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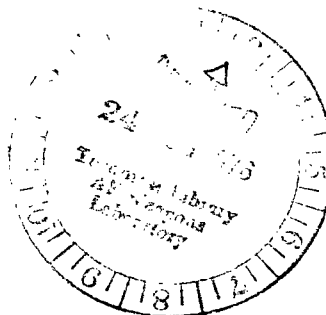
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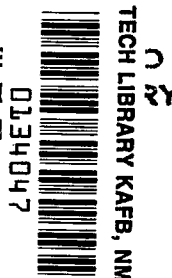
AN EQUIVALENT ENERGY FOR THE OUTGASSING OF SPACE MATERIALS

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16. Abstract

Materials for space applications must have low outgassing rates at normal operating temperatures and the outgassing products should include a minimum of condensables at the temperatures of nearby surfaces. A screening method, developed several years ago and used at many space laboratories, consists of holding a material sample at 398 K (125°C) for 24 hours and measuring its percentage total mass loss (TML) and the percentage volatile condensable mass (VCM) accreted on a 298-K (25°-C) collector. In general, the material is acceptable if the TML is less than 1 percent and the VCM is less than 0.1 percent. This document presents an analysis of the test and its results.

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INTRODUCTION

Materials selected for space applications must maintain structural and chemical integrity when exposed to the environmental conditions of space. They should have low outgassing rates at normal operating temperatures and the outgassing should consist of a minimum of materials condensable at the temperatures of nearby surfaces.

The observation of distant sources of radiation or the measurement of the space medium are affected minimally with spacecraft having low outgassing. In addition, voltage breakdowns and undesirable heat transfer regimes at certain critical regions of the spacecraft are minimized by limiting material outgassing. The requirement on condensables reflects the potentially degrading effect of material deposits on radiating surfaces and on elements of optical instruments. Deposits may change the thermal properties of a surface and attenuate, reflect, and disperse the incoming radiations to be measured.

Materials with the desirable characteristics have been determined from previous use or have been screened by a test developed by Muraca and Whittick (1967), and used at Goddard Space Flight Center, European Space Research Organization (ESRO), and Jet Propulsion Laboratories (JPL). The test, described by Muraca and Whittick (1967), Dauphin et al. (1972), and Park et al. (1973), consists of maintaining samples of about 200 mg of the materials under consideration at a temperature of 398 K (125°C) for 24 hours in a vacuum of about 10^{-6} torr. The sample mass loss and the amount of that mass which condenses on a collector plate held at 298 K (25°C) and located near the sample are used as some of the criteria for the selection of these materials for space use.

In general, the material is considered acceptable if the total mass loss (TML) is less than 1 percent and the volatile condensable mass (VCM) is less than 0.1 percent of the initial sample mass. The criteria for TML reflects the consideration that certain materials show mechanical and physical degradation when they have lost 3 to 5 percent of their mass. For others, such as elastomers, a 1-percent TML is usually detrimental to their mechanical properties. A more definite interpretation can be given to the 0.1-percent VCM criteria. The 0.1-percent condensate of a 1-kg material would cover 100 m² of surface with a uniform 10^{-6} g/cm² layer corresponding to about 20 monolayers and to a thickness of about 1×10^{-6} cm.

Material coatings of these dimensions can be very detrimental for optical thermal applications. Regardless of these considerations, the selection criteria appear to provide sufficient protection against the use of very objectionable materials. It is unfortunate, however, that the test and its selection criteria do not provide direct data that a designer requires to ensure against contamination and the performance of certain systems. The designer needs to know the materials' outgassing rates as a function of temperatures, time, and surface area and the condensation of this outgassing at temperatures other than 298 K (25°C). With this data, the designer can select the materials to use, and can estimate the pressure versus time in compartments and the deposits and contamination which may occur on critical surfaces (Scialdone, 1974).

The analysis which follows is an attempt to obtain a better understanding of the parameters affecting the VCM tests. The analysis points to some of the reasons for the different results obtained for the same materials by different labs. Most important, it gives some insight on the utilization of the test results for the use of the designer.

Relations for the ratio of outgassing rates and vapor pressures at 398 K (125°C) and 298 K (25°C) are derived in terms of the geometry, the temperatures of the apparatus, and the VCM and TML results of the test. An "equivalent" activation energy is also derived in terms of the above parameters. Within the limits of the assumptions made in its derivation, this energy can be used to estimate the outgassing rates at other temperatures. In addition, the analysis shows: the limitations of the test in detecting condensables of certain materials; and the maximum percentage of VCM which can be obtained for certain materials.
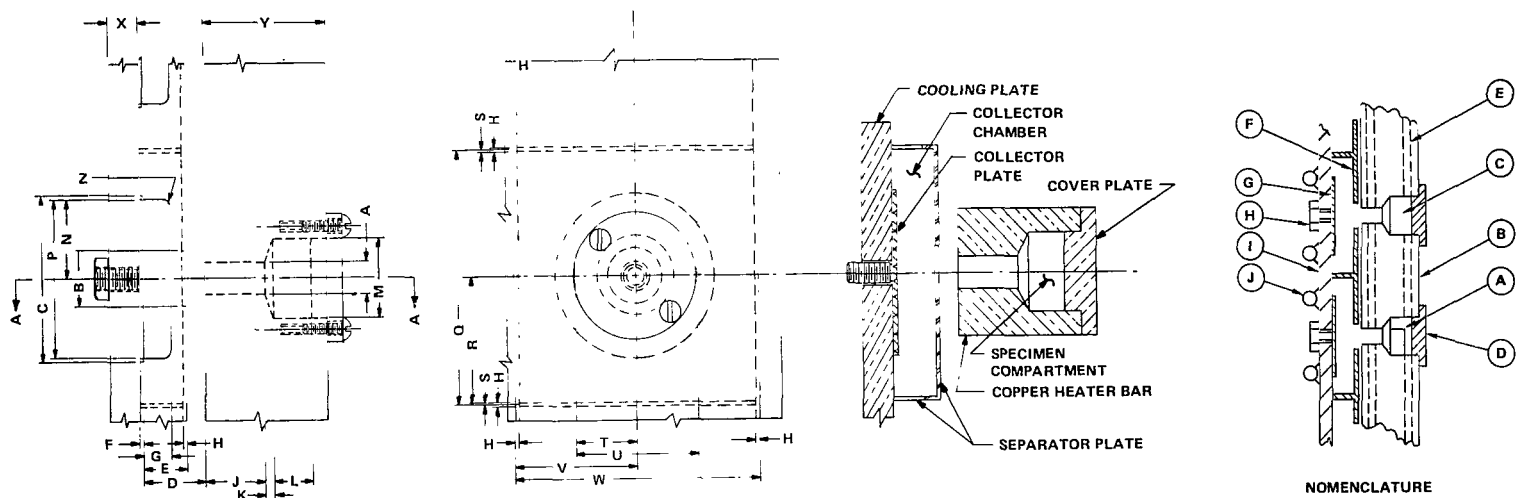
ANALYSIS

The schematic of figure 1 shows the relative locations and dimensions of the test apparatus components used for the determination of the condensables and mass loss of a sample material. From the conservation of mass, the mass, m_c, which accretes on the collector during the 24-hour test, is equal to the difference between the mass impinging and condensing on the collector, $\gamma\varphi\, m_o$, and the mass which departs from the collector, m_L, i.e.,

$$m_c = \gamma\varphi\, m_o - m_L \tag{1}$$

The mass impinging and condensing consists of the mass, m_o, from the opening passage, modified by the view factor, φ, of the collector plate to the opening, and the condensation coefficient, γ. This coefficient accounts for the type of collision (elastic, inelastic) of a molecule condensing on another molecule. The mass, m_o, is also the TML of the sample measured after 24 hours of test, when the continuity relation is applied to the entrance and exit of the passage. The collected mass, m_c, on the other hand, is the measured VCM. Equation 1 rewritten in terms of the mass leaving the collector, the mass loss, and the test results designation is

$$\frac{m_L}{m_o} = \left(\gamma\varphi - \frac{m_c}{m_o}\right) = \left(\gamma\varphi - \frac{VCM}{TML}\right) \tag{2}$$

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COOLING PLATE
COLLECTOR CHAMBER
COLLECTOR PLATE
COVER PLATE
SPECIMEN COMPARTMENT
COPPER HEATER BAR
SEPARATOR PLATE

NOMENCLATURE

A – SAMPLE BOAT
B – HEATER BAR
C – SAMPLE COMPARTMENT
D – COVER PLATE
E – HEATER ELEMENT
F – SEPARATOR PLATE
G – COLLECTOR DISK
H – RETAINING NUT
I – COOLING PLATE
J – COOLING COIL

a. Critical dimensions which must be maintained for test results to be comparable.

b. Diameters must be concentric to ±0.1 mm (±0.005 in) for test results to be comparable.

c. Dimensions include plating thickness. Satisfactory surfaces have been produced by making substrate surface finish 1.6 μm RMS (63 μin RMS), highly polished, plated with electroless nickel 0.0127 mm (0.0005 in) thick and finished with electroplated chromium 0.0051 mm (0.0002 in) thick.

TEST APPARATUS DIMENSIONS

LETTER	MM	TOLERANCE	LETTER	MM	TOLERANCE
A[a, b]	6.3	±0.1	N	16.0	±0.8
B[a, b]	11.1	±0.1	P	32.0	±0.8
C[a, b]	33.0	±0.1	Q	50.0	±0.8
D[a, c]	13.45	±0.1	R	25.5	±0.8
E[a, c]	9.65	±0.1	S	0.4	±0.3
F[a, c]	0.65	±0.1	T	12.0	±0.8
G[c]	7.1	±0.3	U	25.5	±0.8
H[a]	0.75	±0.1	V	25.5	±0.8
J[a]	12.7	±0.3	W	50.0	±0.8
K	1.6	±0.8	X	6.0	±0.8
L	8.0	±0.8	Y	25.0	±0.8
M	16.0	±0.1	Z	1.6	±0.8

Figure 1. Micro-VCM schematic.

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The quantity of gas, m_o (g), which leaves the sample compartment by way of a passage of area, A_o, diameter, D_o, and length, L_o (where a density, n_o (g/cm^3), and temperature, T_o, exists), is given from kinetic theory

$$m_o = \tfrac{1}{4} n_o \, c_o \, A_o \, \alpha \, \Delta t \qquad \text{(g)} \qquad (3)$$

where $\alpha = 4/3 \; D_o/L_o$ is the Clausing factor for molecular flow through pipes and c_o is the gas molecular speed. Similarly, the quantity of gas, m_L, leaving the collector plate, during the same period of time, Δt, can be expressed in the same manner as equation 3, considering the collector an orifice of area, A_c, through which a gas at density, n_c, and speed, c_c, is passing, i.e.,

$$m_L = \tfrac{1}{4} n_c \, c_c \, A_c \, \Delta t \qquad \text{(g)} \qquad (4)$$

The ratio of equation 2, when expressed in terms of equations 3 and 4 with the substitution for $n = P/KT$ from the gas law, and $c \cong \sqrt{KT/m}$ where K is the gas constant and m is molecular mass, becomes

$$\frac{m_L}{m_o} = \frac{P_c}{P_o} \sqrt{\frac{T_o}{T_c}} \, \frac{A_c}{A_o \alpha} = \left(\gamma\varphi - \frac{VCM}{TML} \right) \qquad (5)$$

According to the Langmuir relation (Dushmann and Lafferty, 1962), the rate of evaporation or sublimation per unit area is $w \cong P\sqrt{M/T}$, so for the same material, the ratio of the rates of mass leaving the sample at T_o and the collector at T_c per unit area is

$$\frac{w_L}{w_o} = \frac{P_c}{P_o} \sqrt{\frac{T_o}{T_c}} = \left(\gamma\varphi - \frac{VCM}{TML} \right) \frac{A_o \alpha}{A_c} \qquad (6)$$

Alternately, one can get the ratio of vapor pressure from equation 6 by transposing the temperature ratio.

Before proceeding with the derivation of "an equivalent activation energy" for the material, several comments are needed.

In these tests, the amount of material loss and its molecular nature are not known as a function of time. The process of losing mass may involve a combination of several processes: surface desorption of molecules not indigenous to the material; sublimation of the material molecules from the surface; and diffusion of internal molecules to the surface with subsequent desorption, or other processes. It is also reasonable to predict that certain components of the materials will evolve at different times during the process and each may require a different energy to break away. In this analysis, these temporal variations of mass and energy cannot be taken into account. The TML for the test, m_o, will be considered the result of an equivalent energy, E, which is required for the outgassing of the material.

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The molecules leaving the sample compartment and arriving at the collector may recombine with their own kind or others previously deposited. The total measurable deposits, which are measured with microbalances sensitive to micrograms, will be many monolayers. Here, also, the energies required for the molecules to leave the collector will be variable with time and will involve different molecules and processes. "An equivalent energy," however, is assumed as in the case of the mass loss for the net departure, m_L, of the materials from the collector.

With these assumptions—the correspondence of the processes and energies at the collector and at the sample—one can derive an equivalent activation energy for the material which has undergone VCM test. This energy can be used to better characterize the material and to give an approximate value of outgassing rates and condensation rates at various temperatures.

In view of this, the rates w_L and w_o can be expressed in terms of energy and temperature using the Arrhenius expression, $w = ke^{-E/RT}$, where k is a constant. Equation 6 with these substitutions is

$$\frac{w_L}{w_o} = e^{-\frac{E}{R}\left(\frac{1}{T_c} - \frac{1}{T_o}\right)} = \left(\gamma\varphi - \frac{VCM}{TML}\right)\frac{A_o\alpha}{A_c} \qquad (7)$$

where E (cal/mole) is the equivalent energy, R = 1.98 cal/mole K is the gas constant, and T_c and T_o (K) the temperatures of the collector and sample, respectively. The equivalent energy of the material is then

$$E = \frac{R}{\left(\frac{1}{T_c} - \frac{1}{T_o}\right)} \ln \frac{A_c}{\left(\gamma\varphi - \frac{VCM}{TML}\right)A_o\alpha} \quad \text{(cal/mole)} \qquad (8)$$

where all the terms are defined by the geometry of the test apparatus (φ, A_o, α, A_c), the test results (VCM and TML), and the test temperature conditions (T_o, T_c). Equation 8 has the following asymptotes. The energy is a constant, and a minimum

$$E_{min} = \frac{R}{\left(\frac{1}{T_c} - \frac{1}{T_o}\right)} \ln \frac{A_c}{A_o\alpha\gamma\varphi} \qquad (9)$$

when the ratio VCM/TML = 0 or TML/VCM = ∞. This implies that materials having energy less than the above will show zero condensables for the test. On the other extreme, the energy tends to infinite (E = ∞) when VCM/TML = $\gamma\varphi$ or TML/VCM = $1/\gamma\varphi$. This means that a material which produces the maximum of condensable allowed by the apparatus has a very large energy. The maximum amount of condensable is the product of the TML times the view factor when the condensation coefficient is unity.

APPLICATIONS OF THE THEORY AND SOME EXPERIMENTAL RESULTS

The previous equations have been evaluated employing the following numerical values as obtained from the geometry of the apparatus shown in figure 1. The area of the collector, A_c, is 8.563 cm^2, and the area, A_o, of the opening from the sample holder is 0.3167 cm^2. The coefficient to account for the tubulation has been evaluated using the expression $\alpha = 4/3$ D_o/L_o (Dushmann and Lafferty, 1962). Its value is $\alpha = 0.667$ using $L_o = 0.5$ cm for length and $D_o = 0.25$ cm for the diameter of the passage. The view factor, φ, giving the fraction of the molecules issuing with a diffuse distribution from the passage, impinging on the collector was calculated to be $\varphi = 0.54$ using the computer program of Jackson and Puccinelli (1975). The assumption of diffuse distribution of the molecules should be valid for the majority of the tested materials. But with materials having large mass losses, the exit flow will be collimated and describable by a power function of the cosine. In these cases, the view factor will be approaching one. The condensation coefficient, allowing for the possibility that only a fraction of the incident molecules will condense on the collector before being reemitted, should be close to unity in these tests, where films are of the order of $\mu g/cm^2$ and the temperatures are not too far from each other. As expected, the condensation coefficient has the same effect as the view factor in the results of the selection tests.

The ratio of a material outgassing rate at 298 K (25°C) to that of the same material 398 K (125°C), (w_L/w_o), is shown in figure 2 as a function of the ratio of the total mass loss to the condensate mass (TML/VCM) and for some variation in the view factor. The maximum outgassing ratio is about 1.3×10^{-2} when TML/VCM tends to infinity (small equivalent energy) and the minimum outgassing ratio is obtained when TML/VCM tends to $(\gamma\varphi)^{-1}$ (large equivalent energy). It is seen that the effect of the change in view factor (and condensation coefficient) is mainly to establish the minimum value of the ratio TML/VCM, which is possible with a certain apparatus and a material which is easily condensable at 298 K (25°C).

The equivalent energy as a function of the ratio of the TML to the VCM is shown in figure 3. The energy has been calculated using the nominal dimensions of the apparatus and using different combinations of collector temperatures, T_c, and sample temperatures, T_o. It is seen that the temperature differential establishes a limiting minimum energy for which the material will produce condensables on the collector plate (i.e., VCM = 0). This minimum energy of the material is 10.18 kcal/mole for the normal temperature of 398 K (125°C) and 298 K (25°C) and the nominal test geometry. On the other end, the equivalent energy is very large, approaching infinity if the VCM is equal to the total loss modified by the view factor, i.e., VCM = ($\gamma\varphi$) TML, which implies that all of the mass loss would stick and not leave the collector. Figure 4 shows the same information as figure 3, and also shows the differences in results which may be obtained allowing for tolerances on the geometry and temperatures of the test setup. The minimum and maximum values of the energy corresponding to a given TML/VCM ratio were obtained by using dimensions and temperatures which minimized or maximized the energy. These extreme values were taken to be three standard deviations from the nominal or average values of a Gaussian distribution of values. The nominal, the 3σ and 1σ values, are shown on this plot. The error resulting from these variations is quite large for large values of TML/VCM.
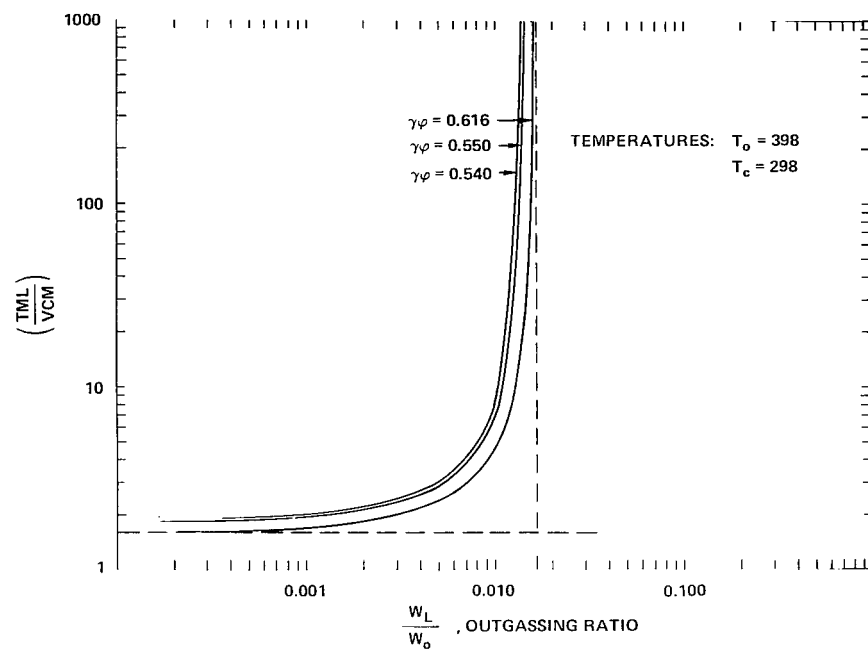
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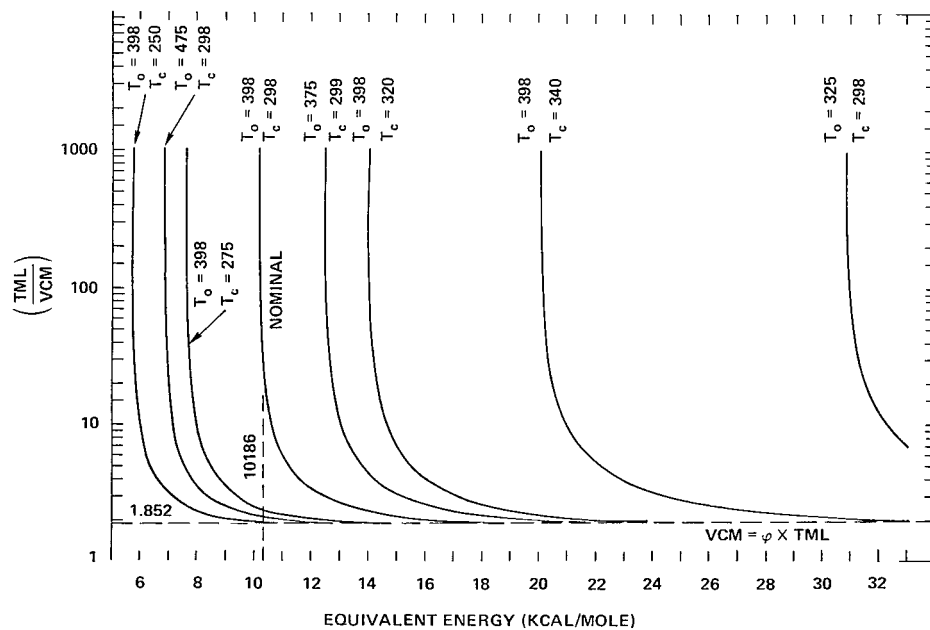Figure 2. Outgassing ratio versus TML/VCM.

Figure 3. TML/VCM versus equivalent energy for various test temperatures.
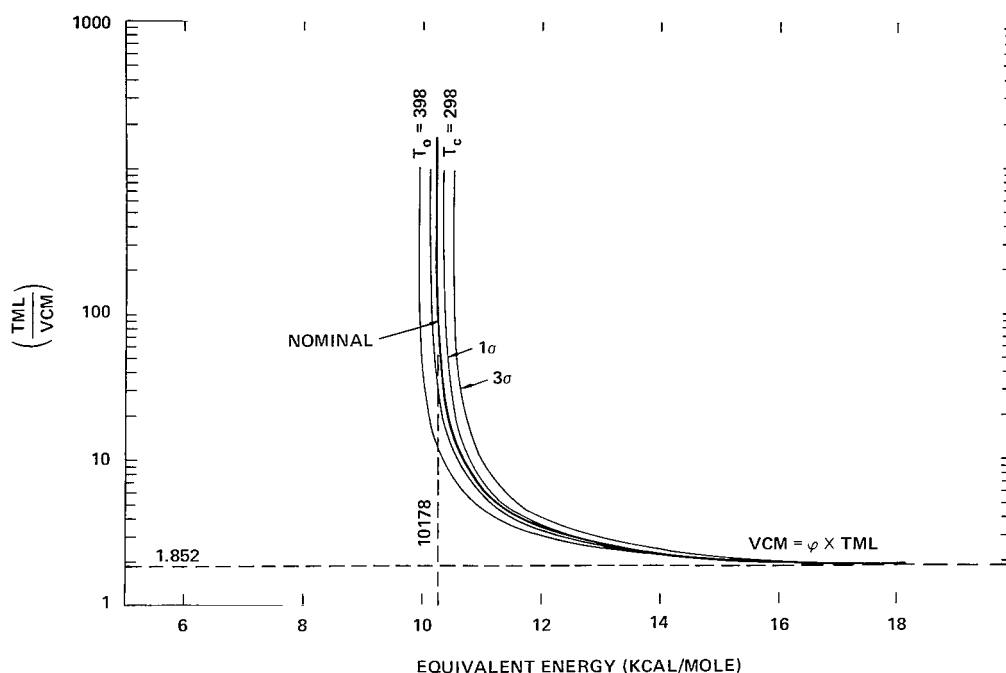
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Figure 4. TML/VCM versus equivalent energy, including tolerances on geometry of apparatus and test temperatures.

Test confirmations of the energy values obtained with this analysis using the data for VCM and TML listed in Campbell et al. (1975) have not been carried out. Only limited data on polymers materials energies are available in the literature. It is hoped that experimental tests will be conducted to obtain these data for several materials of importance. From a general examination of the data to be discussed below and from experience, the energy data from the test appear to be within the expected range of values. Schittko (1963) calculated, from outgassing rates versus temperatures obtained at pressures below 10^{-6}, the activation energies which are attributed to desorption or diffusion from the material. Unfortunately, most of the energies of the listed materials (see also Santeler et al., 1966) are below 10 kcal/mole and the exact nature, preparation, and curing of the materials are unknown. The energies of the recognizable materials appear to agree within 10 percent of the values obtained from this analysis of the VCM tests.

Santeler et al. (1966) indicated that using 10-kcal/mole energy for most polymeric materials gives good results for estimating the outgassing rates at different temperatures. Wilcock (1946) showed that for cyclic and linear methyl polysiloxanes materials, the heat of vaporization increases with molecular weight and is between 8 and 24 kcal/mole, which appears to be the range of energy measurable by the VCM test.

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Jex and Shriver (1975) calculated the energy of RTV 560 adhesive to be 13672 cal/mole. This adhesive is used as a thermal protective surface (TPS). The energy was derived from a plot of outgassing rates versus temperatures. The rates were obtained after about 48 hours in vacuum at 316 K (43.3°C). The materials list of Campbell et al. (1975, p. 118) shows several RTV 560, cured at different temperatures for different lengths of time, and with different components. The TML/VCM ratios vary from 4.96 to 2.19 with an average of 3.6. Correspondingly, the energies vary between 11.2 and 15 with an average of about 12 kcal/mole, which is comparable to the value given by Jex and Shriver (1975). The VCM test giving a ratio of 1.51 in the list has been excluded because that value is not compatible with the apparatus view factor. The minimum TML/VCM should be about 1.85 as discussed.

It appears from the above that the energies provided by the VCM method are comparable to those obtained from tests on outgassing rates at different temperatures.

CONCLUSIONS

An important aspect of the previous analysis is the understanding of the effects of the geometry and temperatures on the results obtainable from the microvolatile condensable material test apparatus for the selection of space application materials. Different results which may occur from small variations in temperatures and geometries between apparatuses have been pointed out. It has been indicated that the maximum amount of condensables which can be obtained from the test is the product of the TML times the view factor of the condenser plate to the passage to the material sample. Also, materials with a certain equivalent activation energy less than about 10.1 kcal/mole will not indicate condensable on the collector due to the nominal geometry and the temperatures used with the apparatus. The equivalent energy has been derived from the test, and is expressed in terms of the ratio of the TML to the VCM, the system geometry, temperature of the material sample, and collector plate. This is an important parameter in the selection of materials. In fact, a material indicating a low equivalent energy implies less deposits of this material on surfaces. The material is easily removed from the surfaces, and probably has a low molecular weight. Most important, this parameter provides the designer with additional data he may use to estimate outgassing and condensation rates of that material at different operating conditions than those of the apparatus. The values of the energy calculated by the method developed here appear to be comparable to data on energy of certain materials given in the literature. It is also apparent that the values are very dependent on the precision of the VCM test results, and the preparation and curing of the material. Tests should be conducted to obtain material equivalent energies for materials commonly used in space applications. The results could be compared to the equivalent values calculated here.

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