Polymer Absorption Sensor Formulations

White Paper

Rev. 1.0.0

Date: 2018-09-25

Author(s): Dr. Aman Bains

Revision History

Revision	Date	Contributors	Description
1.0.0	2018-09-12	Dr. Aman Bains	Initial release

Table of Contents

List of Figures

List of Tables

1 Executive Summary

Commercially available polymer absorption (PA) sensor technologies have not changed considerably since they were first developed in the mid-1950s by Adsistor Corp. Two main factors contributed to the developmental stagnation:

1. material degradation from thermal and hydrolytic weathering, and
2. cross-sensitivity to thermal fluctuations and water absorption (submersion/humidity).

Syscor Controls & Automation Inc. (Syscor), in close cooperation with industry, has driven significant, novel PA sensor research and development, especially in the area of material degradation and water cross-sensitivities. With considerable third-party oversight and support from several major oil and gas industry leaders, including the Pipeline Research Council International (PRCI), Syscor has designed and produced a new generation of cost-effective hydrocarbon detection sensor technology. This technology is engineered, systematically tested and qualified to operate with minimal maintenance and in a multitude of deployment environments (icy, wet, humid, or dry) and temperatures (between -50 and +50 °C), with near zero possibility of false-alarms.

The core of Syscor's solution is three distinctive PA sensor formulations for hydrocarbon detection in air, on water surfaces, and when fully submerged (including when frozen in ice). Their ability to detect hydrocarbons in extreme environments reliably supports real-time, cost-effective integrity monitoring of critical infrastructure. Their seamless integration into existing safety infrastructure allows for easy and rapid deployment into almost any facility. Syscor's PA sensors are uniquely suited for commercialization because of their ease of use, robustness, low-power consumption, low maintenance, self-calibration, and reliable/reproducible detection of hydrocarbon gases and liquids with zero false alarms.

Current applications of these sensors in the petrochemical industry include, but are not limited to, detection of hydrocarbon leaks in transport equipment and facilities (pipelines, pump stations, flanges), aboveground and underground storage tanks and associated piping, mixing tanks, extraction equipment, heat exchangers, reservoirs, lakes, rivers and streams.

The Syscor PA sensors are designed specifically for use with Syscor's Field Transmitter used in the Syscor FR-Tracker™ and HC-Tracker™ Monitoring System Solution Packages. Two models of sensor transducers provide detection of hydrocarbons, temperature, acceleration and liquid height, depending on site and application requirements. Sensor readings are communicated, along with network and battery status, by the Field Transmitter via the WirelessHART communication protocol. A WirelessHART Gateway unit receives and routes the sensor data from the Field Transmitter unit to the monitoring software application and database or other customer systems as required.

2 Background/Challenge

The greatest obstacles that have hindered the widespread use of polymer absorption (PA) sensors in commercial products include degradation due to weathering, especially submersion in water, and false alarms caused primarily by ambient temperature and humidity fluctuations (extreme heat and extreme cold). In real-world applications, PA sensor contact with water (liquid and ice) presents the greatest cross-sensitivity and deterioration challenge for currently available hydrocarbon PA sensor technologies. Understanding and resolving these particular issues has been of primary importance for Syscor Controls & Automation (Syscor).

3 Solution

3.1 Overview

Syscor Controls & Automation Inc. (Syscor), in close cooperation with industry, has driven significant, novel polymer absorption (PA) sensor research and development, especially in the area of material degradation and water cross-sensitivities. With considerable third-party oversight and support from several major oil and gas industrial leaders, including the Pipeline Research Council International (PRCI), Syscor has designed and produced cost-effective hydrocarbon leak detection sensors that are systematically qualified and engineered to require minimal maintenance, achieve near zero false alarms, and operate in a multitude of deployment environments.

The core of Syscor's solution is three distinctive PA sensor formulations for hydrocarbon detection in the air, on water surfaces and when fully submerged (including when frozen in ice).

Application	Sensor Formulation Details
Vapour	The vapour sensor (VS) is optimized to detect gaseous hydrocarbons with a lower detection limit starting at 1000 ppm (calibrated to hexanes; 0.1% v/v of atmosphere or 10% of the Lower Explosive Limit (LEL)) and engineered for vapour detection in air in dry or humid conditions.
Interface	The interface sensor (IS) is designed to detect both gaseous and liquid hydrocarbons and optimized to operate in environments where some temporal submersion in water can be expected (air/water interface).
Water Immersion	The water immersion sensor (WI) is optimized to operate in fully submerged conditions (including hot [T < 60 °C] water or ice) for up to five years.

Table 1: Polymer absorption sensor formulations

These three sensor formulations were qualified from multiple perspectives[1]:

- Qualification (sensor response[2]): Sensitivity to gaseous hydrocarbons (C_3 or greater)
- Qualification: Sensitivity to liquid hydrocarbons (C_3 or greater)
- Sensor cross-sensitivity to temperature
- Sensor cross-sensitivity to water vapour (humidity)
- Sensor cross-sensitivity to water submersion
- Sensor behaviour when fully encapsulated in ice

The rest of this white paper presents results and analysis of the qualification experiments and discusses potential sensor cross-sensitivities.

[1] Material ageing, long-term stability, and mean time before failure are discussed in separate white papers and are not included in this document.
[2] Sensor response is defined as a change in PA sensor resistance (R) relative to its baseline (dR/Ro).

3.2 Solution Details

Summary: Syscor's polymer absorption (PA) sensors are thoroughly tested, systematically qualified devices that are designed to detect hydrocarbons (C_3 and heavier) reliably in air, on water surfaces and when fully immersed in water. Furthermore, they are designed to operate in a wide range of environments (icy, wet, humid, or dry) and temperatures (between -50 and +50 °C) with near zero possibility of false-alarms.

The proprietary composite material that Syscor has developed overcomes the historical shortfalls that have hindered widespread commercial success of existing PA sensor formulations (baseline drift, false alarms due to fluctuating temperature or atmospheric moisture, poor performance due to long-term weathering). Syscor has exhaustively tested all sensor formulations for long-term material degradation due to multiple factors, including thermal-, hydrolytic-, and mechanical-degradation. Furthermore, each sensor formulation has been investigated on a micro- and macroscale for hydrophobicity, sensor topology, and manufacturing reproducibility.

3.2.1 Qualification: Sensitivity to Gaseous and Liquid Hydrocarbons

In general terms, polymer absorption (PA) sensors are devices that are able to repeatedly detect gaseous and/or liquid hydrocarbon substances. Typically, PA sensors are composed of an elastomeric polymer matrix that is embedded with micro- and nano-sized conducting particles. The resulting composite material is typically deposited between two electrodes on a printed circuit board (PCB) and has a characteristic measurable baseline resistance (Ro). PA sensors operate via absorption and subsequent matrix expansion (swelling) resulting from contact with target gaseous and/or liquid hydrocarbons (gasoline, diesel, crude oil, volatile organic compounds). Upon swelling, the interparticle distance of the embedded conducting micro- and nanoparticles increases, resulting in a change in the sensors baseline resistance. If the detected change in sensor resistance is greater than a certain applied threshold, this data can be used to trigger an alarm via an external system.

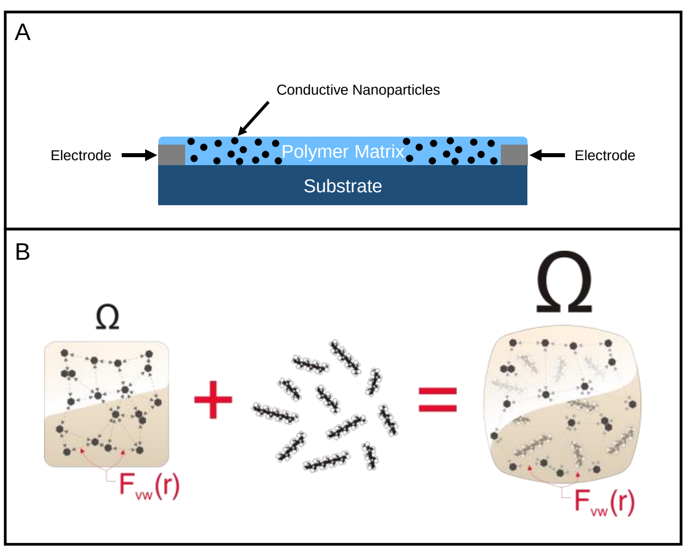

Figure 1 A is a representative schematic of a reversible polymer absorption sensor with highlighted electrode, substrate and conductive particle positions.

Figure 1 B shows the operational mechanism for a standard chemiresistor where the increase in resistance is due to the absorption of hydrocarbons.

Figure 1: Polymer absorption sensor schematic

Generally, PA sensor formulations can detect and absorb only those hydrocarbons that they are specifically designed to target (sensor 'affinity'). All three of Syscor's PA sensors are engineered to detect only propane ($\geq C_3$) or heavier hydrocarbons, eliminating the probability of methane or ethane triggered false alarms.

PA sensor hydrocarbon selectivity and sensitivity are both thermodynamically controlled properties. Sensor hydrocarbon selectivity is determined by the affinity of the sensing material for the analyte (Hansen

Solubility Parameter). The degree of absorption is driven by the analyte's partition equilibria, the system's free energy, diffusive properties (flux), and environmental factors (temperature, wind current, etc.). Diffusive flux, in this context, is a mathematical vector description for directional bulk movement of liquids or gases (i.e. amount of substance per unit area per unit time).

Temperature °C	Vapour Sensor (%)	Water Immersion Sensor (%)	Interface Sensor (%)
-25	18 ± 3	10 ± 2	31 ± 4
0	34 ± 4	9 ± 2	29 ± 1
25	58 ± 3	14 ± 3	25 ± 2
50	78 ± 9	16 ± 2	22 ± 3

Table 2: Summary of PA sensor response to gaseous hydrocarbons (hexanes)

Relative to gases, liquids have a relatively infinite flux. They are capable of instantaneously saturating and swelling a PA sensor's sensing membrane (inducing maximum sensor sensitivity), where gaseous hydrocarbons required longer time periods to diffuse through and completely saturate (<< flux) the sensor material. As a result, typical PA sensors have an inherently lower instantaneous sensitivity to gaseous versus liquid hydrocarbons. Designing a PA sensor that is capable of accurately and reliably detecting gaseous hydrocarbons with zero false alarms was a critical step in the development of a next generation hydrocarbon detection technology. To this end, **Syscor designed a PA vapour sensor (VS) with specific polymeric materials that have a greater affinity for gaseous hydrocarbons even at relatively low vapour concentrations.**

To test these materials and accurately measure the relative gas sensitivity of each PA sensor formulation, experiments with hexane gas were conducted in an environmental chamber test environment (Table 1).

> TEST NOTE: Gaseous hydrocarbon sensor testing was conducted by vapourizing hexane solvent in an environmental chamber at very low concentrations (≤ Lower Explosive Limit) (Figure 2). To address safety concerns, gaseous hexane concentrations were kept to a minimum, and the chamber was quickly evacuated after vapourization (< 10 minutes), ensuring a safe, non-explosive working environment. As a result, the full flux of the vapourized gases was never able to completely contact the test sensors, inhibiting a full scale PA sensor response. Also, the test chamber is not a perfectly closed system and gases are capable of readily exchanging with the surrounding atmosphere. This means that the values presented in Table 1 are qualitative only and represent instantaneous PA sensor response. These values should be used for intra-sensor comparison purposes only. The test does not represent real-world leak scenarios, nor does it present real-world sensor response. Real-world events have hydrocarbon leaks with diffusive flux and PA sensor response, magnitudes higher than what was encountered in the test environment.

Analysis of Table 1 confirms that any deployment scenario where gaseous hydrocarbon detection is prioritized should include installation of a vapour sensor (VS) equipped device. **Compared to the liquid hydrocarbon and water immersion sensor formulations, the Syscor vapour sensor is a superior gaseous hydrocarbon detector. The vapour sensor has two times the sensitivity of any other formulation at 25°C, and nearly four times greater sensitivity at 50°C.**

Sensor sensitivity, however, is not the only metric to consider. **Sensor response time is also crucial.** Rapid leak detection allows for detection of potential events before they become critical emergencies. To this end, **Syscor specifically engineered its PA sensors to not only detect gaseous hydrocarbons with high sensitivity, but to also detect hydrocarbons very quickly. All three of Syscor's sensor formulations have detection response times that are less than 10 seconds** (Figure 2).

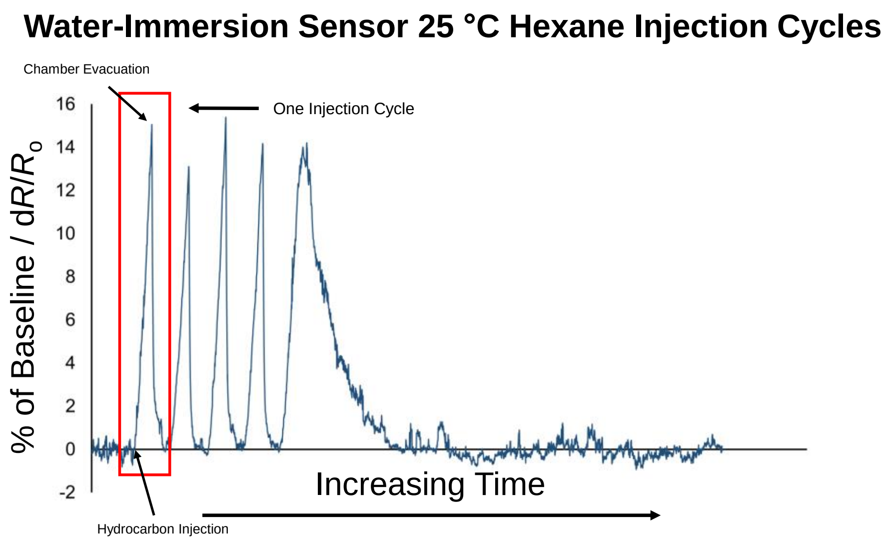

Figure 2: Water immersion sensor snapshot data

Figure 2 shows a snapshot into real data collected during hydrocarbon exposure qualification testing of Syscor's water-immersion sensor. There was a ten second delay between hydrocarbon injection and PA sensor response. Due to safety concerns, the chamber was degassed after ~ 15 minutes of exposure. Each injection cycle was ~ 30 minutes in duration and conducted at 25° C. Presented data was baseline corrected.

In general, sensor response time is a kinetic process that is predominantly driven by the available reaction area (surface area), therefore, materials with high surface area are quicker to react with substances than their lower surface area counterparts. To increase sensor reaction time, Syscor's sensors are specifically engineered to maximize surface area. The 3D surface area for each sensor formulation was systematically studied and confirmed using a standardized approach (ANSI B45.1)[3] and optical focusing microscopy (Figure 3).

Syscor's goal was to engineer the surface topology such that micro-deviations in the Z-direction would increase sensor surface roughness and available reaction area (Figure 3 A). To achieve this, the polymer matrix was doped with high softening point elastomeric polymer materials and utilized extremely volatile solvent deposition techniques. To better illustrate surface topology, scanning electron microscopy (SEM) images of actual sensor surfaces were recorded and analyzed (Figure 3 C, D).

SEM images of PA sensor surfaces provide incredible detail into sensor topology and micro-structure. Figure 3 C is a 45° cross-sectional image of a vapour sensor. Clearly, there are voids present and discontinuities in the polymer matrix material. These voids and discontinuities are representative of a rough, engineered 3D structure. Figure 3 D is a top-down SEM image of a vapour sensor surface. Again, there are a multitude of visible voids throughout the material (highlighted in white). This combination of 3D renderings and SEM images increases confidence and provides meaningful data to scientifically support the observed quick PA sensor hydrocarbon detection times.

[3] ANSI B45.1 categorizes ratios which compare a sensor's 3D surface area (including deviations in the sensor topology, Z direction) to the nominal surface area (2D surface area; length x width, 'x – y' direction).

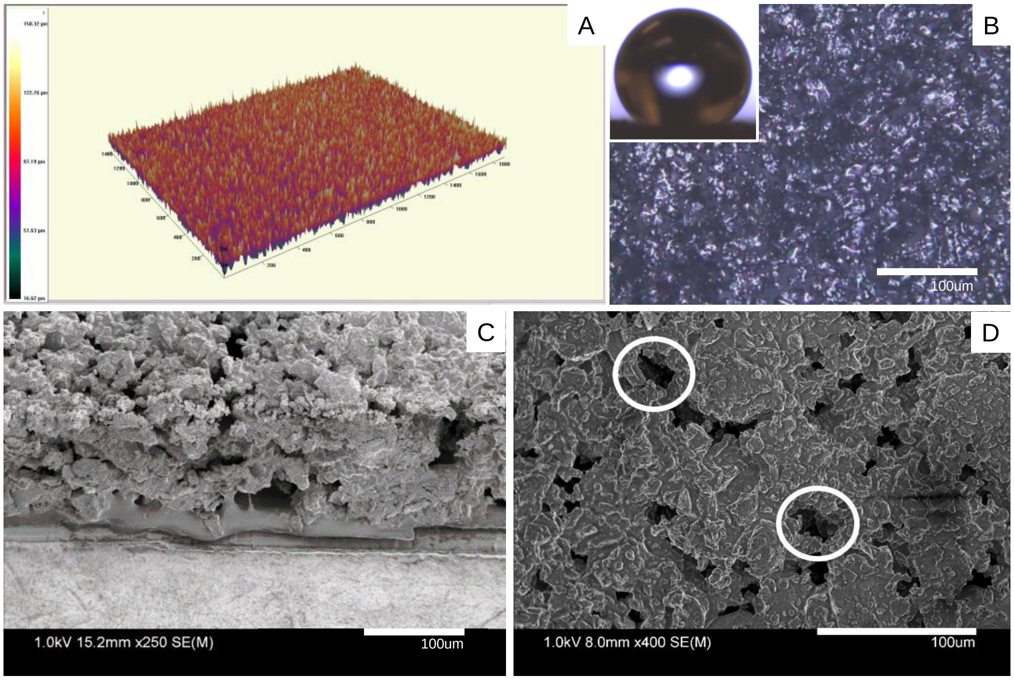

Figure 3: 3D renderings and SEMS images of VS sensor surface

Figure 3 A shows surface topology 3D rendering produced by an optical microscope used for surface roughness calculations; lighter colors represent higher surface amplitudes than dark colors (scale left of A).

Figure 3 B shows a 2D rendering of vapour sensor surface topology; dark regions are lower in amplitude than light regions. Inset in B presents contact angle experiments to measure surface hydrophobicity.

Figure 3 C and D present cross-sectional SEM scans of the vapour sensor. The dark regions are voids within the sensor's composite material; these voids help increase sensor surface area, for faster hydrocarbon detection kinetics.

All scale bars are 100 µm.

3.2.2 Qualification: Sensitivity to Liquid Hydrocarbons

All three of Syscor's PA sensor formulations were tested for their detection of liquid hydrocarbons at four temperature points. All three PA sensor formulations had near instantaneous detection (< 5 seconds) at all four temperature points with baseline changes approaching infinity.

In the tests, all three PA sensor formulations were exposed to diesel, gasoline, and crude oil at four temperature set points (Table 3). During testing, the sensors were submerged into containers containing liquid hydrocarbons and their response was recorded electronically (Figure 4). Sensor response time was determined by averaging the results from 96 sensors of like formulations over five exposure cycles.

Temperature °C	Vapour Sensor (%)	Water Immersion Sensor (%)	Interface Sensor (%)
-25	Open Circuit	Open Circuit	Open Circuit
0	Open Circuit	Open Circuit	Open Circuit
25	Open Circuit	Open Circuit	Open Circuit
50	Open Circuit	Open Circuit	Open Circuit

Table 3: Summary of PA sensor response to liquid hydrocarbons (diesel)

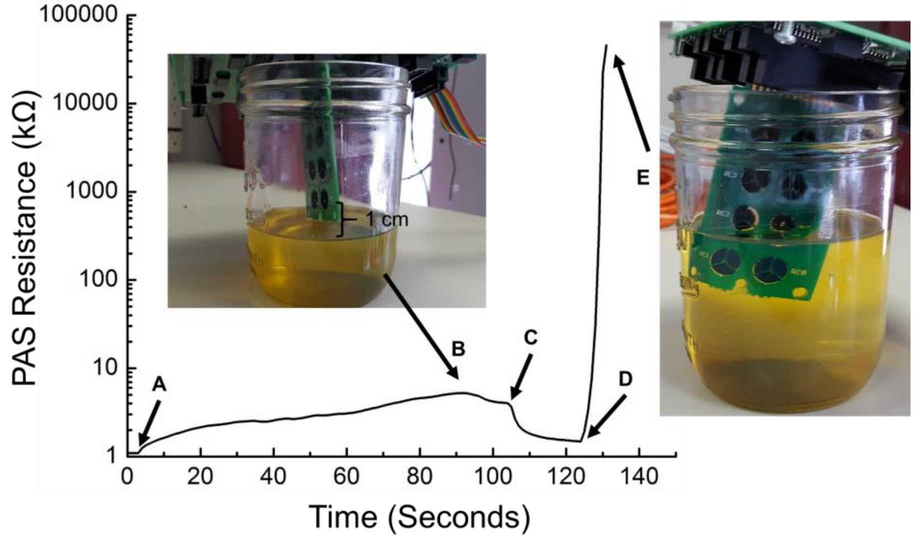

Figure 4: Interface sensor response to gaseous vs. liquid hydrocarbons

Point (A) is the moment the interface PA sensor device was exposed to the diesel vapour in a container. The sensor obtained a maximum resistance of ~6 kΩs (dR/R0 = 500%) after about 90 seconds of exposure (B). At (C) the sensor was removed from the vapour and resistance readings returned to baseline. Next, the sensor was submerged into diesel liquid (D), ensuring direct contact between the hydrocarbons and PA sensors. At this point the sensors reached a maximum of ~ 50 Mohms (E) before the resistance readings became immeasurable.

3.2.3 Cross-Sensitivity to Temperature, Humidity and Water Saturation

Syscor's sensor configurations (vapour, interface and water immersion) are resilient during fluctuations in ambient temperature and atmospheric moisture (humidity) due to their extremely robust, cross-linked polymer matrix and highly hydrophobic surface chemistry. Both the interface and water immersion sensor had very small changes in baseline resistance (≤ 10%) even after prolonged submersion in water, which virtually eliminates the probability of false alarms.

Previously, cross-sensitivities to water and ambient temperature fluctuations have undermined the usefulness of PA sensors and hindered their commercial success. To overcome these historical pitfalls, Syscor developed a proprietary polymer composite formulation that is doped with specific thermoplastics.

Thermoplastics are rigid materials (where T < softening point) that are resilient to mechanical stress. In the context of PA sensors, thermoplastics can mitigate cross-sensitivities to water and temperature by restricting sensor swelling. By varying the concentration of thermoplastics, it is possible to tune sensor performance from highly reactive hydrocarbon vapour sensors (very reactive to liquid hydrocarbons) with relatively high cross-sensitivities to relatively low reactivity hydrocarbon vapour sensors (still very reactive to liquid hydrocarbons) with no cross-sensitivities.

Material hydrophobicity was measured using contact angle measurements (Figure 3 B). These measurements were performed to illustrate the highly hydrophobic nature of Syscor's PA sensor surfaces. Contact angles were measured to be ≥ 140°, classifying these sensors as highly hydrophobic surfaces. Nevertheless, even with the highly hydrophobic surface chemistry, the vapour sensor formulation has an upper level threshold to water saturation where sensor performance deteriorates. This cross-sensitivity is driven by sensor-matrix expansion upon water absorption (similar mechanism to hydrocarbon detection), and is highest in the vapour sensor; especially, when submerged for > 24 hours. This cross-sensitivity of the vapour sensor can potentially mask gaseous hydrocarbon alarm thresholds and may trigger false alarms. To overcome this issue, Syscor revisited the PA sensor chemical formulae and developed the interface and water-immersion sensor formulations.

Sensor Formulation	Cross-Sensitivity			
	Humidity (dR/R_o)	Prolonged H2O Submersion (dR/R_o)	Temperature 25°C (dR/R_o)	Temperature -25°C (dR/R_o)
Vapour	< 40%	< 250%	< 7%	< 2%
Interface	< 10%	< 10%	< 8%	< 12%
H_2O Immersion	N/A	< 1%	< 11%	< 9%

Table 4: Cross-sensitivities for all three PS sensor formulations

The vapour, interface, and water-immersion sensors have low-, medium-, and high- concentrations of thermoplastics, respectively. As seen in Table 4, cross-sensitivity to prolonged water submersion (> 24 hours) is inversely related to thermoplastic concentration.

Syscor conducted exhaustive trials where PA sensor response to water was studied (Figure 5). Water saturation tests were conducted at 25 °C by submerging each PA sensor formulation into water and then measuring its resistance over a 24 hour soak. Both the interface and water immersion sensors had very small changes in baseline resistance (≤ 10%) even after prolonged submersion in water. This is relevant when taken in context of liquid hydrocarbon alarm set points, since alarm thresholds are often set at orders of magnitude higher than their respective baseline resistances. A 10% cross-sensitivity to water submersion virtually eliminates the probability of false alarms.

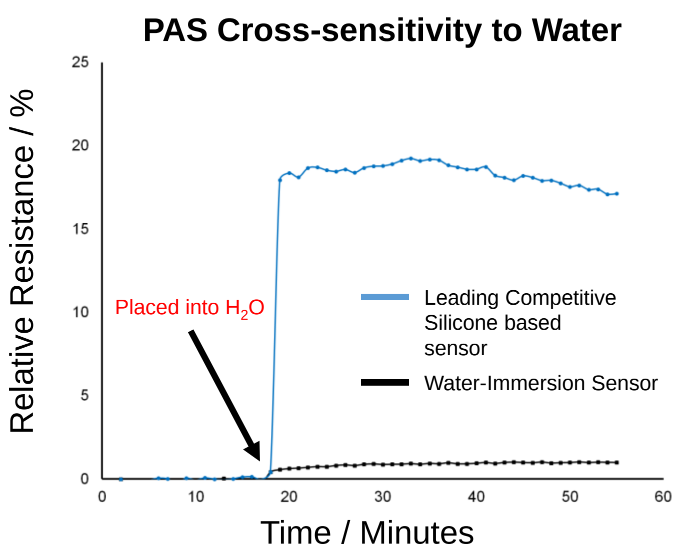

Figure 5: Water Immersion sensor cross-sensitivity to H2O saturation at 25°C

Figure 5 presents the first hour of data from a water saturation test.

This combination of highly sensitive hydrocarbon detectors, with little to no cross-sensitivities or chances of false alarms, delivers very desirable qualities in leak detection devices. Until now, this combination did not exist in commercially available products. Current products are either highly-sensitive and have high probabilities of false alarms, or they exhibit low-hydrocarbon sensitivity and near zero probability of false alarms. **Syscor's devices are unique, as they present a sensor that is both highly sensitive to hydrocarbons with near zero probability of false alarms. This allows for installation and organization of either PA point sensors or facility-wide arrays without the issue of degrading performance.**

3.2.4 Cross-Sensitivity to Freezing Conditions

Hydrocarbon leak detection is especially crucial in scenarios where deployment requires PA sensor installation into bodies of water. Previous generations of commercially available PA sensor formulations had moderate to low success with installation in water. As stated earlier, sensor deployment in these particular applications is problematic due to the water-led accelerated ageing of the polymer material because of the polymer's tendency to absorb water. Once water is absorbed and the PA sensor material is saturated, hydrolysis-driven material degradation is accelerated. Furthermore, this problem is exaggerated when sensors are installed in environments with sustained freezing temperatures.

The expansion of water as it freezes is especially damaging to PA sensors. In instances where water has saturated and penetrated deep into the polymeric material, expansion upon freezing causes microscale structural damage to the sensor. This effect is even more pronounced once the frozen water thaws, confounding the previous structural damage. Freeze/thaw cycles can result sensor delamination, deteriorated performance and, in some cases, complete failure and subsequent false alarms.

Syscor's goal is to provide a reliable hydrocarbon leak detection system that can be used in any deployment scenario, including waterways. **To accomplish this, Syscor developed a proprietary polymer composite (the water-immersion sensor) that is doped with extremely robust and hydrophobic materials. The combination of these polymers dramatically reduces the amount of water that is able to absorb into the material, preventing complete and even partial saturation, dramatically reducing sensor ageing and probability of failure. Also, because very little or no water is absorbed into the sensor, microscale structural damage is prevented during freezing.** All of these measures result in a sensor that can operate within an expected performance threshold regardless of ambient environmental factors.

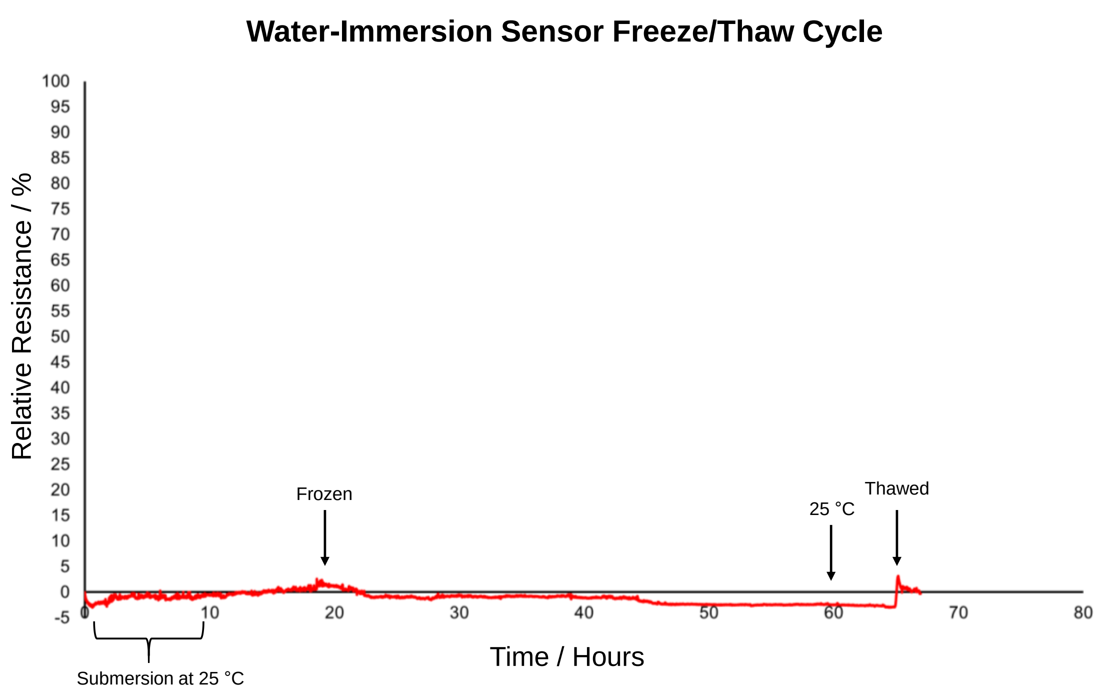

Figure 6: Water Immersion sensors behavioural data during freeze/thaw cycle

Figure 6 shows average behavioural data of 20 water-immersion sensors during a freeze/thaw experiment. The sensors were equilibrated in water for 10 hours before they were frozen. There was no change in baseline resistance during the freeze/thaw period other than signal noise. Alarm thresholds for these sensors are set to over 150% of baseline.

To test the water-immersion sensor formulation, rapid freeze/thaw cycles were induced on batches of 20 water-immersion sensors (Figure 6). These cycles attempted to produce large degrees of chemical and physical stress on the sensor materials. Figure 6 presents some of the collected data.

During testing, the water-immersion sensors were placed in water baths for up to 10 hours at 25 °C before being frozen, which allowed for the sensors to reach their saturation threshold. After 10 hours, the sensors were frozen over ~9 hours at -18 °C. The water-immersion sensor formulation shows no significant change in baseline resistance (no damage) over this period other than signal noise. Next, the sensors were thawed at 25 °C for 5 hours. There were no significant changes in resistance during the thawing process, evidence that there was no physical damage to the sensor material. There was only a 3% bump, signifying the sensor was completely free of ice. Tests identical to those conducted in Figure 6 were repeated three times on each sensor batch. **All water immersion sensor batches showed no deterioration in performance or evidence of accelerated ageing during either freezing or thawing conditions.**

Field Application Note - Polymer Sleeve: To enhance hydrocarbon detection, each sensor transducer is deployed in the field with a polymeric fabric material wrapped around the sensor's metallic housing (Figure 7). This extremely robust polymer sleeve forms a water-tight seal around the sensor housing and acts as an extremely efficient hydrocarbon wick as it facilitates easy penetration of hydrocarbons from the surrounding environment to the inside of the sleeve. The quick concentration of hydrocarbon fumes inside the sleeve ensure accelerated hydrocarbon detection with near zero possibility of false-alarms.

Figure 7: PA sensors in metal housing and polymer sleeve

Figure 7 (left) shows PA sensors encased in their protective metallic housing for general purpose applications. PA sensors for applications in water ways where freezing conditions are expected are wrapped in polymeric sleeves that amplify hydrocarbon flux.

4 Conclusion

Syscor's polymer absorption (PA) sensors are designed specifically to satisfy the petroleum industry's stringent requirements for target hydrocarbon leak detection under extreme conditions in a wide variety of application environments. Syscor's PA sensor formulations are thoroughly tested, qualified and proven devices that provide accurate and reliable hydrocarbon detection in air (humid and dry), on water surfaces, when fully submerged, and even in ice. They are resistant to conditions that have made previous PA sensor formulations undesirable.

The sensors are, however, only one component of a complete Syscor monitoring solution. As an innovator in the field of industrial sensors, Syscor continues to expand our product and solution portfolio based on advanced technologies such as micro-electro-mechanical systems (MEMS), sensor fusion, the Internet of Things (IoT), industrial wireless standards (WirelessHART), inductive power and communications, and more.

The heart of our safety solution, Syscor's FR-Tracker™ and HC-Tracker™ Monitoring Systems can be configured to meet your specific site and application requirements. Current applications of Syscor's monitoring solutions in the petrochemical industry include, but are not limited to, the monitoring of floating roofs on aboveground storage tanks and the detection of hydrocarbon leaks in transport equipment (pipelines, pump stations, flanges), storage tanks, mixing tanks, extraction equipment, heat exchangers, reservoirs, lakes, rivers and streams.

Contact Syscor Controls & Automation Inc. to discuss how to incorporate Syscor monitoring solutions into your specific facility and field applications.

Syscor Controls & Automation Inc.
201 – 60 Bastion Square
Victoria, BC V8W 1J2
Canada
Toll Free Canada/USA: +1-833-361-1681
Tel: +1 250 361 1681
Email: contact@syscor.com
Web site: www.syscor.com

