ONEIDA RESEARCH SERVICES, Inc.
8282 Halsey Road • Whitesboro, New York 13492 • Tel: (315) 736-5480 • Fax: (315) 736-9321

# Gas Compositions in Sealed Medical Device Enclosures

R.K. Lowry*, R.C. Kullberg**, D.J. Rossiter***
Oneida Research Services, Inc., 8282 Halsey Road, Whitesboro, NY13492

* rlowry98@aol.com; +1-321-777-9949; electronic-materials.com; technical affiliate of ORS & consulting engineer
**rckullberg@gmail.com; +1-719-966-4296; asanatechne.com; technical affiliate of ORS & consulting engineer
***djrossiter@ors-labs.com; +1-315-736-5480; www.ors-labs.com; Manager, Internal Vapor Analysis, Oneida Research Services

## INTRODUCTION

There is a growing use of hermetic packages in the medical device industry, particularly for implantable devices. At the same time there is a growing number of high profile failures occurring in the industry.

A key contributor to these failures is moisture. More than 30 years ago, serious field failure incidents demonstrated that too much moisture within sealed microelectronic packages in mission-critical military and space applications impaired the functional reliability of those components. The main cause of failure due to moisture was galvanic corrosion of contacts and metal interconnects on IC chips. Sealed, implantable medical devices are equally mission-critical and are equally vulnerable to the deleterious effects of moisture, particularly in vivo. Implantable devices in vivo must maintain seal integrity with no internal materials outgassing in order to control internal moisture concentrations. This is not reliably occurring in the field with growing consequences, both medically and legally.

The two principal causes of excessive moisture in any sealed enclosure are materials outgassing and/or failure to achieve or maintain the enclosure's hermetic seal. Focus has traditionally been on controlling leaks to prevent elevated moisture. This focus continues with new capabilities for helium leak detection approaching $1x10^{-13}$ cc atm/sec, a more than four orders of magnitude improvement. However, little real data have been published differentiating between hermeticity loss and materials outgassing as root causes of elevated moisture. In fact there is debate as to whether leaks in the $10^{-10}$ to $10^{-13}$ range even exist, or are of practical significance.

Decades of work in hermetic micro electronics packages shows that good seals are achievable, and that control of materials and processes (M&P) becomes much more critical. However, process control efforts have traditionally focused on controlling leaks. This focus on leaks is due to well-developed measurement technology.

Other concerns for M&P control need really long term testing data to demonstrate. Such long-term data is now available thanks to a group of old archival samples. Internal gas analysis data for 200 archival units of various types of microelectronic packages is reviewed. Materials outgassing is the cause for excessive moisture levels in ~75% of the sealed devices that are noncompliant to the 5000 ppmv maximum moisture content imposed by military specifications. Attributing these moisture concentrations purely to leaks is an overly simplistic approach.

## DISCUSSION

A recent description of leak mechanisms[1] confirms that leak avoidance is critical for cavities sealed under vacuum. Further, this work depicts Fick's Law diffusion as the means of moisture ingress for enclosures with no pressure differential with the outside. However, the contributions of outgassing mechanisms are also understood to be significant over the lifetime of a hermetically sealed device. It is important to understand what the internal gas composition ‘finger prints’ are for these various contributors. Consequently, an important benchmark for understanding what is really occurring within a hermetically sealed cavity is the composition of natural air.

If air has leaked into an enclosure sealed in pure inert gas(es) not containing Ar, the internal gas content should show the $O_2$ and Ar components of air in roughly their natural ratio. Absolute concentrations will be less than those in ambient air (i.e. “diluted”) if the leak has not yet caused the enclosure cavity to reach equilibrium with outside air. Moisture content will vary depending on temperature, humidity, and atmospheric pressure of ingressed air and whether materials outgassing has contributed to moisture levels within the cavity. Carbon dioxide in an enclosure exceeding roughly 0.04v%[2] is not from air and clearly indicates outgassing, as does the presence of any volatile organic compounds. Helium (if originally present) retained in any unit would argue against a significant leak mechanism.

The key point is that it is quite possible to engineer and control M&P to achieve dry packages at time zero, so as to create the most protection for the package. It is much harder to engineer and control M&P to be as certain of leak prevention, as it is to be certain of dry initial conditions. Consequently, leak rates and associated testing ought to be the secondary line of defense against moisture problems, while the primary line of defense ought to be M&P selection and process control. This contention is supported by the results of the current work.

## SAMPLES & ANALYSIS

Three different groups of internal gas analysis data and samples were reviewed. Data was generated by three different commercial service laboratories, each with suitability for MIL-STD-883, Test Method 1018.

### Sample Groups

Sample Group 1

This group contained 15 microcircuit packages built 10-20 years ago. The units were never placed in service and were stored for their entire lifetime in a plastic bag in a desk drawer. Eight were TO metal cans, having a nickel lid seam welded to a gold-plated header with eight pins entering through glass-to-metal seals. Seven were gold-plated Kovar flatpacks or DIPs of various sizes and lead counts with braze sealed lids. Most units had cavity volumes ≤0.1cc. The analytical focus for this group was to determine if the concentration of internal moisture was elevated after long storage lifetimes by poor hermeticity (leaks) or by materials outgassing within the cavity. Oneida Research Services performed this testing.

Sample Group 2

This group contained 71 units from a Test Method 5011[3]qualification study of polymeric adhesives.[4] Study of this group evaluated adhesive suitability, so moisture from material outgassing would likely be present. The focus was to determine if poor hermeticity contributed to elevated moisture content.

Sample Group 3

This group contained 114 units from a private database (author R. K. Lowry’s) compiled from many different clients. The group comprised microcircuit packages of a wide variety of styles and cavity volumes. Clients had obtained gas analysis data on the units for a variety of reasons including pre-shipment inspections, materials and process qualifications, DPA, failure analysis, and engineering studies. Details necessarily remain proprietary, but reviewing the gas analysis results with a focus on causes of elevated moisture content is instructive.

### Data Analysis

Except for Group 1, the choice of laboratory was by clients and not authors of this paper. Data were not compared for inter-laboratory differences. The study focus was to generally discern causes for noncompliance to the expectation of 0.50v% maximum internal moisture, as defined by MIL-STD-883.

Numerical values in gas analysis reports were rounded to two decimal places and tabulated as volume percent (v%), where 1v% = 10,000 ppmv. The data sets were exhaustively tabulated. While they do not fit into the space limitations of this extended abstract format, they are available in full detail to the interested reader. Please contact the authors if you wish a copy. No entry in a cell in the data tables indicates that the species reported either as <0.01v% or as not detected.

## RESULTS AND DISCUSSION

Table 1 summarizes the aggregate results for moisture compliance:

| Group | Total Units | Units >0.50v% $H_2O$ |
|---|---|---|
| 1, "Old" units | 15 | 0 |
| 2, 5011 Qual units | 71 | 18 |
| 3, Consultant's database | 114 | 41 |
| Total | 200 | 59 (29.5%) |

Table 1. Non-compliance to the 0.50v% moisture limit of the three sample groups

The first reaction to 29.5% of units noncompliant on moisture is alarm, justifiably if results were solely from pre-shipment inspections or process control measurements. But this study includes units that might have moisture control problems anyway, so the high incidence of noncompliance is not surprising.

Results for each of the three sample groups were tabulated and their overall gas composition "signatures" considered in detail for the likely causes of internal moisture.

### Group 1, "Old" Units

All 15 TO99 cans and braze seal units are free of significant moisture, from either materials outgassing or ingress through leaks, throughout their entire lifetimes. These units had eutectic substrate attach and no polymeric materials inside, which helps achieve and maintain moisture outgassing control over long periods of time.

The results from Group 1 were gratifying. Robust M&P rendered these package styles both dry and truly hermetic for long periods of time of practical significance to device reliability. The materials and technology remain available today.

### Group 2, 5011 Adhesive Qualification Units

All units in this group contain polymeric substrate attach materials which require careful choice and robust pre-seal processing to insure moisture control. There were 71 total units, of which 18 were noncompliant and 53 compliant on moisture. None of the 53 compliant units contain $O_2$ and most contain no Ar. Absence of $O_2$/Ar indicates that up to the time of analysis none of the units had begun to acquire moisture by air ingress.

Three samples contain components of air and fluorocarbon. This defines these units as "variable" or "one-time" leakers, as discussed later. These units are a special case of induced non-hermeticity. They are most likely hermetic except during stresses of burn in or leak test.

One unit contains $O_2$ and Ar in a ratio that, while not identical to air, probably identifies it as a leaking device. The He content in this sample is less than half that of a brother unit and it contains no FC. However, its $CO_2$ content at 0.48v% is too high to be explained by air ingress alone, so outgassing is also occurring in this unit. Units with polymeric materials tend to have levels of $CO_2$ and organics that track with moisture content. On average, compliant units contain only about one-third as much as much $CO_2$ and hydrocarbons as noncompliant units, further indicating outgassing as the source of moisture in units in this group.

The 14 remaining noncompliant units contain no detectable $O_2$ and negligible Ar (though three have somewhat elevated Ar). All contain some level of volatile organics, and most contain $CO_2$ at concentrations far above that of natural air. These units are noncompliant due solely to materials outgassing.

Twelve of the 53 compliant units contained moisture between 0.40-0.50v%. Any loss of hermeticity, or any additional outgassing, would quickly push those units above the recommended maximum moisture content. This underscores the importance of qualifying polymeric materials and their processing with respect to their moisture behavior.

To summarize the results from Group 2, 17 of 18 noncompliant units contain moisture due solely to outgassing from materials. One unit showed evidence of air ingress, however outgassing also contributed to its total moisture content.

**Group 3, Database of Miscellaneous Part Types**

Group 3 included 114 units of a wide variety of package styles and sizes. It had 41 units (from 31 different lots) noncompliant on moisture content. The gas composition "signatures" of the 41 noncompliant parts fell into four distinct categories:

| Category | Status | No. Units |
|---|---|---|
| 1. Nonconforming units with components of air | Non-hermetic enclosure | 7 |
| 2. Nonconforming units with no components of air | Outgassing materials | 20 |
| 3a. Nonconforming units with components of air and FC | Probable one-time leaker | 9 |
| 3b. Nonconforming units with no air, but FC | Definite one-time leaker | 5 |
| Total | | 41 |

Table 2. Categories of nonconforming units among 100 unit (31 sample group) database.

Category 1 is that of probable leakers, in which $O_2$ and Ar are present. Seven of the 41 noncompliant units exhibit this "signature." Several of them contain more-or-less stoichiometric air. The others contain $O_2$ and Ar in "diluted" amounts, with $O_2$/Ar ratios from 3.1 to 11.6, unlike that of natural air. But the $O_2$/Ar presence probably indicates at least some air ingress (though the He in units 8-2 and 8-3 begs that question). Outgassing contributed to the levels of moisture in all units except 8-5, as $CO_2$ is elevated far above that of natural air in the others. These seven units are classified as containing at least some moisture due to air ingress, per the considerations of this study.

Category 2 is a group of 20 units that are noncompliant, but contain negligible or no components of air, and no fluorocarbon. The "signatures" of the various species present point to outgassing mechanisms as the source of nonconformance. Sample to sample variation in this group is impacted by various factors including improper curing of the organic materials present and poor pre-seal baking of package piece parts.

Category 3 is a group of 14 units that are noncompliant and contain fluorocarbon. Within this group, subgroup 3a has 9 that also contain components of air, and subgroup 3b has 5 that do not contain components of air. Such behavior is indicative of units that had a one-time leak event due to stresses during leak check that allowed the ingress of fluorocarbons.

**Pressure-Sensitive Leakers**

Three units in Group 2 and 14 units in Group 3 resemble those with glass-to-metal seals having variable leak rates,[5] e.g. units with leaks apparently induced by external thermal or physical stresses such as clamping during burn-in which temporarily breaks the oxide-sealed surfaces in glass-to-metal seals. Because of this characteristic, noncompliant units in Sample Group 2 or 3 that contain fluorocarbon and/or a gas signature indicative of such temporary breaks are not counted as "on-the-shelf" or "in-service" units with moisture elevated by normal air ingress.

**Peculiar Data**

Not all gas compositions are readily explainable. Table 3 shows some examples to challenge the reader. The data on the explanted hermetic biomedical device was obtained from a legal filing in public record. The device contained negligible air, or at least not enough to explain 33v% $H_2O$. (Not all data were reported in the filing). How can so much water be inside this unit? The large TO's A and B are brother units. A has the right amount of Ar for air, but no $O_2$. The level of moisture is too high to be explained purely by air ingress. Was the $O_2$ consumed by some kind of chemical reaction that produced water? The organic substance reported was specifically methanol. Was there a chemical reaction of $O_2$ with $CH_4$ to make water and methanol? (No balanced reaction is evident unless $H_2$ is available). Unit B also has much water but a completely different gas signature. The LCC is noncompliant by a small amount, but has 23x as much $CO_2$ as air. Where did all the $CO_2$ come from, and is that the explanation for noncompliance? Proposed explanations for these data are solicited from the reader.

| | Explanted Biomed device | Large TO A | Large TO B | 48 ld LCC |
|---|---|---|---|---|
| **Nitrogen** | nr | 70.60 | 87.20 | 98.40 |
| **Oxygen** | 0.17 | | | |
| **Argon** | nr | 0.91 | | |
| **Water** | 32.91 | 24.70 | 10.10 | 0.67 |
| **Carbon Dioxide** | nr | 0.40 | 0.06 | 0.91 |
| **Hydrogen** | nr | | 0.04 | 0.07 |
| **Helium** | 13.55 | | 2.56 | |
| **Fluorocarbon** | nr | | | |
| **Ammonia** | nr | | | |
| **Organics** | nr | 3.77 | | |

nr=not reported

Table 3. Peculiar hermetic enclosure gas compositions.

## RESULTS & CONCLUSIONS

### Results

1) Fifteen TO can and braze seal units more than 20 years old maintained negligible internal moisture due to robust materials processing that prevents both outgassing and air ingress.

2) Seventy-one units from a Test Method 5011 adhesive qualification study had 18 units noncompliant on moisture content. One of these contained an internal gas signature consistent with air ingress. Air ingress did not account for all the moisture in that unit.

3) One hundred fourteen units of a wide variety of package styles and sizes had 41 units noncompliant on moisture content. Seven contained an internal gas signature consistent with air ingress, but only one of these contained air exclusively.

Table 4 summarizes the results with respect to sources of internal moisture:

| Sample Group | Number of Units | Noncompliant Units | Noncompliant: Air ingress | Noncompliant: outgassing exclusively | Noncompliant: variable leak |
|---|---|---|---|---|---|
| 1. Units 10-20 years old | 15 | 0 | 0 | 0 | 0 |
| 2. 5011 Adhesive Qual | 71 | 18 | 1[a] | 14 | 3 |
| 3. Consultant's database | 114 | 41 | 7[b] | 20 | 14 |
| Totals | 200 | 59 | 8 | 34 | 17 |
| Percentages | | 29.5% of units are noncompliant | 13.6% of the noncompliant units | 57.6% of the noncompliant units | 28.8% of the noncompliant units |

a. This unit showed evidence of outgassing also.
b. Only one of these units showed air ingress exclusively.

### Conclusions

Overall, 57.6% of noncompliant units in this study contained elevated moisture due solely to materials outgassing with no evidence of air ingress. An additional 28.8% of the units behaved as variable leakers, a condition not attributed to simple air ingress during storage or service. Only 13.6% of noncompliant units showed evidence of air ingress, and only one of those appeared to contain air exclusively with no evidence of outgassing.

Piece part and materials selection and robust processing are the essential first line of defense for internal moisture control of sealed enclosures. Concern for hermeticity becomes important only after materials and processes are in place to assure that product is dry as-sealed and is as free as possible of outgassing.

It is recognized that certain package types, sealing equipment, suppliers of materials and equipment, and seal processes may be unique special causes of hermeticity issues. Engineers must address these special causes, while maintaining control of materials outgassing, as an integral part of investigating and eliminating special causes of hermeticity failure.

This study is based on a relatively small dataset. Much larger databases are available in industry. The authors solicit inputs from anyone who can share data with the community as a whole to enlarge this study.

## References

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