Nanocomposite Hydrocarbon Detectors for Facilities and Underground/Underwater Monitoring

Introduction

Safe transport of petroleum and other hydrocarbon-based products is an industrial focal point in view of the enormous socioeconomic costs associated with leaks and spills, their remediation, and their impact on sensitive ecosystems. Critical transmission infrastructure is often located in remote regions or at sites providing limited access where active monitoring or spot checking for leaks is extremely cumbersome and expensive. The Petroleum Industry has responded to these challenges through support of the development of real-time hydrocarbon leak detection technologies which can broadly service a multitude of environments—reliably.

Due to inherent vulnerabilities, many commercially available leak detection systems are incapable of meeting industry's remote monitoring needs, especially in underground deployments where water submersion hazards exist. Fortunately, an alternative technology exists which overcomes many of the shortcomings which make the application of conventional leak detection methods unfeasible. Polymer Absorption Sensors (PAS) have demonstrated capabilities in detection of hydrocarbons in harsh environments and recent technological developments led by Syscor Controls & Automation Inc. have overcome many of the impediments that have historically discouraged widespread application of PAS.

This paper introduces PAS, their capabilities and Syscor advancements, and the rigorous qualification process to which the Syscor PAS have been subjected.
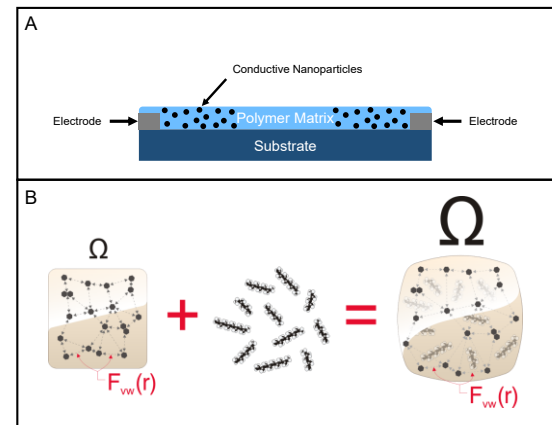

Figure 1: A) Is a representative schematic of a polymer absorption sensor with highlighted electrode, substrate, and conductive particles. B) Shows the operational mechanism for a standard PAS where the increase in resistance is due the absorption of hydrocarbons and subsequent material swelling.

Basis of Operation

PAS are chemiresistor-class devices. Such devices experience a change in their electrical resistance in response to chemicals at or near their surface. In a PAS, the resistance change occurs due an expansion of the polymer matrix on absorption of targeted hydrocarbon chemical analytes. When the polymer substrate is deposited between two electrodes of a circuit board its resistance is readily measured.

PAS Advantages

In polymer-based hydrocarbon sensors, measurements of resistance are generally taken over a short time interval relative to the rate of change of the polymer resistance. This naturally results in a high signal-to-noise ratio (SNR) in PAS devices. Furthermore, their simple detection mechanism (Figure 1) allows PAS with ultra-low power requirements to be realized. Finally—and most importantly—the PAS systems do not require frequent calibration and can be manufactured with highly robust coatings which protect them against mechanical degradation caused by environmental exposure. With application of modern material enhancements, state-of-the-art PAS are now capable of decades of field service without significant performance degradation.

Innovation driven by safety

Emerging PAS Applications

Syscor PAS advancements have opened the door to a wide-range of applications in the Petroleum Industry. Examples of these applications include—but are not limited to— detection of hydrocarbon leaks in transport equipment and facilities (pipelines, pump stations, flanges); in aboveground and underground storage tanks and associated rotating equipment; in field production equipment; and in- and around water bodies (both flowing and frozen) such as collection ponds, lakes, rivers, and aquifers. Syscor's sensor systems (Figure 2) are engineered and qualified for long-term maintenance-free deployment, with underwater service lifetimes > 5 years and above-water service lifetimes > 30 years.
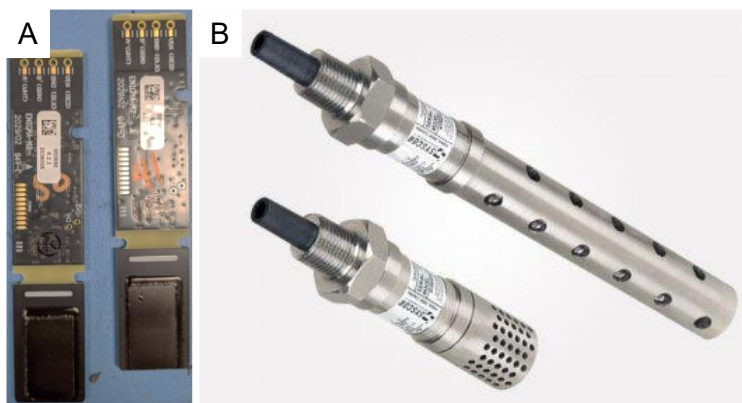

Figure 2: A) PAS on PCB boards ready for assembly; B) Syscor Hydrocarbon Detection sensors ready for deployment.

PAS Hydrocarbon Detection Mechanism

A PAS hydrocarbon detection mechanism centers on an elastomeric polymer matrix undergoing an absorption and deabsorption process[2]. The polymer matrix will favor absorption of chemically-similar analytes.

In a basic PAS conducting particles are deposited between two PAS electrodes forming an embedded sensor pad. In absence of any hydrocarbons the sensor pads possess a characteristic baseline resistance, $R0$. When exposed to chemically-similar analytes the resulting expansion of the polymer matrix will increase the sensor's resistance, R (Figure 1). The concentration of analytes and the rate of change of this concentration will be reflected in the quantity, $dR/R0$. In general, PAS response to hydrocarbons results in a change in resistance orders of magnitude greater than the baseline. These properties and behaviors are common to all PAS. However, testing has concluded that Syscor PAS are typically much more reactive than traditional PAS; that is, given similar factors, the Syscor PAS would be expected to exhibit a larger $dR/R0$.

Historical Limitations Overcome

From the time that chemical-resistive effects were first developed in the 1960s, PAS have held promise as low-power alternatives to traditional environmental monitoring technologies due to their low cost and chemically-selective detection mechanism. Adoption by industry has been slow, however, due to some key shortcomings: (i) traditional PAS systems have been prone to material degradation over time; (ii) weather related cross-sensitivities make the sensors prone to false positives; and (iii) irreversible hysteresis effects resulting from contact with hydrocarbons, damage by freezing in water, and from temperature-cycling.

Through extensive experimental research and test-verification efforts Syscor has developed proprietary materials and manufacturing techniques which solve or mitigate the aforementioned problems.

Material Degradation Problems: The need to expose a PAS polymer material to the environments in which invading hydrocarbons will be detected requires management of trade-offs related to the mechanical durability of the PAS material. PAS must be in contact with the environment in order for hydrocarbons to be absorbed by the polymer matrix but this exposure also leads to material degradation. This degradation results from abrasion and stress/strain caused by weathering, especially freeze/thaw cycles. A second problem relates to corrosion and general breakdown, through oxidation and redox processes, of the metallic traces which connect the embedded sensor to its monitoring system.

The Material Degradation Solution: Syscor has developed special purpose proprietary coatings which are applied at separate stages during the PAS manufacturing process. These coatings separately address the needs for (i) protection of electrical contacts at the PAS circuit board level; and (ii) increased mechanical durability without sacrificing sensitivity to hydrocarbons.

Cross-sensitivity Problem: In particular, susceptibility of traditional PAS to erroneous readings stems from the fact that modulation of the polymer's electrical resistance results from reaction to target analytes and/or fluctuating environmental factors (e.g., weather, temperature, moisture). The two stimuli are virtually indistinguishable because both induce a similar change in the sensor material, affecting its resistance. As a result, despite their promise, legacy PAS have been prone to unreliable sensor readings and have never reached their commercial potential.

The Cross-sensitivity Solution: Recent innovations in materials science, particularly in the area of thermoplastics, have made it possible to resolve the aforementioned cross-sensitivities. Harnessing these new advantages, Syscor has produced and patented a PAS with low susceptibility to environmental cross-sensitivities and exhibiting minimal baseline drift. As demonstrated in both laboratory and customer field applications, the new Syscor PAS (Figure 3) produce near-zero false positives.

Susceptibility to Hysteresis Problem: The nature of the PAS material and absorption mechanism are making these sensors vulnerable to irreversible material changes which result in a permanent indication of the presence of hydrocarbons—hysteresis. The associated material changes inhibit hydrocarbon detection, reduce sensitivity (i.e., the lowest level of hydrocarbon that can be detected).

The hysteresis problem has two disparate causes: (i) mechanical stress (e.g., material stress/strain); and (ii) chemical damage (e.g., material hydrolysis or dissolution). The mechanical stress is primarily caused by (i) cyclical hydrocarbon exposure; and (ii) weathering. Weathering is itself a combination of two processes: (i). Water absorption/deabsorption from the ambient environment; and, (ii) short-term (e.g., day/night) cycles and long-term temperature fluctuations (e.g., seasonal changes). Chemical hysteresis is primarily due to two things: dissolution of the polymer membrane through absorption of hydrocarbons (solubility) and hydrolysis due to the absorbed water from the ambient environment.

The mechanical stresses brought on by hydrocarbon exposure and weathering have similar effects on the polymer membrane: stress/strain causes microfractures to develop within the polymer matrix. The fractures can lead to a inaccurate readings or in acute cases, loss of electrical continuity resulting in complete device failure. All mechanical stress experienced by the sensor material is irreversible. However, the extent to which the sensor material is damaged depends on the length and degree of exposure to the operating environment, and the materials from which the PAS are manufactured.

Chemical hysteresis relates to the ability of a given PAS polymer to exude (i.e., deabsorb) absorbed hydrocarbon and dictates the reversibility of the sensor output dR/R_0. Limited sensor reversibility has been one of the greatest weaknesses of PAS historically. An arguably greater hazard exists in water absorption; a PAS which has become even partially saturated with water will have its electrical resistance increased to such levels that the presence of hydrocarbons is no longer discernible.

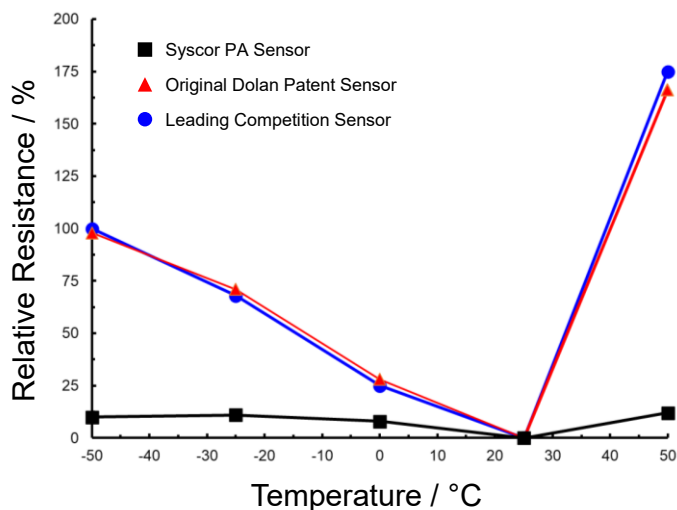**Contrasting PA Sensor Behaviour at Operational Temperatures**

Figure 3: Comparative baseline drift study exploring the influence of fluctuating temperature on PAS stability. Syscor's patented PAS formulation improves baseline stability by a factor between 2 to 3 as compared with *conventional PAS*. Whereas, *legacy* PAS experience large changes in their baseline resistance as a function of ambient conditions, Syscor PAS will not drift by more than 20% from their established baseline.

Susceptibility to Hysteresis Solution: Syscor approached the PAS permanent hysteresis problem by concentrating on preserving the physical integrity of the polymer membrane. By doping the polymer matrix with rigid, thermally conductive thermoplastics, physical cross-links are created within the polymer material which inhibiting membrane movement through constriction. In turn, the resulting increase in rigidity serves to minimize weathering effects by reducing material physical stress and strain, thus preventing cracking and associated material breakdown.

Doping of the polymer matrix also positively impacts reversibility. Although complete deabsorption of certain hydrocarbons is not possible, the reversibility of Syscor PAS when contacting gaseous and/or light liquid hydrocarbons, is significantly improved as compared with legacy PAS.

Finally, the thermoplastic dopants used in Syscor PAS are selected for their extreme hydrophobicity. Legacy PAS materials are prone to water absorption and hydrolysis which leads to material degradation and false positives. Utilization of modern thermoplastics all but eliminates these effects and as a result, Syscor now manufactures a PAS that remains operational (i.e., capable of detecting hydrocarbons) while completely submerged in water, for up to 5 years.

Baseline Drift Hysteresis Problem: Baseline drift is actually a characterization of the aforementioned sensitivity reduction problem. When the PAS material comprising an embedded sensor is damaged—through mechanisms previously discussed above—complete deabsorption of hydrocarbons does not result in return of the sensor's resistance to its previously establish R_0 value. The effective result is that the sensor remains in permanent state of hydrocarbon detection after all hydrocarbons may have been expunged.

Baseline Drift Hysteresis Solution: Unlike all other solutions discussed above, the solution to the baseline drift problem is implemented in embedded software. Syscor embedded systems which report PAS results are self-calibrating. In respect of the baseline, R_0, a PAS processing algorithm regularly updates the PAS resistance, R, and increases R_0 over time when a significant increase in R is detected. Because the change in R in the presence of hydrocarbons, dR/R_0, is orders of magnitude greater than R_0, minor increases in R_0 do not have a significant negative impact on the ability for the PAS to continue to complete its mission.

As part of the self-calibration, R_0 is reduced to the value of R any time the PAS monitoring algorithm detects the condition $R_0 > R$.

Proprietary PAS Technology

Syscor's PAS technology[6] is focused on real-time qualitative hydrocarbon detection and leverages chemiresistor principles with modern composite materials, enhancements, protective coatings, and production techniques. The following advantages are achieved:

- Enhanced material durability
- Prevention of corrosion (i.e., oxidation and redox effects)
- Limited cross-sensitivity to water and temperature
- Increased sensor selectivity (i.e., detection of hydrocarbons only)
- Increased sensitivity (i.e., speed and magnitude of detection) [7–12]

Advanced Research: Syscor utilized a variety of different materials-engineering instrumentation (e.g., scanning electron microscopy, atomic force microscopy, and hydrophobicity testing) (Figure 4) in studying and designing the PAS surface. In particular, Syscor adjusted the sensor's surface topology to increase the surface area of a polymer substrate deposit to quicken analyte detection. In addition, the material's surface chemistry was tuned so as to be extremely hydrophobic thus preventing water absorption and related baseline drifts. Scanning electron microscopy was used to visually confirm changes to the sensor material's surface (Figure 4A) and atomic force/hydrophobicity studies were conducted to confirm the material's ability to reject water and absorb hydrocarbons (Figure 4B).
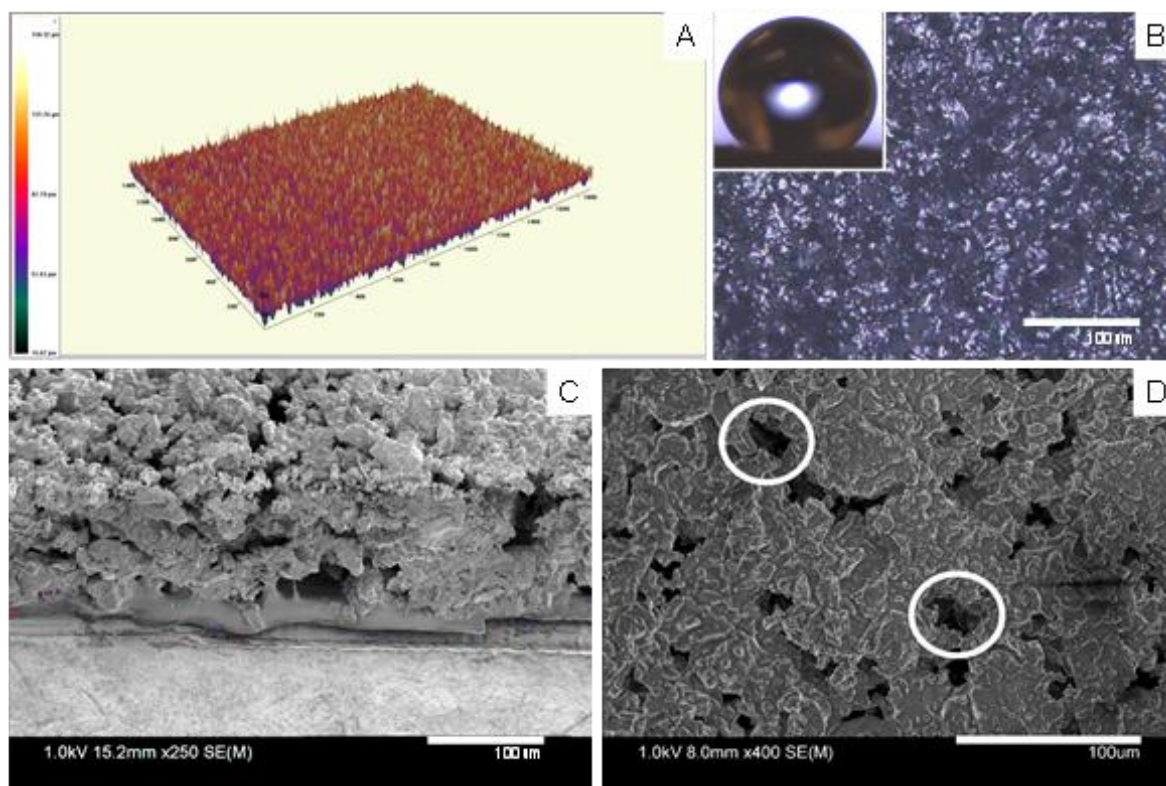

Figure 4: A) Shows surface topology 3D rendering produced by an optical microscope used for surface roughness calculations; lighter colors represent higher surface amplitudes than dark colors (scale left of A). Syscor's sensors were designed to be extremely rough, in an effort to increase surface area. B) Shows a 2D rendering of Syscor PAS surface topology; dark regions are lower in amplitude than light regions. Inset in Figure B presents contact angle measurements that show high surface hydrophobicity, rendering the polymer absorption sensors highly resistant to degradation or false-alarms resulting from extended exposure to water and ice. C&D) Present cross-sectional scanning electron microscopy (SEM) scans of Syscor PAS. The dark regions are voids within the sensor's composite material; these voids help increase the PAS surface area for faster hydrocarbon detection kinetics. All scale bars = 100 μm.

Final Results: The combination of all enhancements has resulted in a net positive effect on the sensor's operational reliability and stability. The advantages provided by the new PAS have been critical to Syscor's successful commercialization of these devices, drastically improving the existing technology without reinventing the wheel.

Syscor PAS Product Types, Attributes and Applications

Standard and Fast Action product types have been developed to cover a wide range of applications. Although the Standard and Fast Action types are designed for differing applications, there are some common aspects in their design and manufacture.

Common Durability and Selectivity: Sensor durability and enhanced selectivity/sensitivity improvements are achieved by doping the PAS matrix with proprietary thermoplastic blends. Specifically, the sensor material is doped with high modulus, highly viscous, thermoplastics which possess low coefficients of thermal expansion and are highly soluble in hydrocarbons. The dopant materials are carefully chosen based on their selective affinity for known target hydrocarbons, reducing the risk of false positives caused by residual substances which may be present in the environment. An added benefit of the dopants is an extreme reduction in problematic baseline drift through stability resulting from physical cross-links created in the polymer matrix (Figure 3).

Common Water Corrosion Protection: The embedded sensor pads of both the Standard and Fast Action PAS are protected against corrosion through a proprietary, highly conductive, water-proof sealant.

Standard PAS Attributes and Applications: Standard PAS are highly robust sensors which exhibit gradual change in response to hydrocarbons. These sensors are specially designed to prevent nuisance alarms and are particularly suited for applications where significant exposure to hydrocarbons is likely or when legacy/residual hydrocarbons may be present.

The Standard PAS is manufactured with an additional proprietary rubber-composite coating that is applied over the PAS material. The coating increases mechanical durability of the embedded sensor. The coating also serves to avoid false positives by blocking direct contact of the hydrocarbon with the embedded sensor; unless hydrocarbons exist in sufficient concentration (threshold) they will not pass the coating to the embedded sensor. Residual hydrocarbons (e.g., micro-sheens) are generally not present in sufficient concentration to trigger an alarm. As a result, the coating avoids instances of detection when insignificant levels of hydrocarbon are present and the sensor only triggers when relatively high amounts of leaked hydrocarbons are present.

The design of Standard PAS allows them to operate in- and underwater making them suitable for deployment scenarios where detection of hydrocarbons in waterways is prioritized. Applications for this sensor include—but are not limited to—tailing ponds, facility infrastructure, and/or monitoring wells in- and around production sites, where some level of previous contamination might be expected.
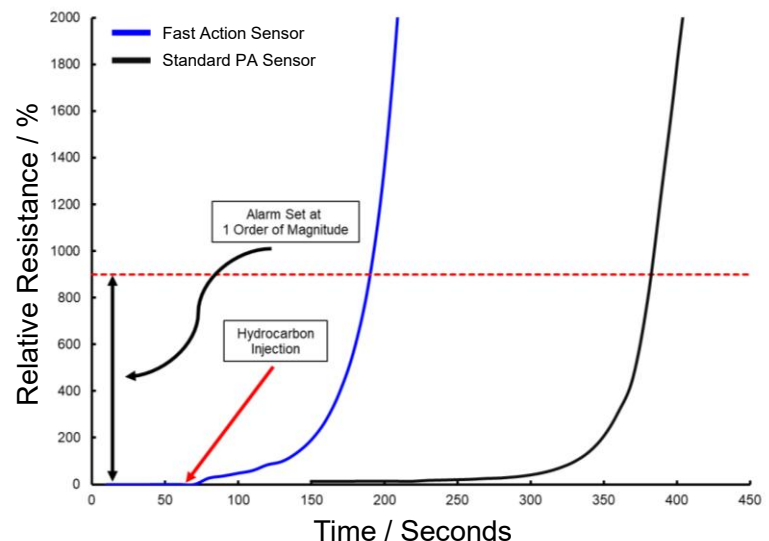

Figure 5: Direct hydrocarbon exposure to the Fast Action and Standard PAS. The Fast Action PAS reacts to gaseous hydrocarbons approximately 2x to 3x as quickly as the Standard PAS. Tests were conducted in a controlled environment, at 25 °C, using hexanes.

Fast Action PAS Attributes and Applications: Fast Action PAS are highly responsive sensors which react quickly to the presence of hydrocarbons and are sensitive enough to detect gaseous hydrocarbons. [1] These attributes result from the exposing the PAS directly to its environment—the Fast Action PAS is manufactured without an exterior rubber coating. This direct exposure enables rapid detection of hydrocarbons.

These sensors are intended for installation adjacent to, or nearby, high consequence ecosystems or critical infrastructure.

Figure 5 compares the sensitivity of the Standard and Fast Action PAS.

PAS Hydrocarbon Detection and Material Qualification

Since 2016 Syscor has maintained an active PAS research and development (R&D) program. A major focus of the program has been the characterization, quantification and validation of certain PAS properties and behaviors. The testing has been concentrated in the following areas:

No.	Name	CAS No.	Detected by Syscor PAS?
1	1,3 Butadiene	106-99-0	No
2	Methanol	67-56-1	No
3	Methylene Chloride	75-09-2	Yes
4	1,2-Dicholorethylene	156-60-5	Yes
5	Methyl Butyl Ether	1634-04-04	Yes
6	Hexane	110-54-3	Yes
7	Butanone	78-93-3	Yes
8	2,2 Dichloropropane	594-20-7	Yes
9	Chloroform	67-66-3	Yes
10	Methyl Acrylate	96-33-3	No
11	Ethyl Acetate	141-78-6	Yes
12	Tetrahydrofuran	109-99-9	Yes
13	Phenol	108-95-2	Yes
14	Bromobenzene	108-86-1	Yes
15	Benzene	71-43-2	Yes
16	Toluene	108-88-3	Yes
17	Ethylbenzene	100-41-4	Yes
18	p-Xylene	106-42-3	Yes
19	Styrene	100-42-5	Yes
20	o-Xylene	95-47-6	Yes
21	Ethyl toluene	622-96-8	Yes
22	Trimethylbenzene	95-63-6	Yes
23	Isopropylbenzene	98-82-8	Yes
24	n-Propylbenzene	103-65-1	Yes
25	Butylbenzene	135-98-8	Yes
26	Isopropyltoluene	99-87-6	Yes
27	Butyl Benzene	104-51-8	Yes
28	Naphthalene	91-20-3	Yes
29	Cyclohexane	110-82-7	Yes
30	Methyl Cyclohexane	108-87-2	Yes
31	Heptane	142-82-5	Yes
32	Octane	111-65-9	Yes
33	Nonane	111-84-2	Yes
34	Decane	124-18-5	Yes
35	Undecane	1120-21-4	Yes
36	Dodecane	112-40-3	Yes
37	Tridecane	629-50-5	Yes
38	Tetradecane	629-59-4	Yes
39	Pentadecane	629-62-9	Yes
40	Hexadecane	544-76-3	Yes

Figure 6: A comprehensive list of target analytes and PAS response when exposed.

- Hydrocarbon detection capabilities
- Material stability
- Environmental cross-sensitivities
- Susceptibility to corrosion.

The greater part of the PAS R&D program has been conducted independently. Additional testing was conducted with oversight from the Pipeline Research Council International (PRCI), Geosyntec Consultants, and C-FER Technologies. Studies were carried out in both controlled laboratory environments and field applications.

Detailed results are provided in the following sections, A through E.

A. Liquid Hydrocarbon Detection

Syscor PAS materials can only detect hydrocarbons with molecular weights greater than that of propane. Due to their chemical/material properties, Syscor PAS are inhibited from reacting to many naturally occurring analytes of interest such as methane, ethane, propane, and hydrogen sulfide. These analytes have no effect on the PAS because the substances are not able to partition into (i.e., mix with) the PAS polymer material.

To determine the range of possible target analytes, the sensors were exposed to a variety of chemicals and their behaviour was monitored in real-time. The testing was carried out in triplicate and the results are tabulated in (Figure 6).

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[1] Although a Fast Action PAS can detect hydrocarbons in gas Syscor only recommends their PAS for liquid detection.
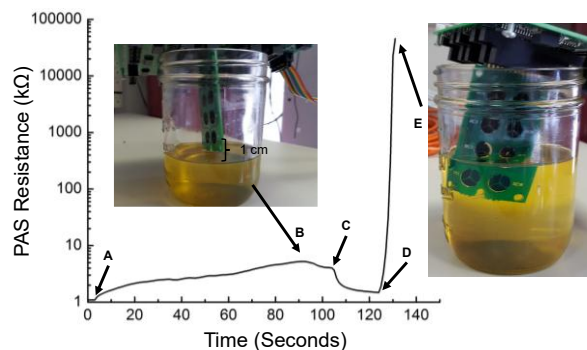
Figure 7: Demonstration of PAS baseline behaviour when exposed to hydrocarbon fumes vs direct liquid contact. The sensors were exposed to diesel fumes at (A) and reached their saturation point at (B). After the sensors were removed at (C) they were directly contacted with diesel at (D). The collected data shows the PAS reaction to liquid hydrocarbons was orders of magnitude higher than when exposed to the same hydrocarbons in the gas phase.

In general, the sensors produced no response when exposed to methane, ethane, propane, or hydrogen sulfide. When exposed to butane, their response was orders of magnitude higher than the established baseline. Furthermore, when exposed directly to liquid hydrocarbons, such as pentane, hexane, gasoline, diesel, crude oil and heavier hydrocarbons, Syscor PAS responded with a clear, strong signal (Figure 7). All hydrocarbons between pentane and C18 were tested and successfully detected by the sensors.

The Syscor PAS were also tested for their response to hydrocarbons at different service temperatures, between -40 °C and +60 °C. The sensors were tested at 3 temperature setpoints: -25, 0, and 25 °C; and exposed to 3 common petroleum products: gasoline, formulated dilbit, and 5-year-old crude oil, with an API of 11° (Figure 8 A-C).

Figure A: Time to Alarm for Syscor PAS After Exposure to Gasoline

Product Temperature → ↓ Sensor Temperature	-25 °C	0 °C	25 °C
Fast Action PAS @ -25 °C	< 10 minutes	< 10 minutes	< 1 minute
Fast Action PAS @ 0 °C	< 10 minutes	< 10 minutes	< 1 minute
Fast Action PAS @ 25 °C	< 1 minute	< 1 minute	< 1 minute
Standard PAS @ -25 °C	< 15 minutes	< 15 minutes	< 10 minutes
Standard PAS @ 0 °C	< 15 minutes	< 10 minutes	< 5 minutes
Standard PAS 25 °C	< 10 minutes	< 5 minutes	< 3 minutes

Figure B: Time to Alarm for Syscor PAS After Exposure to Dilbit

Product Temperature → ↓ Sensor Temperature	-25 °C	0 °C	25 °C
Fast Action PAS @ -25 °C	< 10 minutes	< 5 minutes	< 5 minutes
Fast Action PAS @ 0 °C	< 5 minutes	< 5 minutes	< 5 minutes
Fast Action PAS @ 25 °C	< 5 minutes	< 5 minutes	< 5 minutes
Standard PAS @ -25 °C	< 200 minutes	< 150 minutes	< 50 minutes
Standard PAS @ 0 °C	< 150 minutes	< 10 minutes	< 10 minutes
Standard PAS 25 °C	< 60 minutes	< 10 minutes	< 5 minutes

Figure C: Time to Alarm for Syscor PAS After Exposure to Crude (API 11°)

Product Temperature → ↓ Sensor Temperature	-25 °C	0 °C	25 °C
Fast Action PAS @ -25 °C	< 300 minutes	< 150 minutes	< 20 minutes
Fast Action PAS @ 0 °C	< 120 minutes	< 25 minutes	< 10 minutes
Fast Action PAS @ 25 °C	< 20 minutes	< 10 minutes	< 5 minutes
Standard PAS @ -25 °C	< 400 minutes	< 300 minutes	< 250 minutes
Standard PAS @ 0 °C	< 300 minutes	< 50 minutes	< 20 minutes
Standard PAS 25 °C	< 250 minutes	< 20 minutes	< 20 minutes

Figure 8: Tabulated time to alarm results for the Fast Action and Standard PAS

Figure 9: Crude oil viscosity increase demonstration at -25 °C.

In an effort to reproduce real-world scenarios, two iteration of the experiment at each temperature setpoint were conducted: (1) Petroleum products at the same temperatures as the sensors; and (2) Petroleum products at approximately 25 °C (e.g., simulating product temperatures when flowing through pipelines)[13].

All of the PAS responded relatively quickly—duration between exposure to PAS, and change in baseline—when exposed to products at 25 °C with the Fast Action sensors reacting instantaneously and producing alarms in less than 5 minutes (Figure 8A). The Standard PAS responded to the test products in less than 10 minutes and produced alarms in less than 30 minutes—the slowest detection resulted from testing diesel.

Temperature-dependent decreases in sensor response were an anticipated result because PAS exposure response times are dependent upon analyte mobility and diffusivity (Figure 9). As analyte exposure temperatures were decreased from 25 °C to 0 °C and - 25 °C, response times and time-to-alarm for the Standard PAS did slow considerably. The Fast Action PAS did not, however, exhibit a similar dramatic decrease in detection times and time-to-alarm.

Typically, crude oil is transported through pipelines at between 20 and 50 °C.[13] Therefore, if the ambient temperature is below 0 °C, product flowing through pipelines is considerably warmer than the ambient. Based on Einstein's definition of diffusion kinetics, exposure of PAS to product that is warm relative to the ambient temperature is not expected result in degraded detection performance. To validate this, the -25 and 0 °C exposure tests were re-executed. However, in the second test iteration, the target product was at room temperature and only the PAS were cooled to their target setpoints of 0 and -25 °C. These tests revealed that the PAS were much quicker to detect product with temperature of 25 °C, regardless of the PAS temperature. Nevertheless, when the PAS themselves were cooled to 0 and -25 °C, sensor reaction times and time-to-alarm was significantly slower than their warmer counterpart. Again, this result is related to diffusion and the influence of cold PAS membranes exhibiting slower mixing kinetics at the product-sensor interface.

Oil Sheen Test 25°C

Oil Sheen Test 4 °C

Oil Sheen Test - 25°C

Pre-exposure Frozen Sensors

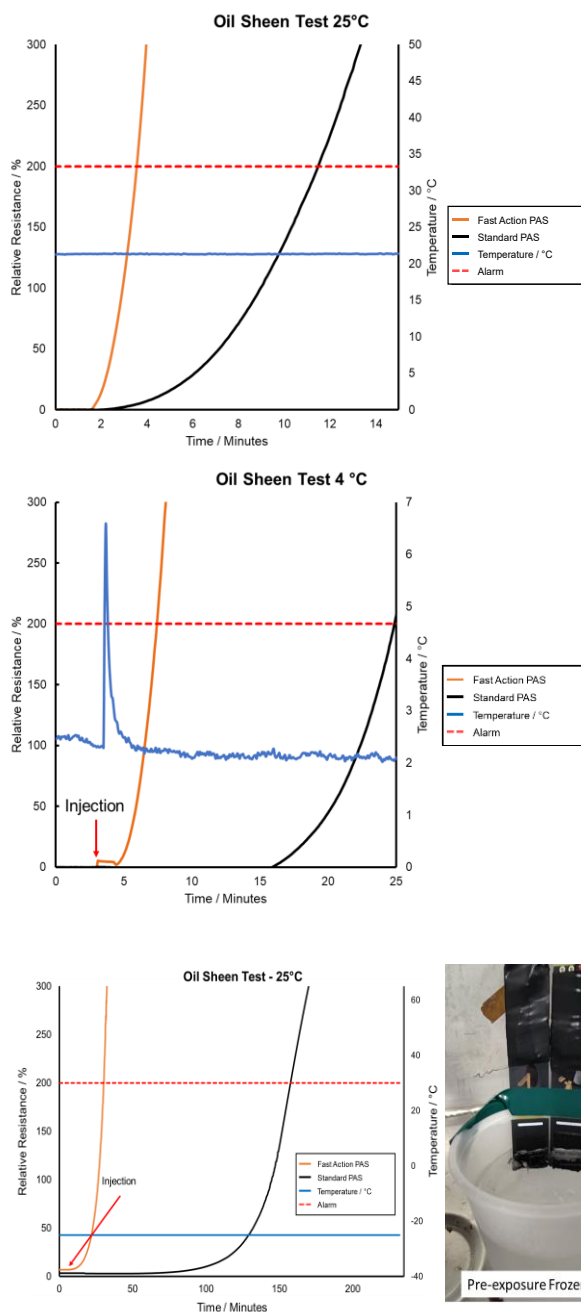Sensors Exposed to frozen, API 11° Crude Oil

Figure 10: Oil sheen exposure testing for the Standard and Fast Action PAS. Tests were conducted using a crude oil sheen that was < 0.1 mm thick. Both sensors produced alarms with the exception of exposures at -25 °C. Sheen thickness was calculated using the specific gravity of crude oil.

Syscor's capacity to detect thin oil sheens (<0.1 mm thick) on water was tested using both the Fast Action and the Standard PAS. Reaction times and time-to-alarm was determined for both sensor systems at three operational temperature setpoints: 25, 0, and -25 °C (Figure 10).

In general, for test temperatures ≥ 0 °C, both the Fast Action and Standard PAS responded to crude oil sheens in less than 20 minutes and produced alarms in less than 25 minutes. The fastest response and time-to-alarm was exhibited by the Fast Action PAS at the 25 °C test temperature (< 1 minute). Conversely the -25 °C tests resulted in response times on the order of 10^2 minutes (Table 1). As stated in the previous section, detection of crude oil at or below 0 °C is exponentially more difficult than at warmer temperatures. As temperature decreases, crude oil viscosity increases (Figure 9) and its diffusivity decreases. Both factors negatively impact sensor reaction times and time-to-alarm.

If customers require sensor systems to quickly detect low concentrations of hydrocarbons over a wide range of temperatures, Syscor recommends installation of the Fast Action PAS hydrocarbon detection system.

Table 1: Time to Alarm for Syscor PAS when exposed to Thin Crude Oil Sheens on Water		
Temperature / °C	Fast Action PAS	Standard PAS
-25 (Frozen Water)	< 30 minutes	< 150 minutes
4	< 5 minutes	< 25 minutes
25	< 1 minute	< 15 minutes

A **Thermal Degradation @ 125 C**

B **Hydrolytic Degradation @ 75 C**
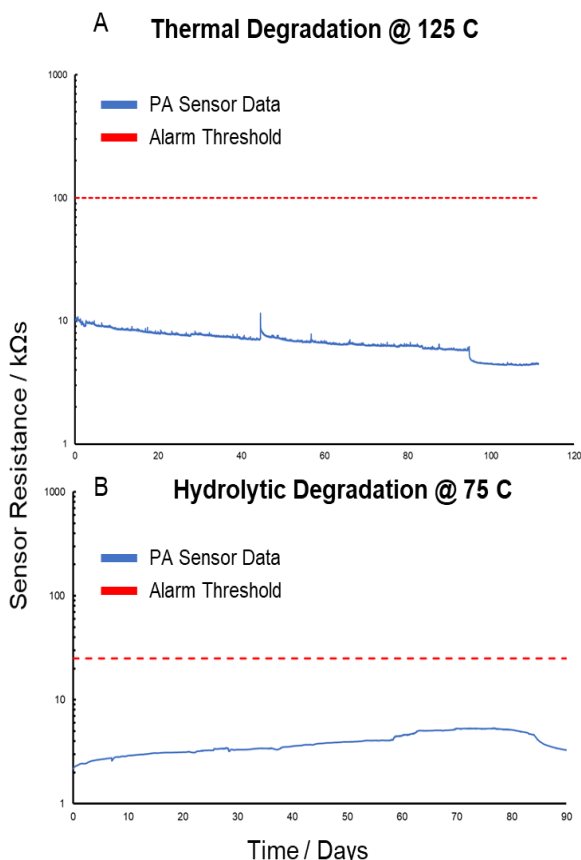
Figure 11: Example data for (A) thermal degradation and (B) hydrolytic degradation tests.

C. Material Degradation

PAS material degradation (ageing) studies were performed under accelerated ageing conditions, as established in the materials science industry. These studies determined sensor material reliability and longevity when deployed in adverse environments. PAS materials were specifically studied for thermal-, hydrolytic-, and mechanical-degradation.[14–16] For example, thermal studies (oxidative degradation)[16] determined sensor lifetimes in heat, and were tested by simulating arid environments (Figure 11A). Hydrolytic studies determined material behaviour in water, and were conducted by simulating humid environments (Figure 11B). Mechanical studies determined material hysteresis and were conducted by simulating day/night cycles and through repeated hydrocarbon exposures (Figure 12C). All of the test parameters were based on expected sensor deployment scenarios.

The material degradation tests were performed with applied heat. Heat is necessary for long-term material studies because it hastens material ageing by actively inducing degradative mechanisms. The extent of degradation was determined by proxy, through sensor resistance. Resistance is an excellent proxy for material degradation because when PAS material degrades, micro-sized voids remain within the polymer matrix. These voids result in a loss of electrical conductivity, leading to increased resistance and false-alarms (Figure 12A and Figure 12B). Thus, observed increases in sensor resistance during testing is a good indication of PAS degradation.

First, PAS thermal material degradation was mapped by exposing the sensor material to elevated temperatures between 100 °C and 300 °C, for > 3 months (Figure 11A). Second, hydrolytic tests were conducted under static conditions, with high humidity (RH > 75%) and relatively high temperature (T > 65 °C) (Figure 11B). Lastly, mechanical stress and material hysteresis tests were performed under dynamic conditions, through two experiments: 1. repeated VOC exposure (at elevated temperature); and, 2. temperature cycling.
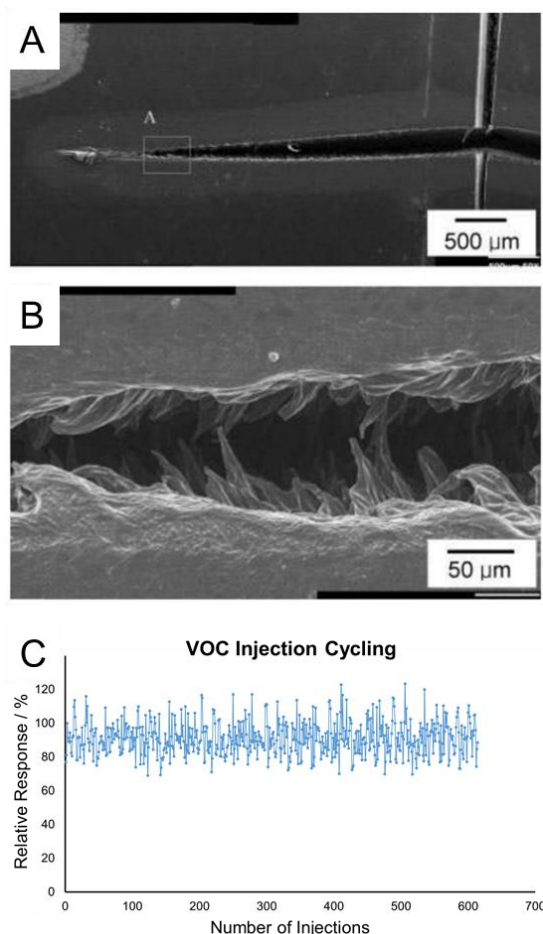
Figure 12: A) Top-down and side-on (B) view of mechanical stress cracking of a polymer observed using scanning electron microscopy. These are example images of what material degradation within the polymer matrix looks like. C) VOC exposure cycling tests on PAS at Syscor's labs.

Once the tests were complete, the raw data was interpreted though the Arrhenius Model (Figure 13). The Arrhenius Model is an industry standard that is used to extrapolate service lifetimes from simulated conditions. Syscor extrapolated all of its test data using the Arrhenius model and concluded that the Syscor proprietary sensor materials can operate in arid or humid environments for up to 30 years without failure or loss of sensitivity.

D. Cross-Sensitivity to Temperature, Humidity and Water Saturation

A major unfulfilled petroleum industry application for hydrocarbon detection is: real-time and reliable monitoring of water bodies, in hot or cold climates. As stated earlier, traditional PAS technologies have fallen short in matching these requirements because of their tendency for false-alarms or other weather-related issues. Syscor's hydrocarbon sensors are specifically designed for the application in these climates and conditions. To test and prove their reliability, Syscor conducted exhaustive cross-sensitivity trials.

These cross-sensitivity tests differ from the degradation tests referenced in 'Section B,' in that the degradation tests were designed to produce material failure. On the other hand, the cross-sensitivity tests were conducted to understand standard operational conditions and limits. Syscor's trials specifically explored: how PAS baseline resistance behaved when exposed to quick temperature cycling (Figure 16A); or, when submerged completely in water (Figure 16B); and, when subjected to repeated freeze/thaw cycles (Figure 16C).

In general, all of the tests produced little to no change in sensor baseline resistance (relative to alarm thresholds) and had no long-term effect on the sensor material (Table 2). The proprietary anchor points within the polymer matrix effectively controlled sensor cross-sensitivities and minimize the mechanisms that might lead to erroneous readings. These results provide confidence that Syscor PAS technology will provide long-term and reliable operation—including the avoidance of false positives—in almost any environment.

Table 2: PAS Cross-Sensitivity to Humidity, Water Submersion, and Temperature

Sensor Formulation	Cross-Sensitivity			
	Humidity (dR/R_o)	Prolonged H_2O Submersion (dR/R_o)	Temperature 60°C (dR/R_o)	Temperature -25°C (dR/R_o)
Syscor PAS	< 10%	< 10%	< 50%[1]	< 10%

A

Arrhenius Plot of PA Sensor Accelerated Thermal Degradation

Raw Data

Line of Best Fit

$y = 89.507x + 7.351$
$R^2 = 0.9943$

B

PAS Humidity Degradation

Raw Data

Line of Best Fit

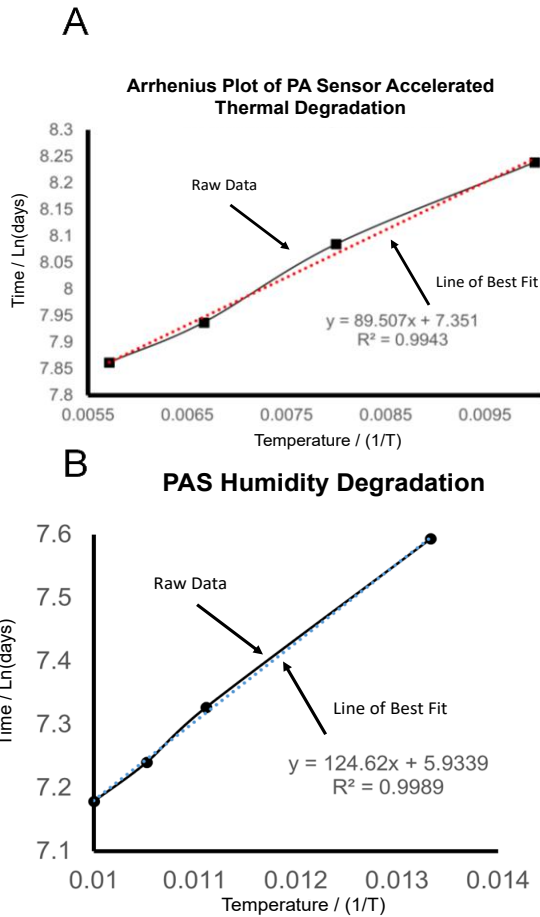$y = 124.62x + 5.9339$
$R^2 = 0.9989$

Figure 13: Arrhenius modeling of (A) thermal degradation and (B) hydrolytic degradation experiments for determining service lifetime of Syscor PAS.

An ongoing long-term cross-sensitivity study is currently being conducted at an Enbridge site in Loreburn, Saskatchewan. This test started in 2018 and is still active today. The test involved the installation of PAS units above a monitoring well in a covered, outdoor transfer facility. The sensors installed here have not deviated from their baseline and have had zero false-alarms due to cross-sensitivities. The sensors have been exposed to wet/dry conditions and temperature ranges between -40 °C and + 40 °C. These results provide real, in-field evidence supporting Syscor's lab simulated long-term ageing, cross-sensitivity and corrosion test results.

E. Corrosion Prevention Coating

Sensor systems that are deployed underwater are generally subject to corrosive effects. As Syscor PAS are designated for underwater deployment, sensor corrosion and long-term operational viability of the devices was studied through simulated lab and comprehensive in-field tests. Corrosion of sensor circuitry through both induced and naturally occurring electrochemical processes is a major hazard faced by commercial sensor systems leading to risk of false-alarms, false negatives, and/or outright instrument failure. To address the hazard, a proprietary protective coating was developed which is applied to the sensor circuit board after the polymer substrate is deposited and cured. The coating protects the sensors from both corrosion and abrasion.
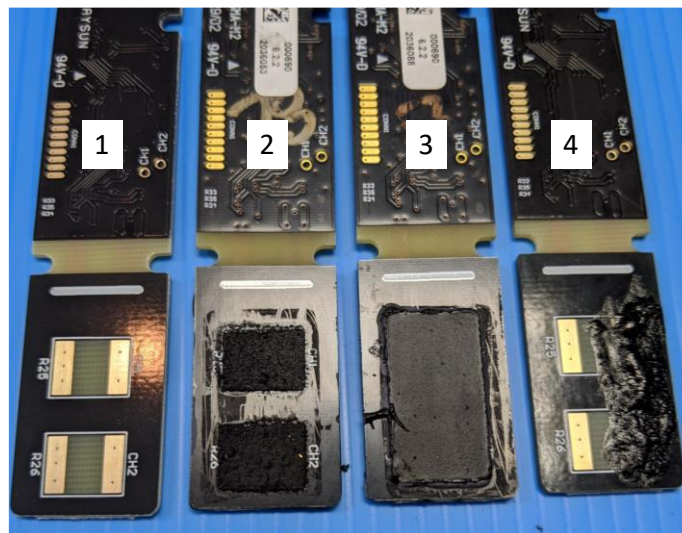

Figure 14: From left to right: 1. PAS printed circuit board; 2. Circuit board populated Fast Action PAS; 3. Standard PAS; 4. Example of corrosion protection coating applied to the printed circuit board electrodes.
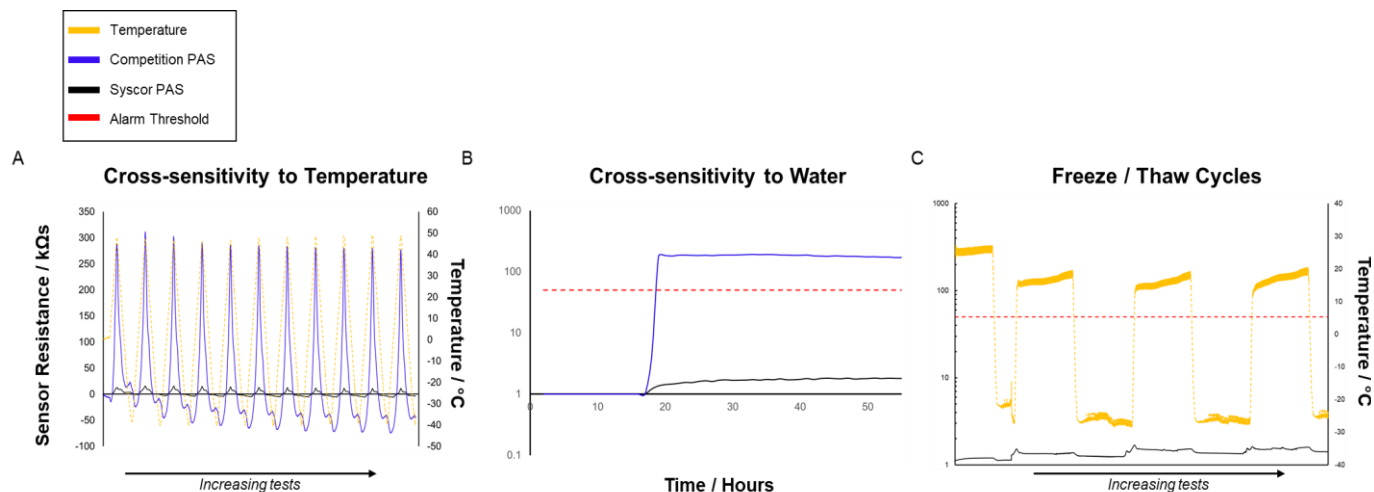
Figure 16: Cross-sensitivity tests against temperature, water submersion, and freeze/thaw cycles. The temperature and water submersion graphical data has competition PAS plotted as a reference. In each case, Syscor PAS formulation outperformed the competition by large margins, with some cases as much as an order of magnitude.

The corrosion-proof coating is comprised of a waterproof thermoset material infused with highly conductive carbon nanotubes. The thermoset prevents water from penetrating through the PAS material and corroding the metallic circuit board electrodes beneath (Figure 14). At the same time, the embedded carbon nanotubes preserve circuit board copper traces thereby all but eliminating degradation of the electrical continuity between the circuit board and the deposited polymer substrate. The coating is applied to both the Fast Action and Standard PAS products.
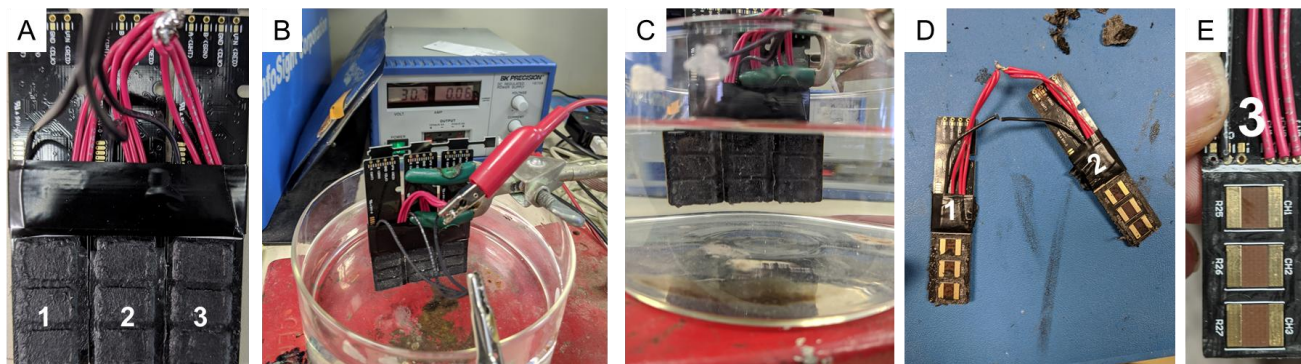

Figure 15: Example of sensor corrosion test. PAS (A) were tested in a simulated corrosive environment (B) with an applied potential of 30V and (C) salt water. The test sensors (D) were completely corrosion free after two weeks of testing (E).

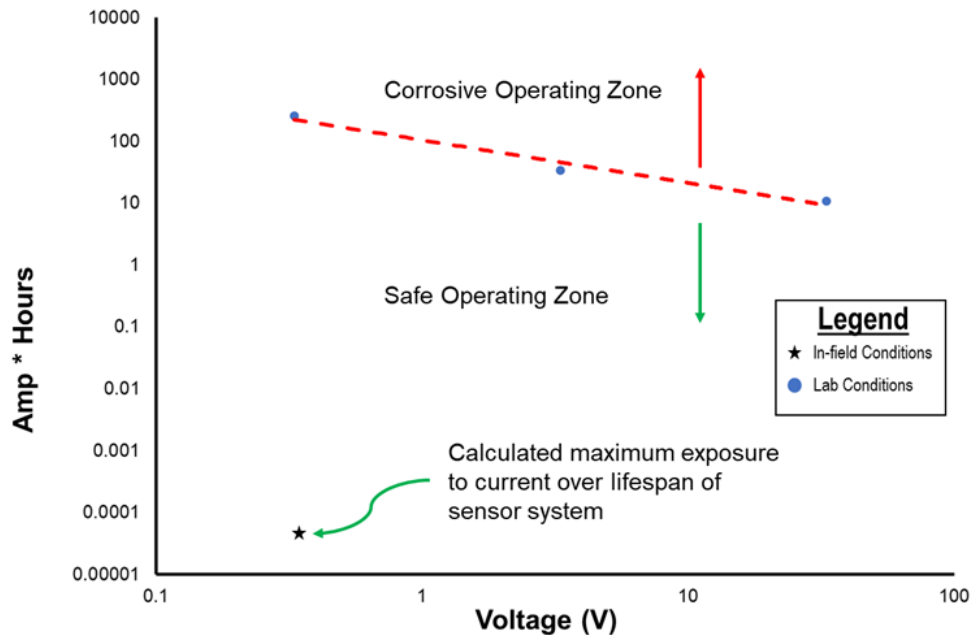## Corrosive and Safe Conditions for Underwater Deployment

Figure 16: Experimental extrapolation of corrosion forces on Syscor PAS sensors. Sensors that exposed to Amp-hours below the dotted red line are within the established safe zone; whereas, sensors above are expected to corrode. Syscor's hydrocarbon detectors are guaranteed to survive in water for up to 3 years under continuous operation.

Syscor tested the corrosion-proof coatings for their effectiveness by exposing the sensor systems to simulated, highly corrosive, underwater environments. These environments were ~5 orders of magnitude more potent (higher applied voltage, dissolved salts in water, elevated temperature) than those levels that the sensors would normally experience. The tests were carried out at 3 different voltages and for up to 8 weeks in duration (Figure 15). Once corrosion was induced (detected by an increase in sensor resistance), the amp-hours required to induce sensor corrosion were calculated and extrapolated to represent real-world conditions (Figure 16).

In general, based on the test results the test sensors will withstand a minimum of ~10 amp-hours without corroding. Syscor's field sensors only experience approximately 1.6×10^{-4} amp-hours over a three-year service lifetime. As a result, the new coatings produce a 'safety-factor' 6 orders of magnitude higher than levels that Syscor's field devices would ever experience in the field, effectively eliminating any cause for concern when considering corrosion related failures.

Conclusions

Syscor Controls & Automation Inc. has developed a hydrocarbon detection system that can detect petroleum products in air, underground or in water. The systems are low power, enabling remote installations, highly robust, intrinsically safe certified, and utilize the Wireless HART communications protocol. The hydrocarbon detection system is engineered to provide seamless environmental monitoring for up to 5 years underwater, and 30 years otherwise.

The systems are completely corrosion- and weather-proof, allowing for installation in any environment. Current applications for Syscor PAS systems include detection of hydrocarbon leaks in transport and field production facilities equipment such as pipelines, pump stations, flanges; aboveground and underground storage tanks and associated rotating equipment; water bodies—still, flowing and frozen—such as collection ponds, lakes, rivers, and aquifers.

References

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Appendix: Field Testing

Standard and Fast Action PAS may be tested in the field through a procedure commonly referred to as a *Bump Test*. The Bump Test exposes PAS devices to butane at concentrations expected to cause a properly functioning PAS to exceed any alarm setpoints configured in an attached supervisory system. A Bump Test is normally preformed during commissioning and at subsequent intervals during the PAS service life.

Syscor provides a PAS Bump Test kit. The Bump Test procedure involves injecting butane into the Test Enclosure containing the PAS device under test. Butane is used because it is absorbed by the PAS within a few seconds. The butane is discharge by the PAS over the course of a few minutes with minimal material hysteresis effects. Butane also has the advantage of being easy to procure as replacement butane canisters are generally available for over-the-counter purchase from local sources.

The Bump Test procedure may be executed in minutes and without significant environmental repercussions. Figure 17 provides an overview of the PAS Bump Test kit and procedure.
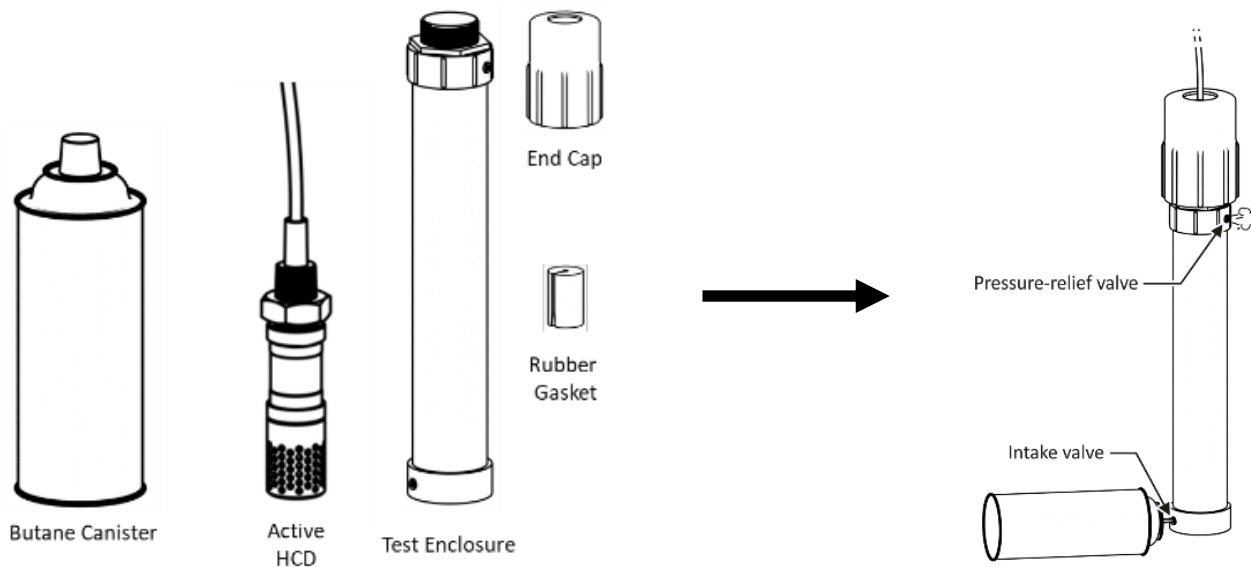

Figure 17: PAS Bump Test kit components and procedure

PAS installed in facilities and locations where the sensors are readily accessed will normally be tested on a recurring maintenance schedule. PAS deployed in areas with limited accessibility (e.g., floating roofs of covered aboveground storage tanks) will only be subjected to a Bump Test during commissioning or following extended periods of field service—as Syscor PAS are self-calibrating this practice does not represent considerable risk. In any case, should a Syscor PAS fail a Bump Test it is recommended that a Syscor field sales associate be consulted.

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