Spacecraft Application of Subliming Materials

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Several materials that have considerable mechanical strength at room temperatures and pressures will sublime rapidly in the hard vacuum of space. Three such materials (camphor, naphthalene, and biphenyl) have been studied in considerable detail both in the laboratory and on orbiting satellites. A principle use of these materials is to actuate electrical switches with predetermined time delays after the spacecraft is in orbit. They can also serve as temporary mechanical structures, which sublime away after the spacecraft is launched. A third use is the encapsulation of delicate instruments during the severe vibration and acceleration environment encountered during launch. Once in orbit, the encapsulation material gently sublimes away, leaving the delicate mechanism free to work in the vibrationless, zero-*g* environment of space Properties of the preceding three materials plus benzoic acid are given, and various means of implementing these applications are discussed.

Introduction

MODERN spacecraft are required to perform increasingly complex and diverse operations. This paper describes some uses of subliming material in several spacecraft components. Camphor, naphthalene, and biphenyl have been used extensively on orbiting satellites. Benzoic acid has been evaluated in the laboratory for applications requiring a very slow sublimation rate. Rapidly subliming materials have been used successfully for the following purposes: 1) time-delay switches, 2) temporary structures or seals, which disappear after launch, 3) encapsulation of delicate devices and operations, and 4) as a source of propulsion impulse for gentle control operations.

Characteristics of Subliming Materials

Sublimation of a material occurs at temperatures below the "triple point" on its phase diagram. The latter defines the coexistence in equilibrium of its three phases. For example, the triple point for camphor occurs at 180.1°C and 385.8 mm Hg.[1] The heat of sublimation is equal to the numerical sum of the heats of fusion and vaporization at a given temperature. The relationship between vapor pressure and maximum sublimation rate G_{max}(g/sec-cm^2) from a solid or liquid surface may be derived from kinetic theory, i.e., the Hertz-Knudsen-Langmuir equation[2]:

$$G_{max} = 0.0583\,P(M/T)^{1/2} \quad (1)$$

where P is theoretical vapor pressure (mm Hg), M is molecular weight, and T is temperature (°K). In the derivation of Eq. (1) it is assumed that no molecules of the vapor return to the solid surface and that the pressure of the vapor just above the surface is exactly equal to the pressure of the saturated vapor at that temperature. The use of Eq. (1) requires a knowledge of $P = P(T)$. For a material with a latent heat of sublimation H_s that is constant over the required temperature range, the Clausius-Clapeyron equation[3] can be integrated to the simple form

$$\log_{10}P = -(KH_s/T) + B(= -A/T) + B \quad (2)$$

Values for constants A and B are shown in Table 1 for camphor, naphthalene, biphenyl, and benzoic acid.[4]

Experimental sublimation rates are usually less than those given by Eq. (1). Some of the factors contributing to this reduction are summarized by Paul.[5] Various in-house tests indicate that the method of manufacture (i.e., molding pressure, particle size, and sample density) greatly affects sublimation rates; samples prepared by casting always sublimed faster than the pressed materials. For example, cast naphthalene (at 255°K) sublimed more than 15 times faster than pressed naphthalene at the same temperature. In Table 1, theoretical values of G_{max} are compared with those measured in vacuum at the Applied Physics Laboratory. Samples were prepared by compressing powders into solid 3-in.-diam disks. The disks were thermally isolated and suspended in a large vacuum chamber. The chamber pressure was held below 10^{-5} mm Hg, and its walls were cooled to <148°K, so that all of the sublimed material "stuck" to the cold surfaces. The sample temperature was held constant (±1.5°K) during each test.

The column headed "In orbit" under G_{max} in Table 1 shows results of measurements of the sublimation of 2-in.-long by 0.5-in.-diam pressed specimens in the Army-NASA-Navy-Air Force (ANNA) satellite. Specimen length was telemetered using a measurement system that was limited to nine discrete steps.

Ultimate strengths of these materials are also given in Table 1. Samples for these measurements were formed at 4000 psig, except for camphor, which was formed at 2000 psig. Tests were also conducted to determine the creep strength of biphenyl pressed into cylindrical form; there was no detectable creep after 13 days at 58.2 psig at room temperature. When formed at high pressure, these materials can be turned on a lathe or milled with considerable ease and precision. Many of the sublimation devices (described later) have been subjected to vibration conditions that exceeded those normally expected during launch; no failure occurred.

Optical properties of subliming materials are important insofar as they affect the equilibrium temperature of spacecraft components in orbit, particularly when a large area of the subliming material is on an exposed surface. Of particular significance is the absorptivity to outer space sunlight α_s and the infrared emissivity ϵ_{ir} for temperatures in the range from 200° to 311°K. Camphor, naphthalene, biphenyl, and benzoic acid all have a white appearance, indicating a low α_s, as reflected by the measured values for absorptivity given in Table 1. Their ϵ_{ir}'s are near unity (Table 1), as one would expect for these organic compounds. The addition of a coloring agent (carbon black or an organic dye) can drastically in-

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Table 1 Properties of four subliming materials

Material	H_s, kcal/mole	Vapor pressure[4] T range, °K	Vapor pressure[4] A	Vapor pressure[4] B	G_{max} (g/sec-cm²)[a] At 255°K Theo.[b]	At 255°K Exp.[c]	At 297°K Theo.[b]	At 297°K Exp.[c]	In orbit[d]	Ultimate strength,[e] psi σ_t	σ_c	σ_s	Optical α_s	ϵ_{ir}
Camphor	. . .	273–453	2797	8.80	3.0⁻⁴	7.1⁻⁵	1.0⁻²	1.5⁻⁴	2.73⁻⁴	. . .	178	162	0.37	>0.96
Naphthalene	14.23	273–353	3729	11.45	2.8⁻⁵	8.9⁻⁸	3.0⁻³	1.0⁻⁵	4.95⁻⁵	150	1080	175	0.09	>0.90
Biphenyl	17.37	314–367	3799	10.38	. . .	1.5⁻⁹	1.6⁻⁴	3.4⁻⁶	1.32⁻⁵	300	825	180	0.20	>0.95
Benzoic acid	. . .	333–383	3333	9.00	. . .	1.5⁻¹¹	. . .	1.8⁻⁸	. . .	100	≥700	210	0.23	>0.89

[a] Exponents in the G_{max} columns indicate negative powers of 10, i.e., required decimal shift to left.
[b] Theoretical values of G_{max} are computed from Eq. (1), using P from Eq. (2).
[c] Measured values of 3-in.-diam pressed disks in vacuum ($\leq 10^{-5}$ mm Hg).
[d] Measured sublimation rate for 0.5-in.-diam by 2-in.-long pressed cylinders in ANNA satellites. Sublimation temperature is ~300°K.
[e] Measured for $\frac{5}{8}$-in.-diam cylinders pressed at 4000 psi (except camphor, pressed at 2000 psi). Subscripts t, c, and s designate tension, compression, and shear, respectively.

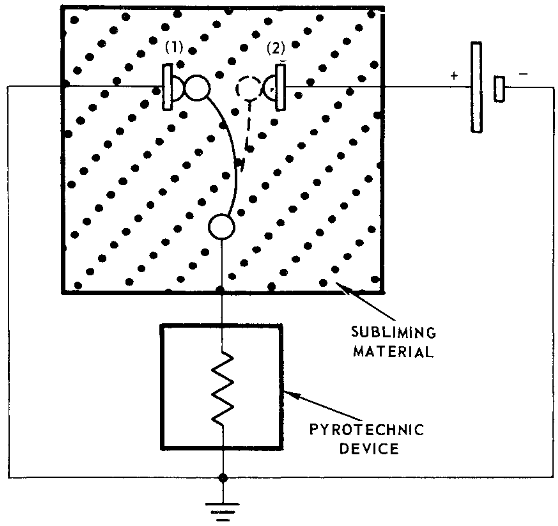

Fig. 1 A sublimation-actuated time-delay switch.

crease α_s without appreciably affecting ϵ_{ir} or $G_{max}(T)$; this technique can be used to raise the equilibrium temperature of exposed subliming material, thereby increasing the rate of sublimation.

These are chemically stable organic compounds. No interaction with aluminum or with other commonly used metals is known to take place at normal spacecraft temperatures. Although they have pungent odors, especially at high temperatures, they are not known to be toxic when inhaled in small quantities.

Time-Delay Switches

One of the most useful applications of subliming materials is in electrical switching contacts, which operate after the satellite is in orbit, e.g., to initiate payload separation or to separate multiple payloads from each other. Figure 1 illustrates a switch that was used successfully to separate the payload from the X-248 rocket on several missions. Two single-pole, double-throw switches were mounted near the forward end of the rocket. The subliming material (biphenyl) holds a leaf-spring contact at position 1 during the launch operation, so that the pyrotechnic bridge wires are electrically shorted to prevent inadvertent detonation by an rf or other electrical signal. If no heat were applied, this switch would actuate approximately three hours after lift-off. After the solid propellant burns there is a rapid increase in the skin temperature of the rocket; within 10 min it exceeds the melting point of the biphenyl, which then sublimes rapidly, causing contact 1 to open and contact 2 to close and "fire" the pyrotechnic device. This initiates the deployment of a yo-yo device, which removes most of the angular kinetic energy of the spin-stabilized X-248 rocket. The second switch, separated from the rocket case by a thermally insulated sheet of glass-fiber-encapsulated epoxy resin, operates approximately 5 min later to initiate the separation of the satellite from the rocket. The total time delay of 15 min is desirable so that most of the residual rocket impulse is dissipated before separation of the payload.

Another type of switch (Fig. 2) employs a spring acting against a subliming cylinder to move a central disk contact through a segmented outer cylinder (i.e., a series of contacts), thus providing a number of sequential switching operations. Actuation speed is controlled by heating the fixed metallic grid at the top. Sufficient power to cause complete sublimation can readily be stored in a small silver-zinc cell. After several successful laboratory tests, this switch was used for two multiple-payload launchings as a backup for the rocket's programer, but since the latter worked in both

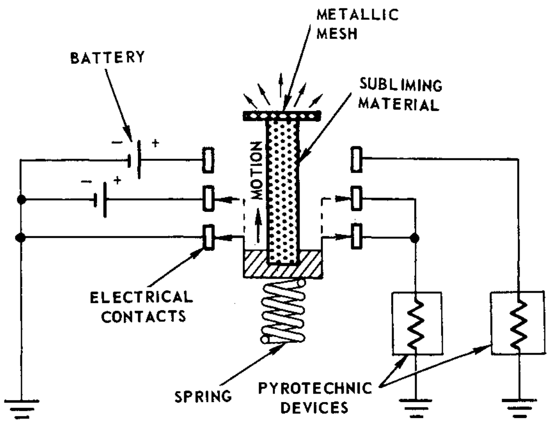

Fig. 2 Sublimation timer.

cases, the only flight result was that the switches did not operate prematurely. This type of switch, employing biphenyl without heating, was successfully used to impose a 12-hr time delay on the activation of a high voltage experiment in a satellite. This high-voltage experiment was timed to avoid the altitude region where air is easily ionized, ~120,000 ft.

On one payload, a five-day timer was used successfully to prevent excess battery charging, which might have occurred early in the satellite's life before proper attitude control was established. This switch had the configuration shown in Fig. 2, except that a small diameter orifice was used. If a series of orifices were used, delay times of years could be achieved, e.g., to turn off a satellite after it accomplished its mission.

These subliming time-delay switches are simple, lightweight, and reliable. A total of 13 switches have been used in conjunction with six orbiting satellites without even a partial switch failure.

Temporary Mechanical Structures

The cylindrical joint shown in Fig. 3 is supported in shear according to

$$F = \pi d h \sigma_{su}$$

where σ_{su} is the ultimate shear strength of the subliming material. Using biphenyl (σ_{su} = 180 psi) with d = 10 in. and h = 2 in., one can obtain a holding force of more than 1000 lb with just a few ounces of material. This type of structure has been used successfully on six satellites. In each case the joint rigidly held a comparatively massive piece of equipment during launch and released it after the vibrationless, zero-g orbital condition was achieved.

Another mechanical structure is shown in Fig. 4. In this case a great mechanical strength advantage is achieved by

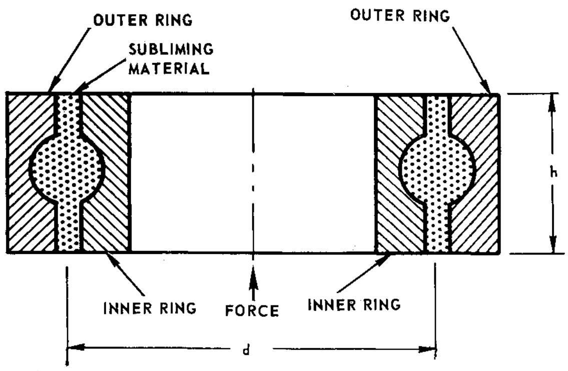

Fig. 3 A mechanical structure using subliming material.

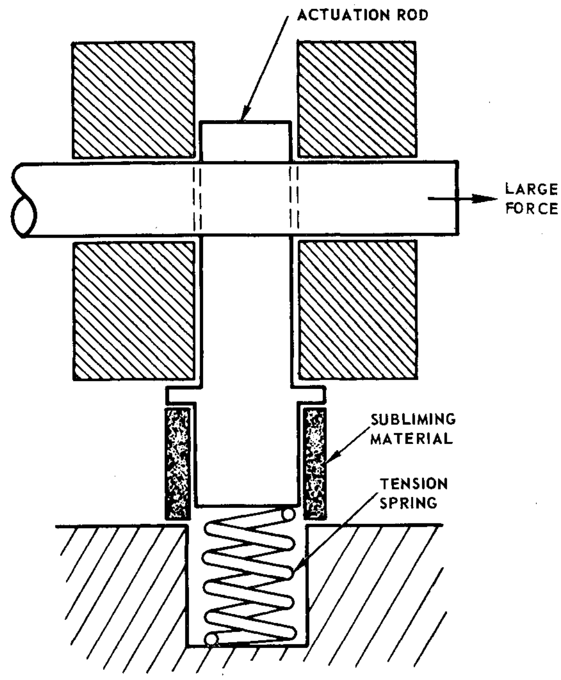

Fig. 4 Sublimation-actuated mechanical latch.

using a high-strength pin to resist a strong force, so that the subliming material is required only to resist the thrust of the spring. This type of device has been designed into a clamp release for separating a payload from the launch vehicle. It does have the disadvantage that it requires a delayed separation (may exceed 2 hr), but this may not be a serious drawback for many missions.

Temporary Encapsulation or Sealing Applications

The permanent encapsulation in plastic of fragile devices is well known, but a subliming material can also be used profitably as a temporary constraint of sensitive elements during launch, followed by gentle sublimation to allow the device to perform its intended function. An example is the encapsulation of an extremely delicate damping spring on a gravity-gradient stabilized satellite.[6] One such spring consisted of 142 turns of 7-mil-diam copper wire. The mean diameter of this helical spring was 6 in., and its spring constant was only 1.5×10^{-6} lb/ft. The biphenyl slowly sublimed, releasing one coil at a time over a period that was as short as 12 hr for one satellite and as long as three days for another. This technique was successful on each of four satellites on which it was used.

Temporary Pressure Seal

In one application it was desired to study radiation damage characteristics of a transistor filled with dry nitrogen as compared with the same transistor under vacuum conditions. Since this transistor was not available as an evacuated, hermetically sealed unit, a small hole was drilled in the case, and then it was sealed with biphenyl. The subliming material prevented contamination of the transistor during ground operations with the satellite, but it sublimed in orbit. The experiment showed that the nitrogen-sealed transistor was considerably more susceptible to radiation damage than the transistor that operated in a vacuum environment.

Source of Impulse

Measurements on the thrust of subliming biphenyl indicate that approximately $\frac{1}{3}$ dyne/cm^2 is obtained when biphenyl is illuminated at normal incidence with outer-space sunlight. This thrust level can be increased by electrical heating, by increasing the exposed area, or by causing the material to sublime through a nozzle. There is considerable merit in the use of a low-thrust, long time source of impulse for station-keeping of a comparatively fragile satellite, such as a gravity-gradient stabilized satellite in a synchronous orbit. Another possible use would be in the control of spin rate by mounting one of these devices so that its direction of thrust would have a long moment arm with respect to the center of mass of the satellite.

Conclusions

Subliming materials can be utilized for performing a large variety of functions to increase the effectiveness of a spacecraft mission. These mechanisms can be made extremely light, simple, and highly reliable. Several subliming materials investigated for this purpose provide a wide variance in actuation times. Mixtures of these materials can be used to obtain virtually any sublimation rate that might be desired. A record of 100% reliability has been established in using these devices on many different earth satellites.

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Space Engine Performance Prediction

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In-space engines, typified by low chamber pressures and high expansion ratios, undergo the major part of their development at sea level. Correct inference of combustion efficiency from sea-level test data and accurate prediction of vacuum thrust coefficients are therefore essential to satisfactory system development. An experimental technique was developed for determining nozzle stagnation pressure and hence combustion efficiency from measured thrust rather than from injector face pressure. This method requires the use of a low area-ratio nozzle of known thrust coefficient. Nozzle divergence losses are based on the ratio of thrust coefficients found by using the axisymmetric method of characteristics to those given by ideal one-dimensional flows; frictional losses are found by integration of wall shear drag for this family of nozzles; and nonequilibrium efficiencies are derived by using the sudden-freezing analysis of K. N. C. Bray. A method of combining these factors to establish over-all performance is presented. Experimental data for both sea-level and simulated altitude-firing tests of liquid rocket engines agree well with the predicted values.

Nomenclature

a = constant in reaction rate constant equation
A = area, in.^{2}
b = constant in reaction rate constant equation
B = $|R_f/X_f|$
c = constant in reaction rate constant equation
c^* = characteristic velocity, fps
C_D = discharge coefficient
C_f = skin-friction coefficient
C_F = thrust coefficient
$C_{\epsilon D}$ = drag loss
$C_{\epsilon G}$ = geometry loss
$C_{\epsilon K}$ = chemical dissociation loss
F = thrust, lbf
F_w = shear drag, lbf
g = 32.174 ft/sec^2
I_{sp} = specific impulse, lbf-sec/lbm
k_f = forward reaction rate constant of the freezing reaction, ft^6/lb-mole^2-sec
M = Mach number
P = pressure, psia
R = gas constant, 1545 ft-lbf/lb-mole-°R
Re = Reynolds number
R_f = forward reaction rate of the freezing reaction, lb-mole/ft^3-sec
R_t = throat radius, in.
s = distance along nozzle contour, ft
T = temperature, °R
v_{ir}' = stoichiometric coefficient, ith reactant in the rth chemical reaction
v_{ir}'' = stoichiometric coefficient, ith product in the rth chemical reaction
V = velocity, fps
w = viscosity exponent
$\dot{w}$ = mass flow rate, lb/sec
W_T = total molecular weight
x = distance along nozzle axis, ft
X = difference between forward and backward reaction rates, lb-mole/ft^3-sec

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