

On Excess CO₂ within a Hermetically Sealed 14-Pin Butterfly Package: Solubility of CO₂ within Fluorocarbon Liquids

Mark M. De Luna and Todd Uramoto
Northrop Grumman Mission Systems
21240 Burbank Blvd
Woodland Hills, CA 90660 United States
Ph: 818-715-2272;
Email: Mark.DeLuna@ngc.com

Abstract

In this paper, we examine the presence of excess CO₂ found within a hermetically sealed 14-pin butterfly package. Excess CO₂ within a hermetically sealed package can suggest that the internal structures of the package have degraded significantly over the lifetime of the package. The level of CO₂ discovered within the butterfly package was inconsistent with the controlled sealing gas environmental composition, and the gas composition of concurrently sealed packages. A literature review of industry technical papers and academic studies show that fluorocarbon liquids preferentially absorb CO₂ at levels 4-5 times greater than other gasses such as oxygen and nitrogen. Previous experimental and computational methods found that fluorocarbon liquids can absorb CO₂ at levels of 1.5-1.6 mol%, which is greater than the calculated maximum amount of absorbed CO₂ (0.91 mol%) found within the butterfly package. The Internal Gas Analysis (IGA) of the butterfly package confirmed that it is highly likely that when butterfly package ingested the fluorocarbon liquid, the CO₂ was absorbed in solution and thus ingested into the device. Given that the butterfly package was initially filled with 12% ppmv of helium and it retained the helium at a significant level, the phenomenon of a one-way leaker preserved the evidence of CO₂ absorbed in the fluorocarbon liquid.

Key words

Fluorocarbon, Hermeticity, Absorption, Butterfly Package

I. Introduction

Hermetically sealed packages are an important for many industrial, government, and military applications. In certain applications, analyzing the gas content at the conclusion of extensive testing provides valuable information on the integrity of the hermetic seal. Typically, the result is that the gas content internal to the package is consistent with expected gas content from the nominal fill gas composition. If there is a differing gas content, it is assumed that the package is no longer hermetically sealed. However, the device typically undergoes leak testing to ensure the package is hermetic. Therefore, if the package internal gas content differs from the fill gas composition and the package was deemed hermetic from multiple industry-standard leak tests, then the phenomenon of a one-way leaker is hypothesized.

The internal gas content of five 14-pin butterfly packages was analyzed via IGA at the end of the qualification test

sequence to confirm that the package retained its fill gas composition, contained less than 5000 ppmv of moisture, and contained less than 50 ppmv of fluorocarbon. Of the five packages tested, one package (Package 1) contained high levels of oxygen, fluorocarbon, and moisture indicating that it had been exposed to atmosphere around the time of the beginning of qualification gross leak test (Table 1). Leak tests subsequent to the gross leak tests showed Package 1 was hermetic.

Table I - IGA Results

SAMPLE ID		Package 1	Package 2	Package 3	Package 4	Package 5
Pass/Fail		FAIL	PASS	PASS	PASS	PASS
Inlet Pressure	torr	180.7	179.8	178.7	175.7	181.3
Sys. Pressure	torr	9.7e-6	9.9e-6	9.9e-6	9.7e-6	1.0e-5
Sample Temp.	°C	100.3	99.9	99.5	100.1	100.1
Volume	atm cc	1.09	1.08	1.08	1.05	1.10
Nitrogen	ppmv	783,769	834,479	833,649	831,596	835,332
Oxygen	ppmv	150,383	31,269	28,160	37,716	30,615
Argon	ppmv	10,590	13,288	13,262	13,263	13,341
Carbon Dioxide	ppmv	1,886	146	179	117	128
Moisture	ppmv	10,764	2,066	2,301	2,142	1,415
Hydrogen	ppmv	165	512	736	716	417
Methane	ppmv	ND	ND	ND	ND	ND
Ammonia	ppmv	ND	ND	ND	ND	ND
Helium	ppmv	38,905	118,240	121,714	114,451	118,753
Fluorocarbon	ppmv	2,452	ND	ND	ND	ND

The amount of nitrogen, oxygen, and moisture present within Package 1 suggested that it had moved towards equilibrium with atmospheric gas for some time. However, the amount of CO₂ was abnormally high for atmospheric gas exchange to be the only source of CO₂. Atmospheric levels of CO₂ are around 400 ppmv outdoor and between 400-1000 ppmv indoors (Table 2) [1]. Indoor CO₂ levels can reach as high as 2000 ppmv, but this is unlikely in most rooms with a modern HVAC system. Excess CO₂ within hermetically sealed packages is of particular concern because it may indicate that the internal inorganic structures may have undergone a redox reaction, which may deteriorate or destroy device function. While CO₂, to the best of our knowledge, has never been linked to a hermetically sealed device failure; however, the mere presence of CO₂ indicates that the package integrity has been compromised.

The hypothesis for why Package 1 was hermetic throughout the qualification is that Package 1 was a leaker up until the gross leak test; at the conclusion of the gross leak test, Package 1 ingested fluorocarbon and was plugged by the fluorocarbon, rendering Package 1 hermetic once again.

Table II - Gas Compositions of Package 1 versus Atmospheric Conditions

	Package 1	Atmosphere	Indoor*	Indoor Measured
Nitrogen	783,769	780,000	780,000	
Oxygen	150,383	210,000	210,000	
Argon	10,590	10,000	10,000	
Carbon Dioxide	1,886	400	1,000	< 450
Moisture	10,764	Variable	10,000	
Helium	38,905	Trace	Trace	
Fluorocarbon	2,452	None	None	

*Note: Worst case indoor

The hypothesis for the presence of the high levels of CO₂ is that the CO₂ (between 800-1400 ppmv) was dissolved in the

fluorocarbon bath, and when Package 1 ingested 2,452 ppmv of the fluorocarbon, the absorbed CO₂ was ingested with it.

II. Literature Review

In reviewing the literature, many studies have been conducted on the solubility of CO₂ in fluorocarbon liquids [2], [3]. Gomes and Pauda studied the interactions of CO₂ with liquid fluorocarbons using molecular simulation and found that molecular dynamics predicted a greater solubility of gases within fluorocarbons when compared to their hydrocarbon counterpart [2]. In their literature review, they noted that CO₂ solubility in fluorocarbon liquids is greater than other gases, such as oxygen and water vapor, but the molecular mechanism is unknown and there is much conflicting information. Using computational methods, Gomes and Pauda found that fluorocarbons present larger cavities of a given size to solubilize gas and that the free energy of cavity formation is always smaller than the equivalent hydrocarbon. However, they were unable to uncover a mechanism for the preferential solubility of CO₂ in fluorocarbons when compared to O₂. The predicted fraction of CO₂ in fluorocarbons was compared to experimental studies and the trend was found to agree (Table 3). We may interpolate the simulation data to obtain the 90 °C (363.15 K) data point, and the fraction of CO₂ within the fluorocarbon liquid at 90 °C is ~1.6% CO₂.

Table III - Simulated and Experimental Solubility of O₂ and CO₂

	Simulation[2]		Experimental	
	10 ⁻³ x ₂			
T (K)	C ₆ H ₆	C ₆ F ₆	C ₆ H ₆	C ₆ F ₆
	O ₂			
200	5.9 ± 0.4	10 ± 1		
300	3.0 ± 0.1	5.4 ± 0.1	0.815	2.41 ⁴
400	3.1 ± 0.1	5.1 ± 0.1		
	CO ₂			
200	174 ± 30	231 ± 39		
300	16.6 ± 0.4	24.3 ± 0.8	9.70 ⁴	22.0 ⁴
400	7.9 ± 0.1	11.2 ± 0.2		

To determine if the excess levels of CO₂ within Package 1 were from CO₂ solubilized in the fluorocarbon bath, data sheets detailing the solubility of gases within fluorocarbon liquids was examined. F2 Chemicals Ltd released a technical article describing the solubility of gases in their series of fluorocarbon liquids (PP1 – PP9) and found that the solubility of CO₂ was about an order of magnitude greater than the solubility of nitrogen and oxygen (Table 4). They also found that as molecular weight increased, the solubility of the gas decreased.

Table IV - FT Chemical Ltd Solubility Data
(units: 100 ml gas/100 g liquid)

	FLUTECH™ liquid				
Gas	PP1	PP2	PP3	PP6	PP9
Helium	6.6	5.5	4.6	3.9	3.4
Hydrogen	10.7	9	7.4	6.3	5.6
Nitrogen	26.3	22	18.3	15.6	13.8
Carbon monoxide	26.3	24.2	20	17.1	15
Argon	39.8	33.5	27.7	23.7	20
Oxygen	41	34.6	28.6	24.4	22
Carbon dioxide	156	132	109	93	82
Sulphur hexafluoride	167	140	116	99	87
Ethane	263	221	183	156	138
Chlorine	781	657	542	463	408
Increasing Molecular Weight 					

The fluid used in the gross leak test is Galden D02 (Solvay), which is a perfluoropolyether (PFPE) with a molecular weight of 760 g/mol. While the data sheet does not provide the solubility of CO₂ in the D02 fluid, it does provide that the solubility of air is 26 cm³ of gas /100 cm³ of liquid. To compare that with the solubility data in Table 4, we can convert the units:

$$\text{solubility of air} = \frac{26 \text{ cm}^3 \text{ air}}{100 \text{ cm}^3 \text{ D02}} = \frac{26 \text{ ml air}}{100 \text{ ml D02}} \times \frac{1 \text{ ml D02}}{1.77 \text{ g D02}} = \frac{15 \text{ ml air}}{100 \text{ g D02}} \quad (1)$$

This shows that the solubility of air is on the same order of magnitude as the solubility of oxygen and nitrogen in the PP9 liquid (similar MW to D02), so it is likely that the solubility of CO₂ in D02 is about an order of magnitude greater than the solubility of air. While the exact number for the solubility of CO₂ in D02 is not available, we can conclude that the properties of fluorocarbon liquids are approximately similar to one another based on their similar molecular weights.

The Solubility Data Series of “Carbon Dioxide in Non-Aqueous Solvents at Pressures Less Than 200 kPa” from IUPAC contains numbers for the relative concentration of CO₂ in a variety of fluorocarbons from a variety of peer-reviewed publications[3]. In particular, we can examine the solubility of CO₂ in the larger fluorocarbon molecules, which would have similar properties to D02. A study by Tham et al. noted that the CO₂ mole fraction in a mixture of isomers of heptafluorotetrahydro (nonafluorobutyl) – furan (C₈F₁₆O) (MW = 416.06 g/mol) was 0.0223 at 298.2 K (25 °C), and 0.01550 at 323.2 K (50 °C) at a CO₂ partial pressure of 101.2 kPa.5 These results indicate that CO₂ could reach a mole percent between 1-2 mol% in a fluorocarbon liquid.

III. Calculation

We can use the data from Gomes and IUPAC as upper limits of CO₂ solubility to assess whether the excess levels of CO₂ can be explained by the solubility of CO₂ in the ingested fluorocarbon. To do this, we can convert the levels of D02 and CO₂ from ppmv to mol%. As noted in Table 2, a

minimum of ~800 ppmv is hypothesized to come from the ingested fluorocarbon. The conversion is shown in (2) below:

$$800 \text{ ppmv CO}_2 \times \frac{1}{V_M} \times V_{IVA} = 2.58 \times 10^{-8} \text{ moles of CO}_2 \quad (2)$$

Where, V_M is the standard molar volume of an ideal gas (1 bar and 363.15 K), and V_{IVA} is the volume of gas taken during IVA (~1 mL). For simplicity, the unit conversions are not shown in the equation above. The standard molar volume of an ideal gas was calculated using the ideal gas law with a temperature of 363.15 K.

Since the D02 fluorocarbon is a relatively large molecule, the ideal gas law does not apply. To obtain the molar volume of D02 (V_{D02}), we can divide the density (1.54 g/ml at 125 °C) by the molecular weight (760 g/mol), which gives a molar volume (V_{D02}) of 0.494 L/mol. A temperature of 125 °C was used because density data for D02 at 90 °C was not available; however, since the density is greater at 90 °C than at 125 °C, the number of moles would be greater than the mol% calculated in (3) below:

$$2430 \text{ ppmv D02} \times \frac{1}{V_{D02}} \times V_{IVA} = 4.92 \times 10^{-6} \text{ moles of D02} \quad (3)$$

The resulting percent mole fraction of CO₂ within the fluorocarbon is 0.52 mol%, which is below the 1.6 mol% predicted by the simulation and below the 1.5 mol% limit measured in the experimental study. If we assume that 450 ppmv CO₂ was from gas exchange with room air and the remaining 1436 ppmv of CO₂ was solubilized in the ingested fluorocarbon, then the resulting mol% would be 0.91 mol%, which is also below the limits stated above. Since the D02 bath is kept exposed to indoor conditions, it is likely that the CO₂ slowly absorbs into the bath and, at the time of test of Package 1, was at a level of ~0.5-0.9 mol%. We do not see elevated levels of other gases because studies have shown that fluorocarbon preferentially absorbs CO₂ over other atmospheric gases [2],[4]. More importantly, the initial concentrations of oxygen and nitrogen within the Package 1 likely masks any increases due to gas absorbed in the ingested fluorocarbon.

IV. Conclusion

The phenomenon of a one-way leaker is supported by the analysis of the CO₂ gas content. It is likely that Package 1 was a leaker on the order of ~10⁻⁶ for some time before the gross leak test, allowing for gas exchange between the indoor atmosphere at the test site. Then, Package 1 was placed into the fluorocarbon bath where it is likely that Package 1 ingested fluorocarbon liquid. The leak path was plugged by the fluorocarbon liquid, preserving the state of the gas composition and rendering Package 1 hermetic. The IVA showed elevated levels of CO₂ which can be attributed

to CO₂ absorbed by the D02 fluorocarbon liquid based on the relative concentrations.

References

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