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HUMIDITY CONTROL SIMULATION FOR ELECTRONICS PACKAGING

David G. Myers/Raytheon Missile Systems

ABSTRACT

An important aspect of environmental control is the protection of equipment from the harmful effects of humidity. It is often desirable to desiccate a sealed volume in order that it satisfy a dryness requirement over the duration of its service life. Desiccant sizing, along with proper sealing, become important design elements in ensuring that such a requirement is achieved. To this end, Raytheon has developed a simulation tool to analyze and predict the humidity within sealed volumes. The pertinent physical principles that are modeled are permeation of water vapor by diffusion, pneumatic leakage, the hygroscopic properties of sealed materials, desiccant characteristics, and the kinetic model of ideal gas mixtures. The simulation has the capability of imposing any external environmental condition, consisting of diurnal cycles of temperature and humidity. The physical principles which underlie the simulation are described. An example of simulation results, design decisions and lessons-learned are presented.

KEYWORDS: humidity, permeation, water, desiccant, leakage

INTRODUCTION

Analysis of the humidity within a sealed volume, such as a missile guidance section or electronic subassembly box, can be undertaken by means of the simulation program VIPER (Vapor Intrusion Program with Environmental Recognition). VIPER models the pertinent physical processes within the sealed unit and the external environments to which the sealed unit is exposed. Included among these physical phenomena are (1) permeation of water vapor by diffusion through the seals, (2) pneumatic leakage around the seals, (3) the dynamic hygroscopic properties of the sealed materials—that is, how they adsorb and desorb water, (4) the beneficial effects of desiccant, and (5) the kinetic model of ideal gas mixtures. The simulation has the capability of imposing any external environment, including multi-year usage scenarios having dormant storage and active field use phases, consisting of diurnal cycles of temperature and humidity. The end product of the simulation is a rendering of the predicted humidity of the entrapped air within the sealed unit, as well as the water content of the sealed materials. A recognized benefit of VIPER is that it may be used as a tool for establishing a desiccant size and for

performance verification, once a dryness requirement has been ordained for the unit in question by systems engineering or product assurance interests.

The VIPER simulation is an outgrowth of knowledge and experience gained during humidity control design activities for a variety of missile programs. This knowledge and experience base has come by way of both experiment and research. The benefit of VIPER over simple closed-form models of moisture penetration into sealed volumes is that the closed-form solutions (1) do not model the dynamics of adsorption and desorption of water into and out of the hygroscopic contents (the "desiccant equivalent") of the enclosure, (2) assume a constant external environmental forcing function, and (3) are not capable of effectively modeling leakage in the viscous mode. VIPER, on the other hand, simultaneously integrates—with a time step size amounting to several minutes—the differential equations governing all of the physical processes. Some of these differential equations are nonlinear or have non-constant coefficients and forcing functions, making a closed-form solution intractable.

During the initial stage of analysis for a particular application, the simulation parameters are fashioned based upon design information that is available at the time: seal dimensions and material type, predicted leak rate, expected service environment, and an estimate of the moisture content of the sealed materials. The VIPER simulation will furnish a preliminary estimate of humidity in the unit for any hypothetical desiccant size. (Experience has shown that purely analytical methods produce results that are conservative, and agree with subsequent experiments to within a factor of two or three.) Later, experiments may be performed to establish more accurately such quantities as the permeation rate of water vapor through a particularly prominent seal, the mass of latent moisture in the sealed materials, or to measure the dynamic properties of water adsorption into and desorption out of these materials during temperature cycling. An appropriate employment of these experimental results yields a fully calibrated simulation model, which can be used (1) to establish sensitivities as to what are the main contributors which consume the desiccant capacity, (2) to determine the effect of altering seal materials, (3) to determine the consequences of exposing the unit to different external environments, or (4) to

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determine the effect on system design of altering the internal dryness requirement.

The subjects addressed in this paper are as follows: First, an overview of the physical principles is given, followed by a set of assumptions. These assumptions establish a foundation for all of the computations performed in a humidity analysis. This is followed by a more detailed treatment of the mass transport phenomena that are modeled. Finally, there follows a section which illustrates the results of using the VIPER simulation program—including some design decisions, a case study and lessons-learned.

NOMENCLATURE

A area (normal to direction of flow), m^2
C gaseous conductance, m^3/sec
D binary diffusion coeff. of water vapor in air, m^2/sec
M molal mass of a gas, kg/kgmole
P permeation coefficient, m^2/sec
Q gas flow rate, Pa m^3/sec
R universal gas constant, J/(kgmole °K)
T absolute temperature, °K
V volume, m^3
a characteristic dimension of leak passageway, m
l length, m
m mass of gas, kg
p pressure, or partial pressure, of gas, Pascal
q quantity of gas, Pascal m^3
v_a mean molecular speed, m/sec
x spatial variable, m
η viscosity, Pa sec
ρ density, kg/m^3

OVERVIEW OF PHYSICAL PRINCIPLES

The penetration of moisture into a sealed missile assembly and the adsorption and desorption of water into and out of sealed materials, under any variety of external conditions, can be predicted analytically by applying certain physical principles and utilizing known or experimentally-determined physical parameters. The computer simulation VIPER has been specifically created to make these predictions by furnishing the discrete time-integrated solutions to the pertinent differential equations governing the processes involved.

The physical processes that are modeled in the simulation are primarily concerned (1) with the transport of water past solid seal materials, and (2) with the hygroscopic properties of air and solid materials.

The transport phenomena are often referred to (all-too-generally) as "leakage." More precisely, there are two categories of "leakage" or transport that are considered in this analysis. The first, which is not properly "leakage" at all (and will not be referred to as such again), is the process of permeation of water by means of diffusion through a solid medium. When the material is a solid seal barrier this process is sometimes defined by a parameter called the WVTR, or Water Vapor Transmission Rate. Permeation is the process whereby gas molecules dissolve in the solid material and diffuse to the other interface under a concentration gradient, where they vaporize.

The crucial item to remember regarding the permeation of water vapor is that mass transport through a solid medium is proportional to the differential concentration of the penetrant only. That is, the rate of mass flow of water vapor depends only on the partial pressure differential of water vapor across the seal, not the total pressure differential of the gas mixture across the seal.

The second mass transfer category that is considered in the VIPER simulation is what may be called pneumatic leakage. VIPER considers two distinct modes of flow—the so-called viscous and molecular flow modes—in the category of leakage, thereby discounting the obscure transitional flow mode, and the peculiar modes of choked flow and turbulent flow. In one leakage mode (that is, viscous) the mass flow is a function of the total pressure differential of the gas mixture across the barrier. In the other mode (that is, molecular), mass flow of a particular constituent gas of the mixture is proportional to the partial pressure differential of that gas. Leakage is differentiated from permeation in that, unlike permeation, the gases pass through interstices in the nominally solid seal and remain in a gaseous state. The physical property that determines which of the two modes of pneumatic leakage is in operation is the dimension of the leak passageway in relation to the mean free path length of the molecules in the gas mixture.

In the molecular flow mode, water vapor leaks in or out of a sealed unit according to the direction of the concentration gradient of water vapor only, regardless of the total pressure differential across the seal. In the viscous flow mode, water vapor passes into or out of the sealed unit according to the direction of flow of the mixture, of which it is only one constituent. This type of leakage, when it occurs during daily cycling of temperature, with the resulting reversal in the direction of mass flow, is commonly referred to as "breathing."

Achieving and maintaining dryness within any sealed unit is dependent upon the properties of the desiccant that is used (if any), and upon the hygroscopic properties of the solid materials which compose the interior of the sealed unit, that is, the ability of these materials to adsorb, retain and desorb moisture. The reader is urged to inspect an article by Mueller [1] for an excellent discussion of the dynamic solubility of water in sealed materials (desiccant equivalent), which is vastly more important than the water content of the sealed air. As stated in that paper, the "air is merely a transfer agent" rather than being the primary factor in determining the humidity of the unit.

A fact that was often unrecognized in the past is a dry gas purge alone is not an effective means of removing moisture from a sealed unit containing electronic hardware. Very roughly speaking, the free air volume of, say, a missile guidance section may contain a water vapor mass on the order of a hundred milligrams, while the sealed solid materials may contain a mass of water vapor on the order of ten grams. Within moments after a dry gas purge, water endeavors to fill the "vacuum" of water vapor within the sealed air volume by desorbing out of the sealed materials. The potential capacity of water in the vapor state in the sealed air is very small compared to the reservoir available in the sealed materials. It does not take long, therefore, for the system humidity to nearly revert to its original state prior to the purge.

Desiccation is the most reasonable solution for truly dry, long-term storage because desiccant removes residual moisture in the sealed materials, and consumes and retains water vapor

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that permeates and leaks into the sealed volume. As a consequence, the water adsorption characteristics of molecular sieve desiccant, that is, its water adsorption capacity versus the concentration of water vapor in the surrounding air, is modeled in the VIPER simulation. The initial moisture content of the molecular sieve desiccant—amounting to several percent of its weight—needs to be controlled by the supplier and user. The initial moisture content of the desiccant is also modeled in VIPER, since it is a liability against the available desiccant capacity.

Finally, the VIPER simulation also models the desiccant equivalent capacity of the sealed materials. The dynamic characteristics of adsorption and desorption of water are most precisely determined on the basis of experiments on the unit. The experiments involve the monitoring of the absolute and relative humidity of the air within the sealed unit while it is undergoing temperature cycling (simulating diurnal variations). The dynamics are informed by the so-called "lag loop" time constant. Mueller [1] also contains a discussion of the lag loop phenomenon.

ASSUMPTIONS

The computations and simulation results rendered by VIPER are entirely dependent upon the set of assumptions that are put forth here. Therefore, it is important to understand the nature of these assumptions, which are concerned with the physical laws of gases, gas flow, and the hygroscopic properties of materials. The assumptions are generally considered to be on the conservative side.

The major assumptions are stated as follows:

(1) The application and use of (i) the equation of state of an ideal gas and (ii) the Dalton principle, as models of the behavior of gases, are valid. Heavy reliance is placed upon these physical principles in the computations that are performed by VIPER.

(2) The operative form of the permeation equation as used in this paper is a valid model of the transport of water vapor through the elastomeric seals.

(3) The equations for molecular and viscous flow of a gas through leak pathways are valid models of pneumatic leakage. In practice, predictions of water vapor penetrating into a sealed unit by means of leakage are based upon either the leak rate specification or a measured leak rate.

(4) Water vapor mass transport into the sealed volume by means of permeation and by means of pneumatic leakage proceed simultaneously with one another. Moreover, these phenomena act independently of and additively with one another. This assumption is a conservative one for, if anything, the process of permeation would tend to impede the process of leakage; water diffusing through the elastomeric seals might cause them to swell slightly (Buchter [2]), creating a tighter seal against pneumatic leakage.

(5) The mode of pneumatic gas leakage in operation in a sealed volume is either entirely molecular or entirely viscous in nature, but not both.

The mode of pneumatic leakage that is in operation is sometimes difficult to determine. One solution to this difficulty is to use the general guidelines given in the leak testing handbook (McMaster [3]) for determining the mode of flow. Or it is sometimes possible to resort to a kind of dimensional analysis to determine to mode of leakage. For example, the hypothesis that the mode of flow is molecular might lead to the conclusion that the leak pathway is on the order of microns in length; because this dimension is not possible, we reject the hypothesis. If this method is not fruitful, then sometimes the analyst can do no more than assume, in the interest of conservativeness, that the mode of flow in operation is the one that yields the higher cumulative quantity of water vapor penetration.

This assumption excludes the possibility of the so-called transitional flow from occurring. The elimination of transitional flow is a result of the nature of this mode of flow, which, as its name implies, is an intermediate form between molecular and viscous flow. The analytical approach to transitional flow is somewhat dodgy. Transitional flow incorporates elements of both molecular and viscous flow. Indeed, Turnbull, *et al* [4], have pointed out that "as the gas pressure is lowered, the change of flow characteristics from viscous to molecular is by no means clear-cut." Furthermore, "this region is somewhat difficult to treat mathematically, but for most practical purposes it is sufficiently accurate to consider a duct in this pressure region as having a viscous conductance...in parallel with a molecular flow conductance...." Thus the total gaseous conductance is given by the sum of the viscous and molecular flow conductances. Since transitional flow can evidently be approximated by the superposition of molecular and viscous flow, the assumption put forth here is sufficient to eliminate the transitional flow case.

(6) Dry gas purging and overpressurization of a sealed volume (while having some minor benefits) will not impede water vapor permeation through the seals. The so-called activated diffusion process, by which water vapor permeates through the seals, is driven only by the partial pressure differential of water vapor across the barrier. The physical laws governing the solubility and diffusion of gases through seal materials show a dependence on the concentration of the penetrant only, without reference to the concentration of other substances. This assumption is supported by experiment, where it has been shown (van Amerongen [5]) that "the permeability of a [rubber] membrane to a given gas is not affected by the presence of a second gas."

(7) Water vapor adsorption dynamics of the desiccator unit is modeled mathematically as a first-order lag. The value of the time constant is a function not only of the rate at which the desiccant alone will adsorb water, but also the permeability of the material intervening between the desiccant—resident in a kind of housing—and the free air volume of the sealed unit. This permeable membrane is usually a kind of porous plastic that allows the (more-or-less) free flow of water molecules into the desiccator housing, but prevents potentially harmful dust from the desiccant beads or granules from escaping.

(8) The dynamics of adsorption and desorption of water into and out of the sealed materials (desiccant equivalent) are modeled as a first-order lag, with a time constant estimated most effectively by experiment. Establishing a precise value of the time constant will not appreciably affect long-term humidity predictions, but only the humidity during the dry-out period.

(9) The change of state of water—that is, condensation, sublimation and vaporization—are not considered in the VIPER simulation. Provision for this possibility may be considered in the future as a growth option for the VIPER simulation model.

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Among a variety of models (References [6-8]) that address the vaporization of water, the one that ought to be selected is the Hertz-Knudsen relation.

(10) Elastomeric seal materials are incompressible in the sense that the volume remains constant during compression, and only the shape is changed (Buchter [2]). The compressed dimensions, based upon the depth of the bladder (groove) between mating surfaces, are the dimensions used in the operative form of the permeation equation.

(11) Where there is metal-to-metal contact between mating surfaces of the unit structure, it is assumed that the size of the interstitial space does not alter the concentration of the water vapor penetrant at the boundary of the seal material and, thus, does not affect the way in which permeation is modeled. A discussion in Buchter [2] supports this conservative assumption.

(12) No attempt is made to provide a thermal model of the sealed unit as it responds to daily temperature cycling. Furthermore, the change in energy state (heat lost or added as a result of condensation, evaporation, sublimation) of the gas mixture and the water in its various phases is ignored. The benefits derived from adding such complexity to the VIPER simulation would be minimal.

FUNDAMENTAL PHYSICAL PHENOMENA

Kinetic Theory of Gases

A major assumption of the analysis is that the air and water vapor mixture trapped within the sealed unit obeys idealized laws of thermodynamic physics, particularly the ideal gas law and the Dalton principle for the mixture of nonreactive gases.

The ideal gas law may be stated as follows:

$$pV = \frac{m}{M}RT \qquad \text{(Reynolds \& Perkins [9])}$$

The VIPER simulation concerns itself not only with water vapor, but with various constituents of dry air, namely, nitrogen and oxygen gas, and argon. Altogether, these gases account for more than 99.96% of the actual atmospheric content. The total pressure exerted by the atmosphere is the sum of the pressures exerted by the constituent gases. These constituent pressures are called the partial pressures. It has been found that the partial pressure of each of the constituent gases of a mixture is very nearly the same as would be the actual pressure of that constituent alone if it occupied the same volume as does the mixture. This has given rise to the Dalton principle, which states that the total pressure of a mixture of gases is equal to the sum of the partial pressures of the component gases. Thus, under this assumption, each of the constituent gases in the gas mixture behaves independently of the others, and can be analyzed as such by using the ideal gas law, with p equal to the partial pressure of the particular constituent.

Hygroscopic Properties of Air

The vapor pressure or saturation pressure of water expresses the ability of air to retain water. Tables of the saturation pressure of water versus temperature (replicated in VIPER) may be found in the literature (e.g., Weast [10]). Warmer air can hold much more water than colder air. For example, saturated air at, say, 25 °C (77 °F) has a partial pressure of water vapor (3167 Pa), which is some ten times as high as that (310 Pa) when the temperature is −8 °C (17.6 °F). The mass of water vapor in a given volume of air is proportional to its partial pressure. Therefore, air at 25 °C can hold ten times as much water as air at −8 °C.

Is evident that the partial pressure of water vapor can never exceed the saturation vapor pressure of water at that particular temperature. The ratio of the partial pressure to the saturation vapor pressure at the same temperature is the relative humidity, usually expressed as a percentage. Because the water vapor in the air is saturated when its partial pressure equals the saturation vapor pressure at the air temperature, saturation can be brought about either by increasing the water vapor content or by lowering the temperature. The temperature at which water vapor in a given volume of air becomes saturated is called the dew point (or frost point if that temperature is below freezing). If the temperature of a sample of air is lowered below the dew point, condensation (dew or frost) will occur to reduce the water content to correspond to the vapor pressure at the lower temperature. (If the temperature is below freezing, the process is called sublimation, which is the direct formation of ice from the vapor state, bypassing the liquid state. Oddly enough, the term sublimation also refers to the opposite process, the vaporization of ice.)

The absolute humidity of a sample of air is simply the density of water vapor. Another quantity of importance is the humidity ratio (sometimes called the specific humidity), defined as the ratio of the mass of water to the mass of dry air in the sample.

Diffusion of Water Molecules in Air

The fact that sealed units are usually tightly packed volumes, having narrow diffusion corridors between different sections, with associated localized areas of higher humidity, is usually ignored, and is not a standard feature of the VIPER simulation. The diffusion of water vapor molecules in air is a rapid process compared to the other phenomena that are modeled. But occasionally it is necessary to analyze the diffusion of water molecules within a sealed volume from a region of higher concentration to another region of lower concentration. This circumstance might arise, for example, in a very tightly packed electronics subassembly or missile guidance section that has permeable seals at one end and a desiccant package at the opposite end, with a narrow corridor in between. This corridor is postulated to be too large to be considered a "leaky" seal, but small enough to permit a water vapor concentration gradient under steady state conditions. Clearly, the gas mixture at the desiccated end will have a lower concentration of water molecules than the end with the permeable seals. In the absence of convective transport of the gas mixture within the unit, water molecules will diffuse through the narrow diffusion corridor in a predictable way. The physical law that applies in this case is Fick's law of diffusion, which can be expressed for a one-dimensional case as follows:

$$\frac{dm}{dt} = DA\frac{\partial \rho}{\partial x} \qquad \text{(Rogers [11])}$$

Let l be the diffusion path length. If Fick's law is integrated with respect to the spatial variable x over the interval from $x = 0$ to $x = l$, we get

$$\frac{dm}{dt} = \frac{DA(\rho_l - \rho_0)}{l}$$

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where ρ_0 and ρ_l are the concentration values at the boundaries. The so-called binary diffusion coefficient D of water vapor in air has been experimentally determined. A value of 0.000026 m^2/sec (Klopfer [12]) may be used.

MASS TRANSFER OF GASES BY MEANS OF LEAKAGE AND PERMEATION

The VIPER simulation models two primary forms of gaseous mass transfer, namely, permeation and pneumatic leakage. Recall that permeation is the process whereby the gas penetrant dissolves in the surface layer of a barrier material, diffuses through it under a concentration gradient, and evaporates from the low concentration surface. Pneumatic leakage of gas occurs through interstices or passageways, such as pinholes, cracks and other porosities, by the more or less free flow of molecules in the gaseous state.

Pneumatic Leakage

The most important modes of pneumatic flow are viscous flow and molecular flow. (There are other modes and sub-modes of leakage that are not pertinent to the topic at hand, and are not treated in VIPER. Choked flow, occurring when the flow velocity approaches the speed of sound in the gas, is seldom encountered in small leaks. Turbulent flow is also seen infrequently in leaks. The transitional flow case, representing the "transition" between viscous flow and molecular flow, has been eliminated by assumption.)

In describing the modes of gas flow that operate in a leaking system, it is helpful to utilize the kinetic theory of gases as a model in interpreting the events that occur. Dushman [13] provides a fine discussion of the distinctions among the primary modes of pneumatic leakage. A summary of this discussion is as follows (where it must be borne in mind that gas flow is assumed to be isothermal): Gas flow may be divided into its different modes by specifying ranges of values of the Knudsen number, a dimensionless parameter that is the ratio of the mean free path of a molecule to a "characteristic dimension" of the leak passageway. If the mean free path is small compared to this "characteristic dimension" then collisions between gas molecules occur more frequently than molecular collisions with the leak passageway walls. These intermolecular collisions dominate the characteristics of the flow. In this case, then, (small Knudsen numbers) the gas acts like a continuous medium, in particular, a viscous fluid—giving rise to the name viscous flow. In contrast, when the mean free path is large compared to the "characteristic dimension" the flow of the gas is limited and characterized by molecular collisions with the leak passageway walls. Since there are relatively few intermolecular collisions, each gas species in the mixture acts independently of the others. Flow at large Knudsen number values is therefore called free-molecule, or molecular flow.

Viscous Flow

The equations governing viscous leakage are developed in consideration of the theoretical fully-developed flow of an incompressible fluid, wherein friction between the medium and the walls of the leak pathway induce a condition of zero flow velocity at the wall. The point of departure in the development is the Navier-Stokes equations of fluid flow. The reduction and integration of the Navier-Stokes equations results in the so-called Poiseuille (or Hagen-Poiseuille) equation, described in Dushman [13] for the case of a cylindrical tube with radius a:

$$Q = \frac{\pi a^4}{8\eta l} p_a (p_2 - p_1)$$

where p_1 and p_2 are the pressures across the leak, and p_a is the arithmetic mean of p_1 and p_2. In the range of applicability, this equation has been substantially verified experimentally.

Flow rates for, say, the cases of annular, elliptical and rectangular cross-sectional channels can also be developed, by means of imposing the appropriate boundary conditions on the Navier-Stokes equations.

The following excerpt from McMaster [3] summarizes the characteristics of the viscous flow of gases: "The two most important characteristics of [viscous flow] leaks are (1) the flow is proportional to the difference between the squares of the pressures across the leak and (2) the leakage is inversely proportional to the leaking gas viscosity.... Viscous flow occurs when the mean free path length of the gas is significantly smaller than the cross-sectional dimension of a physical leak."

Molecular Flow

The equations describing the rate of flow of gas under the conditions of free-molecule flow stand in contrast to the viscous flow mode. Scheiddegger [14] gives a theoretical development, wherein it is noted that, "The theorems obtained from the continuous matter theory have been observed to be in need of correction if the distance between the walls confining the fluid is of the same order of magnitude as the free molecular path length in the fluid.... [T]he quantity of gas flowing through a capillary is larger than would be expected from Poiseuille's formula [for viscous flow]." The development of the so-called Knudsen's law describing this mode of flow, is described as follows in Dushman [13]: "At pressures...where the mean free path is greater than the characteristic dimension, the rate of flow is limited, not by collisions between molecules, but by collisions of molecules with the walls. The manner of attacking the problem of flow in this range theoretically and the first experimental verifications of the theory are due to Knudsen...." For the case of a cylindrical tube with radius a, Knudsen's equation can be written as

$$Q = \frac{2\pi a^3}{3l} v_a (p_2 - p_1)$$

where p_1 and p_2 are, respectively, the downstream and upstream pressure of the leaking gas under consideration.

It is crucial to understand the characteristics of molecular flow in relation to the pressure differential across the leak. McMaster [3] observes: "In molecular flow, molecules travel independently of each other.... Therefore, a certain amount of separation of gaseous species takes place during flow through a leak. In molecular flow, the gas molecules travel independently of each other. Thus, it is possible for random molecules to travel from a part of a system at low pressure to another part of the system at a higher pressure."

Therefore, in the application of molecular leakage theory to the penetration of water vapor into sealed volumes, the pressures p_1 and p_2 appearing in Knudsen's law are taken to be the partial pressures of water vapor on either side of the seal barrier. In this sense, the molecular flow of gas through leaks

resembles the permeation of water through barrier materials by means of diffusion.

Diffusion by Permeation

We begin with a basic definition of permeation within the context of solid barrier materials, such as those used to seal electronics packages. Rogers [11] declares, "The transmission of penetrant through a polymer membrane free from cracks, pinholes, or other flaws normally occurs by an activated diffusion process. The condensed penetrant dissolves in the surface layers, migrates through the bulk material under a concentration gradient, and evaporates from the other, low concentration surface. After a relatively short transient-state build-up, a steady state of flow is attained with a constant transmission rate, provided a constant pressure difference is maintained across the film."

A great deal of discussion exists in the literature on models of permeation on the molecular level. These address the microstructure of the material itself, and involve such concepts as "interstitial" transfer of mass (Roff [15]) and "convective diffusion" [16-17]. It is only the so-called activated diffusion that concerns us here. In spite of many molecular-level descriptions of permeation, there has been a need to formulate a macroscopic mathematical model of the permeation process.

Equations Governing Permeation

Numerous sources in the literature [3, 5, 11, 15] give comparable theoretical development and presentation of the equations governing the permeation of a barrier material by a penetrant gas. Fundamental in the development of these equations are the laws of Fick and Henry. Fick's first law of diffusion expresses that in steady-state flow, the rate of permeation is directly proportional to the concentration gradient across the barrier. When Henry's law is obeyed, there is a linear relationship between the concentration of the penetrant in the surface layer of the barrier and the (partial) pressure of the penetrant at the boundary. When these two fundamental laws are combined, we obtain the operative form of the permeation equation:

$$\frac{dq}{dt} = P \frac{A}{l} (p_1 - p_2)$$

This is the working model of the permeation equation used in the VIPER simulation. The analyst needs to understand the limits of applicability of this model. Variability from the basic, operative form of this mathematical model can occur under the influence of temperature variations [18] and material thickness [16, 19-22], the presence of fillers in the seal material [16, 18, 23], aging of the seal material [18], and even radiation [24]. Thus, one of the primary conclusions of literature research is that the analyst may not use the operative form of the permeation equation with total impunity. Flagrant disregard of the limitations of applicability will reward the user with inaccurate predictions.

Permeation Coefficient, Gaseous Conductance, and WVTR

The rate of permeation by diffusion of water vapor is modeled as a process which is directly proportional to (1) the instantaneous partial pressure differential of water vapor across the seals, (2) the area of the seals normal to the direction of flow, and (3) a "permeation coefficient," whose value depends upon the seal material type. Furthermore, the rate of permeation is inversely proportional to the length of the permeation pathway. Diffusion through "parallel" pathways into a sealed volume is additive. The analog of the permeation of water through seals is heat flow, wherein parallel thermal conductances are summed to form the total conductance. (Seal conductances in series are combined analogous to thermal resistance components that are in series with one another.) Therefore, to model the water vapor penetration into a sealed volume consideration must be given to the number, material type, dimensions, and compression of all its seals.

For any seal, we define a quantity called gaseous conductance for permeation to be $C = PA/l$, having units of volume per unit time. The total permeation characteristic of a sealed volume with multiple permeation pathways—for seals in parallel with one another—may be summarized by the total gaseous conductance, which is the combination of the individual seal gaseous conductances.

The permeation coefficient P represents a quality of the material itself, with other elements—the seal dimension and partial pressure gradient across the seal—factored out. Published values of the permeation coefficient P do not exist as such in the literature, however. A common parameter that is published (e.g., Helander & Tolley [25]) is the Water Vapor Transmission Rate, or WVTR. The WVTR of a material, in order to be meaningful, must be referenced along with a material sample thickness and humidity condition for which the WVTR is valid. A proper conversion from WVTR to the permeation coefficient P is accomplished as follows:

$$P = \text{WVTR} \frac{RT}{M} \frac{l}{\Delta p}$$

where T was the absolute temperature, Δp was the partial pressure differential across the material and l was the sample thickness, all applicable for the conditions under which the material was tested.

SOLID ADSORBERS

Molecular Sieve Desiccant

The kind of desiccant that is preferred for humidity control in missile electronics packages is molecular sieve Type 4A. Molecular sieve desiccants are physical (not chemical) adsorbents that are designed to have high equilibrium adsorption capacity for water, even at very low concentrations of water in the surrounding air. This is illustrated in Figure 1, where, for a fixed desiccant temperature, the curves (called isotherms of the desiccant) show the capacity (or equilibrium loading) of the molecular sieve versus the partial pressure of the surrounding air. Often it is glibly stated that a molecular sieve can adsorb 20% to 25% of its weight in water. This may be true under certain circumstances, but from the isotherms it is obvious that long before the desiccant reaches its maximum equilibrium loading, the humidity in the surrounding air has reached a level that is too high for many defense applications. The sizing of molecular sieve desiccant for a particular application must take into account the desired level of dryness for the system. For example, suppose it is desired to maintain a dew point of −25 °C within a sealed package which is at room temperature (25 °C, or 77 °F). The partial pressure of water that

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corresponds to this dew point temperature is 63.5 Pascal, or 0.0092 psi. From the molecular sieve isotherm, we see that the equilibrium loading of the desiccant will be 18.6% (not 20% to 25%). If higher temperatures are expected, then the appropriate isotherm must be used, and the desiccant efficiency will be lower.

Figure 1
Molecular Sieve (Type 4A) Equilibrium Adsorption Isotherms
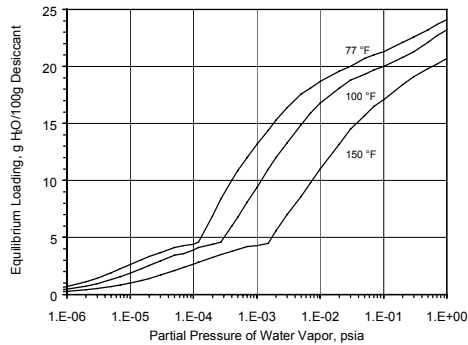
Source: "Union Carbid Molecular Sieves: Water and Air Data Sheets," Union Carbide Corporation, Molecular Sieves Department, Tarrytown, NY

Another important consideration is that the equilibrium loading of the desiccant represents the mass of water vapor per mass of activated (unused) desiccant. Typically, when sizing a desiccant for an application one needs to budget an extra amount because the water content of the desiccant as it is installed may already be about 2% to 5% by mass. This budgeting allows for water adsorption during manufacture, shipping, storage and installation.

Desiccant Equivalent and the Lag Loop Phenomenon

All materials adsorb a quantity of water that depends upon the temperature and humidity of the surrounding air to which they are exposed. In this regard, all materials act as a "desiccant equivalent." The adsorption characteristics of various types of desiccants are well-known. See, for example, Figure 2, where the superior qualities of the molecular sieve desiccant are illustrated. Molecular sieve has a high adsorption capacity for water at low humidities, while the other desiccant varieties possess a somewhat linear relationship between adsorption capacity and relative humidity.

The adsorption characteristics of many non-desiccant materials are known as well. The adsorption capacity for plastics, painted metals, fibers and many other materials also show an approximately linear dependence on the relative humidity of the surrounding air. This is illustrated by the dashed line in Figure 2, which is representative of the total adsorption characteristic of a variety of desiccant equivalent materials sealed within, say, a missile guidance section or electronics subassembly box.

It may seem from Figure 2 that the desiccant equivalent would provide a very insignificant contribution to the analysis of humidity within a sealed volume, since the slope of its graph is very small. But it must be remembered that the mass of the desiccant equivalent is relatively large, which offsets its small adsorption capacity rate. For example, it is interesting to note that as a result of a dry-out test on an air-to-air missile guidance

section (Myers [26]) the desiccant equivalent capacity was found to be nearly 10 grams of water.

The equilibrium water content of desiccant equivalent materials also vary at a given relative humidity with changes in temperature. As a rule, materials can hold more water at a cooler temperature for a constant relative humidity. (This is also true for molecular sieves; note the relative placement of the three isotherms in Figure 1.) Adsorption of water from the surrounding gas mixture by a material takes place whenever the partial pressure of water vapor in the surrounding air exceeds the vapor pressure of the water in the material, and desorption occurs when the opposite condition is in effect.

Consider the case of a sealed unit that is subjected to continual diurnal variations in temperature. The amount of water in a material exposed to air in a sealed volume is continually undergoing change as a result of two factors. First, the moisture content of the air (and hence the partial pressure of water vapor) varies constantly, and second, the temperature of the air and the material is continuously changing. These two interrelated factors can be most easily explained in terms of the so-called "lag loop" phenomenon, which is a graphical method of plotting the dew point temperature versus the relative humidity. The lag loop is explained in Mueller [1].
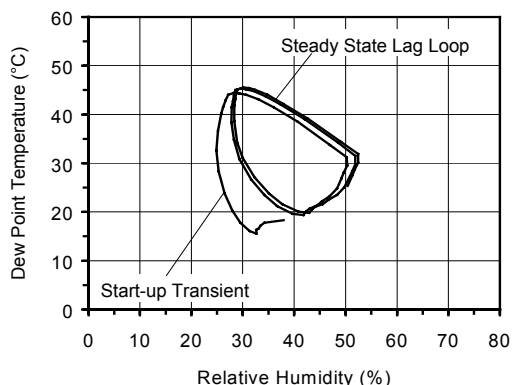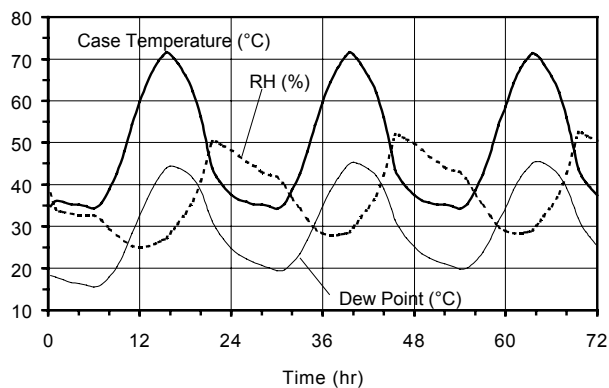
Figure 2
Relative Humidity Effect on Desiccants
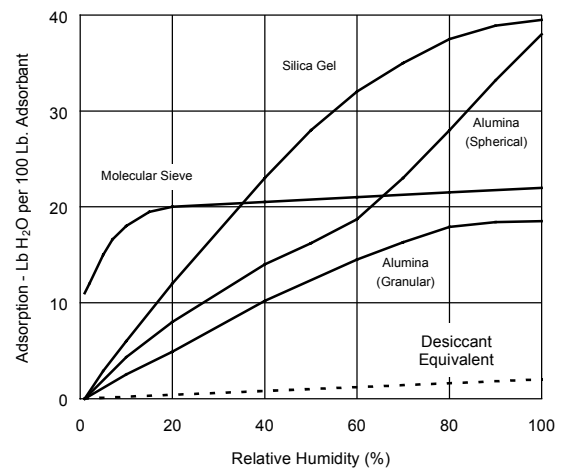
From monograph "Davison Molecular Sieves," W. R. Grace & Co., Davison Chemical Division, Petroleum Chemicals Dept., Baltimore, Md.

In the VIPER simulation, the quantity of water in the desiccant equivalent is modeled as a first-order lag. The value of the time constant will determine the shape of the lag loop. The size of the loop and the positioning of the loop on the lag loop graph will be determined by the adsorption capacity of the desiccant equivalent and the volume of air in the sealed unit. The lag loop time constant and adsorption capacity are quantities that can be determined experimentally. The adsorption capacity can be determined by a dry-out experiment, and the lag loop time constant can be determined by the kind of experiment described in the previous paragraph, where an instrumented test article is subjected to several temperature cycles, while dew point temperature and relative humidity are monitored.

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Figure 3
Lag-Loop Experiment for Surface-to-Surface Missile

A revealing illustration of the lag loop is given in Figure 3. A surface-to-surface missile, encased in its launch tube/storage case, was instrumented with dew point and relative humidity sensors. (No desiccant was present.) The temperature was cycled over a period of three days to simulate a severely hot storage environment. The resulting internal relative humidity and internal dew point temperature are plotted along with the temperature profile in the upper graph of Figure 3. When the relative humidity and dew point are plotted against each other, the outcome is the lag loop illustrated in the bottom graph of Figure 3. Note how the absolute humidity, represented by the dew point, varies in response to the rising and falling of the temperature. Also note that there is a lag between the adsorption and desorption of water in response to the forcing function, which is relative humidity.

COMPUTER SIMULATION

The computer model VIPER was constructed in order to simulate the physical processes discussed in this paper. It has been adapted to analyze many kinds of sealed units, such as missile guidance sections, sensor and electronics subassemblies, and even an entire missile inside its desiccated launch tube/storage canister.

The input data set consists of the initial conditions of the air and materials of the sealed unit, the quantity of desiccant, the desiccant equivalent dynamic parameter (time constant), parameters defining the permeable membrane of the desiccator unit, plus simulation control variables such as the integration

time step size and print interval. The output consists of a wide variety of program variables that can be used to monitor the performance of a simulation run: the humidity of the sealed air (measured in relative or absolute humidity, dew point, concentration in parts per million, or partial pressure of water); the water content of the desiccant and the sealed materials (the desiccant equivalent); the instantaneous rate of water vapor flow into (or out of) the unit by means of leakage and permeation; and the cumulative water vapor mass leaked and permeated into or out of the system since the time of sealing.

The executive routine of the simulation controls the initialization, time integration, printout and plot file generation functions. Separate modularized subroutines exist for the following simulation elements:

(1) gaseous conductance of the seal set
(2) permeation coefficients for seal materials
(3) desiccator dynamics
(4) molecular sieve adsorption equilibrium characteristic
(5) desiccant equivalent adsorption dynamics
(6) ambient environment
(7) functions for determining dew point and the vapor pressure of water
(8) simulation utilities, the most important of which perform -

• the time integrated solution of a dynamic system (specified in the s-domain)

• interpolation (one- and two-dimensional)

• secant and bisection methods for finding the zeros of nonlinear functions

The "heart" of the simulation is a subroutine that maintains a kind of dynamic equilibrium, at each integration time step, within the sealed unit. What is meant by "equilibrium" is explained as follows. We know that the ideal gas law must be obeyed, that is, there is a relationship between the partial pressure of water and the mass of water vapor within the unit. But in addition, at each instant of time the mass of water within the air volume of the unit must be consistent with all of the dynamic processes that are occurring simultaneously: permeation; leakage; and adsorption (or desorption) into (or out of) the desiccant and desiccant equivalent. The law of conservation of mass must also be implicitly obeyed. Each of these dynamic processes is also dependent upon the instantaneous state of the unit humidity, that is, the partial pressure of water vapor in the sealed unit. Thus, there is a kind of "circular" interdependence among all of the physical processes that are modeled in the simulation. The consequences of all of these physical processes must be solved simultaneously to maintain the dynamic equilibrium just described. Such a solution cannot be achieved in closed form. The way in which the solution is obtained in the simulation program is by a numerical method. A (highly) nonlinear function of water vapor mass in the unit is solved by means of the secant method, whereby an initial posit of the water vapor mass is iterated until specified convergence criteria are met.

Simulation Example

An example of VIPER simulation results is presented here for the Guidance Section of an air-to-air missile. This simulation has been calibrated by extensive testing. The Guidance Section is assumed to have 135 grams of molecular sieve to maintain dryness. Figure 4 shows the absolute

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humidity, in terms of dew point temperature, as a function of time for 15 years after sealing of the Guidance Section. The first year, during which a dryout of the desiccant equivalent materials occurs, is spent in ready storage. During the second year the missile is subjected to an alert status environment. The next eight years are spent in dormant storage. This is again followed by one year each in ready storage and alert status. The final three years are spent in dormant storage. The ready storage and dormant storage environments have a diurnal temperature cycle that varies between 91 °F and 160 °F, while the alert status environment ranges between 78 °F and 95 °F. The ambient humidity for all three environments is quite high.

Figure 4
**Air-to-Air Missile Guidance Section**
Humidity Analysis
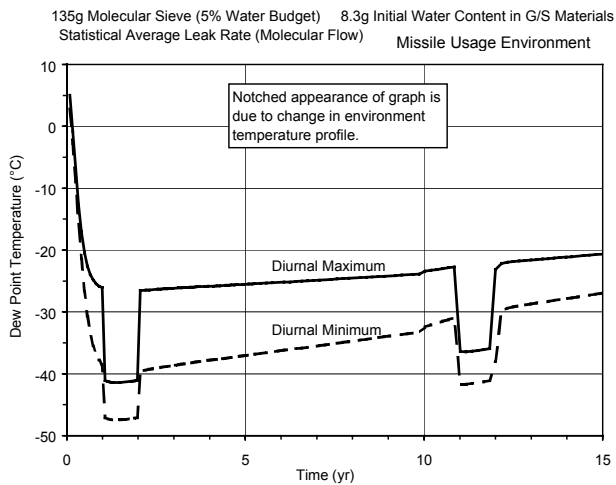
Note that during the first year there is a prolonged dryout process, during which the desiccant package is pulling water vapor out of the sealed air, to which the desiccant equivalent responds by desorbing its water. High temperature cycling aids this process, since, as we have seen, materials can hold less water at higher temperatures.

The fact that materials can hold less water at higher temperatures explains the appearance of two features of the graph in Figure 4. First, there is a noteworthy variation in dew point temperature over the period of a single day as the temperature cycles. Therefore, the "Diurnal Maximum" and "Diurnal Minimum" curves are separated by about 10 C° dew point temperature. This shows that the "lag loop" is in operation even within a desiccated sealed volume at very low humidity. (Compare this with the results of the lag loop experiment for the encased missile in Figure 3, where there was a 25 C° swing in dew point temperature.) Second, the "notches" in the graphs during the periods of alert status (the second and eleventh years of the simulation) are due to the cooler temperature profile in effect during these periods, in contrast with the higher temperatures of the storage environments, when less water can be retained in the desiccant equivalent.
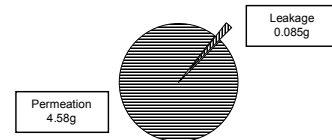
Note that after the initial dryout period there is a relentless rise in dew point temperature during the life of the missile. This is owing to the continual addition of water vapor to the sealed unit, mostly due to permeation.

Figure 5
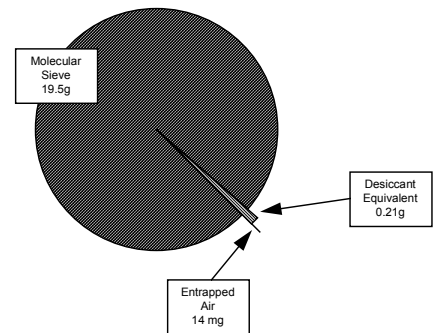**Air-to-Air Missile Guidance Section**
Humidity Analysis
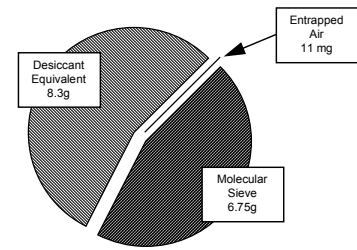
The pie charts in Figure 5 illustrate the disposition of water in the Guidance Section at the time of sealing, the contribution of permeation and leakage which adds to this initial water quantity, and the final disposition of the water. The areas of the graphs represent mass of water vapor. These graphs illustrate the relative unimportance of water vapor in the entrapped air versus the latent water in the desiccant equivalent. Also, the magnitude of water vapor penetration due to leakage relative to that due to permeation is shown. Although this example is given for a specific application, the results are in many ways typical of what is seen in general for missile guidance sections.

Lessons Learned and Design Decisions

Extensive humidity analysis activity at Raytheon, utilizing the VIPER simulation tool, has resulted in a useful collection of lessons learned and design decision guidelines:

(1) Molecular sieve is the desiccant of choice for defense electronics.

(2) For the purpose of long-term control of humidity in guided missile electronics, a dry nitrogen purge is not very beneficial.

(3) Pre-dying the desiccant equivalent of a unit does not necessarily reduce the desiccant size significantly. In any case, pre-drying can be costly, because the unit must be protected (in

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a desiccated dry-box) from factory air prior to and during assembly, until the unit is sealed.

(4) Permeation is usually the largest contributor of water. Therefore, select relatively impermeable seal materials to keep the desiccant size reasonable. Also, use seals in series to reduce permeation.

(5) Since the contribution of leakage is usually small (barring a gross leak in the system), the benefit of a leak test ought to be seen more as confirmation that all seals are in place as a barrier against permeation, rather than as a test to ensure that the leak rate is very, very small. (Paying careful attention to leakage while being unmindful of permeation is an illustration of "straining out gnats while swallowing camels.")

(6) Great care must be taken when interpreting or communicating units of leak rate with its applicable differential pressure. Attention must be also given as to whether the reported leak rate is that of a tracer gas (at its pressure differential) or whether a specified leak rate has been converted to the equivalent value for, say, nitrogen gas.

(7) Long-term humidity predictions are weakly dependent on an estimate of the free air volume of the interior of the sealed apparatus under consideration.

(8) Consider using impermeable metal seals if there is only a minimum space available for desiccant.

(9) Conformal coating provides many benefits, such as protection against salt fog and liquid water. However, it is not effective as a long-term protection against humidity.

(10) Humidity indicators are not useful in guided missile applications because they are not sensitive enough to indicate a problem until the dryness requirement has been exceeded for a significant period of time.

(11) The ambient temperature and humidity environments used in an analysis are extremely important to the outcome of long-term humidity predictions for the interior of the desiccated volume. These environments should be tailored to maximize exposure to worst-case high humidity at elevated temperatures, as this will provide the most severe trial for the seal permeability against water. Therefore, for the purposes of determining maximum water loading, it is not important to include captive carry (for air-to-air missiles) or cold temperature storage episodes. (These events may be important for other reasons, such as determining the likelihood of condensation or sublimation.)

(12) The dryness requirement should be a prominent consideration throughout the entire design process, and should be communicated clearly to subcontracting suppliers.

(13) It is preferable to specify the dryness requirement in terms of an absolute humidity (i.e., dew point temperature or concentration), not a relative humidity.

CONCLUSION

The VIPER simulation is a comprehensive engineering tool that is used to ensure the compliance of missile systems designs with dryness requirements. VIPER has been calibrated against test results, adapted to a wide variety of package designs, and has become an integral part of Raytheon's efforts toward the attainment of cost savings and high reliability.

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