Oxygen Plasma Effects on Several Liquid Droplet Radiator Fluids

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The Liquid Droplet Radiator is one of several radiator systems currently under investigation by NASA Lewis Research Center. It involves the direct exposure of the radiatior working fluid to the space environment. An area of concern is the potential harmful effects of the low-Earth-orbit atomic oxygen environment on the radiator working fluid. To address this issue, seven candidate fluids were exposed to an oxygen plasma environment in a laboratory plasma asher. The seven fluids studied included three siloxanes and four perfluoropolyethers, and were chosen on the basis of chemical family, physical properties, and likelihood of resistance to oxidation. The fluids were characterized by noting changes in visual appearance, physical state, mass, and infrared spectra. Of the fluids tested, the perfluoropolyethers were the least affected by the oxygen plasma. The only effect noted was a change in mass, which was most likely due to an oxygen-catalyzed depolymerization of the fluid molecule.

Introduction

THE Advanced Radiator Program at the NASA Lewis Research Center is currently investigating the Liquid Droplet Radiator (LDR) for potential use by spacecraft power systems. This concept uses a radiator fluid (in the form of small drops ejected from an orifice plate) directly exposed to space as its heat-transfer medium. The LDR has several potential advantages; among these are a large radiator surface area per unit mass, invulnerability to puncture by small particles, and ease of stowage and deployment.[1] In order for such a system to be feasible, several problems must be resolved. These include droplet loss, spacecraft contamination, and fluid degradation in the space environment.

Any fluid proposed for use in the LDR must meet several requirements. Among these are 1) high emissivity for optimum radiator cooling, 2) low solar absorptivity, 3) a surface tension high enough to induce rapid droplet information but low enough to inhibit wetting of the orifice and collector surfaces, 4) low viscosity to minimize pump power requirements, and 5) low vapor pressure to minimize fluid losses and possible spacecraft contamination through evaporation.

In addition to the above requirements, any proposed fluid must also survive the space environment to which it is exposed. At low-Earth-orbit (LEO) altitudes (generally 180–650 km), the principal chemical specie is neutral atomic oxygen,[2] which is highly reactive. At proposed space station orbital altitudes, atomic oxygen impacts spacecraft surfaces with an energy of about 4.25 eV. Since the radiator fluid in the LDR system would be directly exposed to the LEO environment, it must be able to withstand successfully this atomic oxygen exposure. The present paper is concerned with the effect of the low-Earth-orbit atomic oxygen environment on several candidate radiator fluids.

Seven fluids were chosen for this study. They were selected on the basis of availability, fluid family (e.g., silicone-based oil and perfluorinated, carbon-based oil), viscosity, and vapor pressure. The fluids selected included 1) pentaphenyltrimethyltrisiloxane (Dow Corning 705 Diffusion Pump Fluid), 2) polymethylphenylsiloxane (PMPS, an experimental fluid made by Dow Corning), 3) polydimethylsiloxane (PDMS, another experimental fluid made by Dow Corning), 4) Fomblin Z25, a perfluoropolyether made by Montedison, 5) Krytox 143AB, 6) Krytox 1502, and 7) Krytox 16256. Fluids 5–7 are from the Krytox line of perfluoropolyether oils made by DuPont. These candidate fluids cover a wide range of values for viscosity and vapor pressure, as shown in Table 1.

Experimental Procedure

Fluid samples were exposed to the simulated low-Earth-orbit environment by placing a small quantity (1–7 g) of each fluid in separate 10 ml beakers and then placing the beakers inside the reaction chamber of a Structure Probe, Inc., Plasma-Prep II plasma asher. The exposed fluid surface area was 3.8 cm^2. This device creates a plasma environment by passing a carrier gas (in this case, ambient air) over the samples and then dissociating and ionizing the gas with 100 W of continuous wave rf power at 13.56 MHz. (Electromagnetic radiation of this energy is insufficient by itself to dissociate molecules in the liquid state.) The operating pressure is about 50 μ. Although it is difficult to calculate a direct relationship between exposure time in the asher under these conditions and lifetime in LEO, use of the asher does allow gross determination of the likelihood of survivability of a particular material in LEO.

Several different kinds of measurements were made on the fluid samples as a function of time of exposure to the plasma. All fluids were examined by infrared spectroscopy, which is highly sensitive to chemical structure, before and at regular intervals during exposure to the plasma. Where such spectra

Table 1 Properties of candidate liquid-droplet radiator fluids

Fluid	Vapor pressure at 20°C, Torr	Molecular weight, amu	Viscosity at 20°C, cS
DC 705	3×10^{-10}	546	175
PMPS	6×10^{-7} (120°C)	1 300	148
PDMS	3×10^{-8} (120°C)	2 700	25.4
Fomblin Z25	3×10^{-12}	9 500	355
Krytox 143AB	5×10^{-6}	3 700	230
Krytox 1502	5×10^{-7}	1 465	17
Krytox 16256	5×10^{-14}	11 000	2 560

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were not featureless, uv-visible spectra were obtained as well. In addition to the spectroscopic measurements, changes in mass, physical state, and visual appearance were noted.

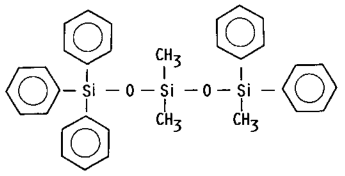
Results and Discussion

For the purpose of discussion, the fluids will be divided into three categories based on their chemical composition. The Dow Corning (DC) 705 will be discussed individually; the PMPS and PDMS fluids will be discussed together; and the Fomblin Z25 and three Krytox fluids will also be discussed as a group.

Dow Corning 705

Of the seven fluids tested, the asher plasma environment had its greatest effect on the DC 705. The fluid, which was initially a clear, colorless, odorless liquid of moderate viscosity, rapidly (in less than 10 h of exposure) became a clear, lavender-colored, high-viscosity liquid with a rather sweet odor. Changes in color and viscosity became apparent after only a few hours of exposure. After 66 h of exposure the fluid had almost solidified. An approximately 2 g sample showed an increase in mass of about 3.5% during this time.

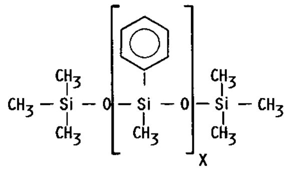
A comparison of i.r. spectra taken prior to exposure and then after 43.5 h of exposure indicated several changes (Fig. 1). The presence of a new, broad peak centered at about 3400 cm^{-1} is a strong indication of hydroxy functional groups. The exact nature of these functional groups was not determined. Any water or low-molecular-weight alcohol or acid would have evaporated off under vacuum. (No attempt was made to collect and analyze any volatile products.) One likely explanation is that these new functional groups are attached to a much larger molecule, possibly the parent compound itself. The small increase in mass supports this conclusion. The chemical structure of Dow Corning 705 follows.



The broad, relatively weak peak centered at about 1700 cm^{-1} suggests the presence of carbonyl groups. This would be consistent with the presence of esters, ketones, or carboxylic acids. In addition, the sweet odor noted above also indicates the possible presence of ester groups. Regardless of the exact structure, it is clear that the DC 705 undergoes significant degradation, including significant oxidation, when exposed to the plasma environment.

PMPS and PDMS

The plasma environment also had significant effects on the fluids PMPS and PDMS. After 43.5 h of exposure, each fluid had developed a film of solid material both on the walls of the beaker and across the top of the fluid itself. A very small gain in mass (less than 0.3%) was noted for each fluid over this exposure time. Both fluids remained clear and colorless. Spectroscopic data yielded little information. I.R. spectra taken before and after exposure for both the PMPS and PDMS fluids showed no differences. UV spectra obtained on the PMPS also showed no changes. The solidified material most likely results from an oxygen-catalyzed polymerization of these materials, perhaps by a cross-linking between substituents on individual molecules. The chemical structures of PMPS and PDMS follow.

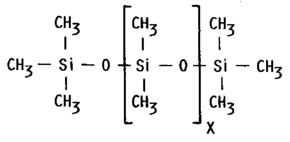


PMPS

X = 7-10

PDMS

X = 33-41



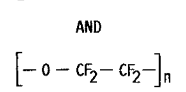
Fomblin Z25 and the Krytoxes

The Fomblin Z25 and the three Krytox fluids showed the least detrimental effects from exposure in the plasma asher. No changes were noted in clarity or color. No changes of any kind were noted in the i.r. spectra of these fluids, even after many (160–380) hours of exposure. The only effect of the plasma noted was a slow, linear loss in mass for each fluid. Figure 2 shows the mass loss vs time for two of the fluids, Fomblin Z25 and Krytox 143AB. The calculated mass-loss fluxes for Fomblin Z25 and the Krytoxes are given in Table 2.

An attempt was made to determine the exact cause of the observed mass losses. Under the conditions in the plasma asher, the fluids are exposed to a vacuum of approximately 50 μ and a temperature of about 50°C, in addition to the plasma. It was thought that perhaps either the vacuum or the vacuum in conjunction with the elevated temperature might be responsible for the observed mass loss. To this end, one sample each of Fomblin Z25 and Krytox 143AB were exposed to vacuum conditions at both room temperature and 50°C.

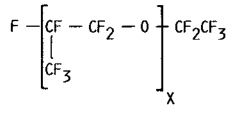
No mass losses were observed for either fluid when exposed to these special conditions. (This is not surprising since these are vacuum-pump oils and are specifically designed to withstand this kind of environment.) Clearly, the plasma environment causes the mass loss. The oxygen may react with the fluids, but only to form one or more volatile products. The chemical structures for Fomblin Z25 and the Krytoxes follow.

FOMBLIN Z25



(RANDOM MIXTURE)

KRYTOX



X = 7-9 FOR KRYTOX 1502
= 21-23 FOR KRYTOX 143AB
= 64-66 FOR KRYTOX 16256

The most probable explanation for these observed mass losses is an oxygen-catalyzed depolymerization of the parent molecule. The ether α-carbon at the ends of the molecules is the most likely point of attack. The resulting fragments are then evaporated away, leaving no change in the remaining fluid.

Table 2 Calculated mass loss fluxes of Fomblin and Krytox fluids

Fluid	Mass-loss flux gm × cm^{-2} h^{-1}
Fomblin Z25	1.38×10^{-5}
Krytox 143AB	0.977×10^{-5}
Krytox 1502	2.84×10^{-3}
Krytox 16256	2.79×10^{-5}

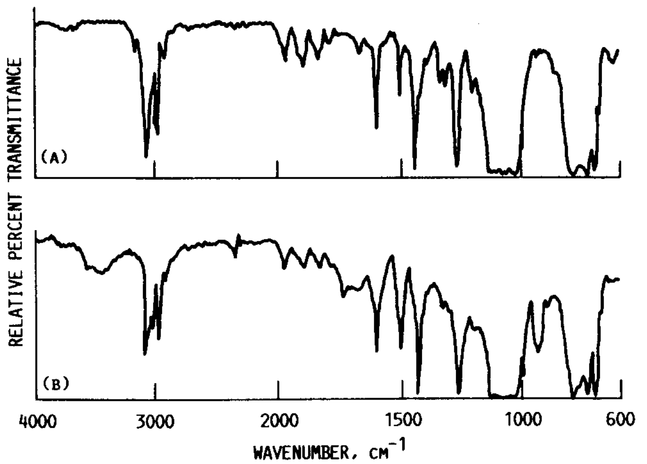


Fig. 1 **Infrared spectra of Dow Corning 705 diffusion pump fluid: a) before exposure to the asher plasma and b) after 43.5 h of exposure to the asher plasma.**

Recommendations

The results presented herein indicate that, as a general class, the perfluoroethers are acceptable as a atomic-oxygen-durable candidates for use in the LDR. By this, it is meant that these fluids showed no physical or chemical changes upon exposure to an atomic oxygen environment. In most instances, the measured mass-loss fluxes were quite low. If the proper combination of vapor pressure and viscosity could be found in a perfluoroether (two of the fluids tested here, Krytox 143AB or Fomblin Z25, might be satisfactory), the mass-loss problem could be overcome by maintaining a sufficiently large reservoir onboard the spacecraft to replenish the circulating fluid as necessary. Additional studies must be made to determine if these fluids have the other requisite properties (emissivity, etc.) described earlier.

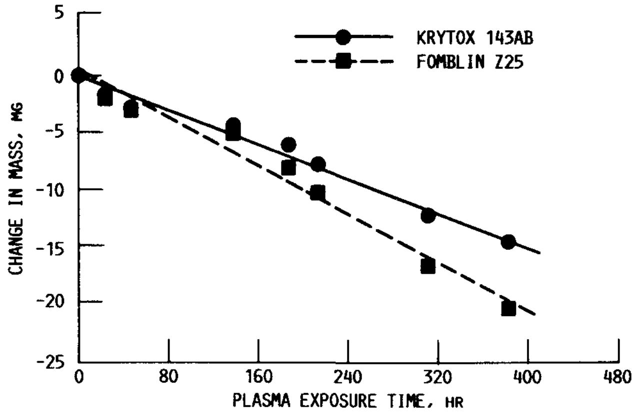


Fig. 2 **Change in mass vs plasma exposure time for Fomblin Z25 and Krytox 143AB showing a linear mass-loss rate for each fluid.**

References

[1]Taussig, R.T. and Mattick, A.T., "Droplet Radiator Systems for Spacecraft Thermal Control," *Journal of Spacecraft and Rockets,* Vol. 23, Jan.-Feb. 1986, pp. 10-17.

[2]*U.S. Standard Atmosphere, 1976,* U.S. Government Printing Office, Washington, DC, 1976, p. 30.

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The scope of the chapters and the focus of the papers presented in this volume were developed in two workshops held in Orlando, Fla., during January 1982. In putting together the individual papers and chapters, one of the first obligations was to establish which concepts are of interest for the 1995-2000 time frame. This naturally leads to analyses of systems and devices. This open and effective advocacy is part of the recently revitalized national forum to clarify the issues and approaches which relate to major advances in space propulsion.

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