frac{r\gamma}{4\eta\ell} \tag{8}$$

gives the rate at which fluid enters if the driving force is capillary pressure (the Young and LaPlace equation) and the retarding force is viscosity (the Poiseuille equation). The time required to fill the capillary completely by this mechanism is

$$t=\frac{2\ell^2\eta}{\gamma r}=\frac{2\times 1\ \mathrm{cm}^2\times 1.39\ \mathrm{poises}}{30\ \mathrm{dynes/cm}\ \times 3.5\times10^{-4}\mathrm{cm}}=264\ \mathrm{sec}$$

a factor of 4×10^6 faster than the vapor phase.

Another reason for considering the vapor phase as secondary is that the final equilibrium is not dependent on the mechanism by which it is reached. This consideration is important if we attempt to determine whether PNB would be useful if they were not in direct contact with any fluid but placed such that they would contact the system only through the vapor phase. As an example, the PNB would be rested on a teflon coating, which would essentially prevent oil from creeping into the PNB. Although this type of configuration would not change the final equilibrium, it would decrease the rate by which fluid could be imbibed from an adjacent member, e.g., a bearing.

Alternative methods of replenishing lubricant lost to space have been proposed but not actively pursued, probably because it was assumed that PNB were adequate. The results of this study, however, show clearly that PNB reservoirs in lubricated spacecraft mechanical assemblies will be nonfunctional under isothermal conditions. Further research is required to determine the "effectiveness" of PNB under nonisothermal conditions. Until such results are available, the use and the effectiveness of PNB reservoirs in spacecraft hardware are at best doubtful.

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