

Use of Passive Age Sensors for Projecting Remaining Thermal Life of Materials

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ABSTRACT

This paper proposes use of passive thermal age sensors and empirical correlation models to project remaining useful life of thermally degradable products and materials. Thermal age sensors, comprising a selected polymeric matrix and conductive fillers, change resistance as the matrix thermally degrades in the same thermal environment as the monitored product or material. Thermal age sensor resistance represents the integrated time-temperature condition of the sensor at its characteristic activation energy. Empirical models correlate sensor resistance to a selected property of the material utilizing multi-temperature thermal aging data of the monitored material. These correlation models project the current condition of the selected product property, or, if end-of-life properties are specified, these models project the percentage of remaining design life of the material. Several applications of this approach are discussed utilizing thermal age sensors attached to monitored materials. An approach utilizing two thermal age sensors is introduced that allows a single tag to predict selected properties of many different materials. PHM tags utilizing passive thermal age sensors do not require an internal source of electrical power or internal memory, eliminating the need for batteries and significantly reducing data management issues. This approach can be expanded to a wide range of products and materials when sufficient thermal age data is available.

1. INTRODUCTION

Projecting remaining thermal life of products and materials is a complex undertaking requiring collection of data representing the entire thermal history in which the target material exists. It also requires an understanding of the effect of the thermal history on one or more selected properties of the material. It is well known that most materials are affected by other environmental conditions

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such as humidity, gases, and ionizing and non-ionizing radiation. An exhaustive evaluation of material degradation in a complex environment is extremely complex and beyond the scope of this paper. However, the thermal environment of many materials is often the primary environmental stressor, and a simple method which is capable of adjusting the expected life of a material based on thermal conditions only is very useful, especially when it provides an economical improvement over simple “shelf life” methods where the thermal environment must be assumed.

A common method of incorporating thermal history in both diagnostic and prognostic analysis is the use of thermal data loggers in conjunction with physics-based modeling or empirical algorithms. For example, thermal data, such as thermal history from data loggers can be used together with algorithms to predict the future reliability of electronic products, (Vichare, Pecht, 2006).

The approach utilized in the present method utilizes an empirical model to project a selected material property based on the current thermal age of the material. The current thermal age of the material is represented by the resistance of a thermal age sensor thermally associated with the material. The empirical models require multi-temperature aging data of the selected property of the target material or product.

The thermal age sensor comprises a conductive composite sensor element whose resistance at any time represents the integrated time and temperature at its characteristic activation energy (E_a). These thermal age sensors are placed in the same or similar thermal environment as the product or material they are monitoring.

If an end-of-life value of the selected property is specified, these empirical algorithms can predict the remaining thermal life of the product or material as a percentage of remaining life. Or, they can predict the remaining life in time with an assumed effective temperature or use of a similar temperature environment in the future.

2. THERMAL AGE SENSORS

The methodology of this paper utilizes a conductive composite thermal age sensor as the primary sensor element for predicting material or product thermal degradation. Thermal age sensors act as “coupons” of the target material or product in that they respond to the thermal environment of the product. They are small, light and low cost since they inherently integrate time and temperature without batteries or memory requirements. Electrical power to read the sensor comes from a reader such as a multi-meter or RFID reader.

The thermal age sensors of this method comprise conductive composite elements that employ conductive fillers dispersed in a polymeric matrix. Sensors utilize electrodes to allow measurement of the sensor resistance. The resistance of the sensor depends on many factors including the matrix selected, the conductive filler, the geometry of the sensor element, and the processes used in mixing, curing and conditioning of the sensor. Thermal age sensors are typically hermetically sealed so that they respond to thermal environments only and minimally affected by the presence of humidity and other gases which may affect the sensor.

Figure 1 below shows the so-call electrical percolation curve for a conductive composite.

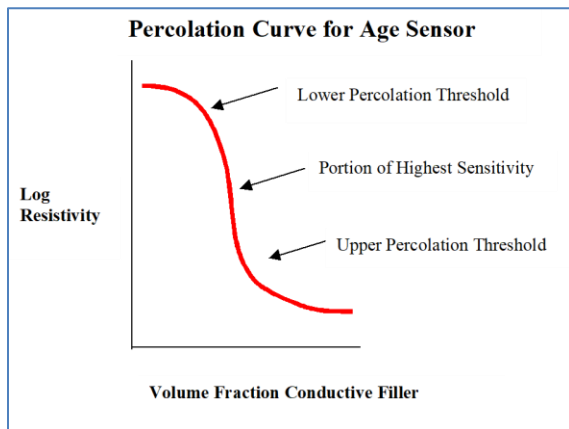


Figure 1: Electrical percolation curve for a conductive composite material.

The resistivity of the conductive composite decreases as the volume fraction of the conductive filler increases due to reduced distance between conductive particles. Note the large change in resistivity with small changes in volume fraction of the conductive filler in the steep portion of the curve. This amplification effect is useful in a thermal age sensor, where shrinkage of the matrix due to chemical and physical aging mechanisms is very small.

Figure 2 below shows an example of a sensor element with an epoxy matrix, carbon black conductive filler, and embedded electrodes. Sensor packaging provides desired sealing, mechanical protection, and electrical connectivity to a PHM tag.

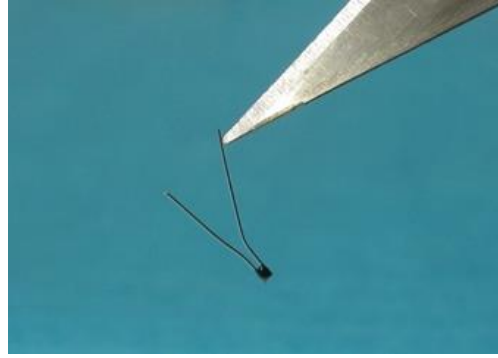


Figure 2. Photograph of epoxy-based thermal age sensor element.

Multiple aging effects on the sensor matrix including chemical and physical aging mechanisms result in changes of sensor resistance with time. For example, chemical reactions such as crosslinking and oxidation and physical reactions such as loss of volatile fractions result in volumetric fraction changes in the conductive composite element over time. These reactions normally result in a decrease in the volume fraction of the matrix with a resulting decrease in sensor resistance. Since these reactions are temperature dependent, the rate of sensor resistance change with time increases with temperature. This effect is shown in Figure 3 below for a cellulose acetate (CA) matrix sensor element.

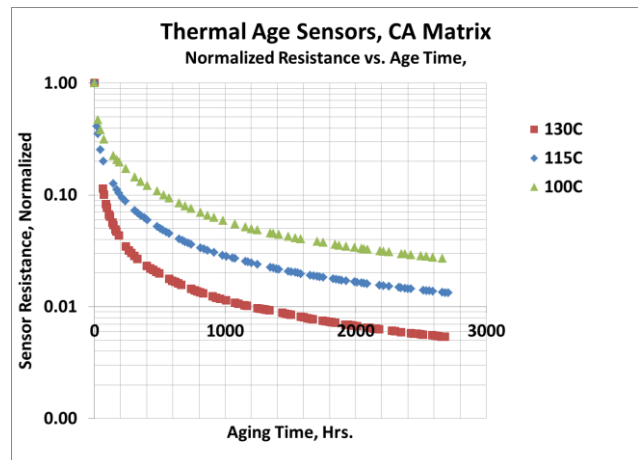


Figure 3: Thermal age sensor resistance vs. age time. Note temperature dependence on rate of resistance decrease.

The temperature-dependence on the rate of resistance change allows numerical and graphics-based analysis of this dependence for use as a thermal age sensor. For example, time-temperature superposition (TTS) may be used to determine Arrhenius behavior and activation energy (E_a) of the aging processes as suggested by Gillen, Bernstein and Celina (2017). TTS can also be used to determine Arrhenius behavior of the resistance decrease phenomenon of a

conductive composite sensor. An experimentally determined time shift or acceleration factor is applied to sensor resistance data for each temperature so that the resistance-time curves are superimposed. The figure below shows a TTS graph of the resistance-time response of the CA sensor data of Figure 3 at multiple temperatures.

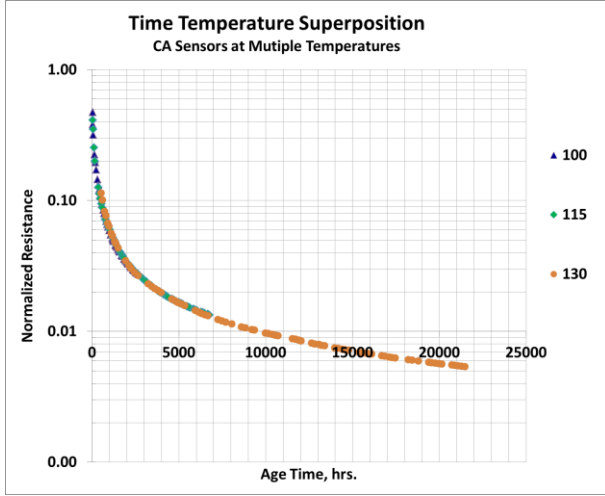


Figure 4: Time temperature superposition graph of the resistance response of CA thermal age sensors at multiple temperatures.

Table 1 shows the acceleration factors (AF) at each temperature (base temperature 100C) which produce the superposition shown in Figure 4.

Table 1: Acceleration Factors (AF) for sensor resistance vs. time for superposition.

TEMPERATURE (C)	ACCELERATION FACTOR
100	1.0
115	2.5
130	8.0

Since the acceleration factors above represent the reaction rate of sensor resistance to temperature, they can be used to determine the Arrhenius behavior of sensor resistance to temperature during aging. By plotting the natural logarithm of this acceleration factor (representing the relative rate of the reaction at different temperatures) to the inverse absolute temperature, linearity can be used to determine Arrhenius behavior of the thermal age sensor. The figure below shows Arrhenius behavior for the sensor example above.

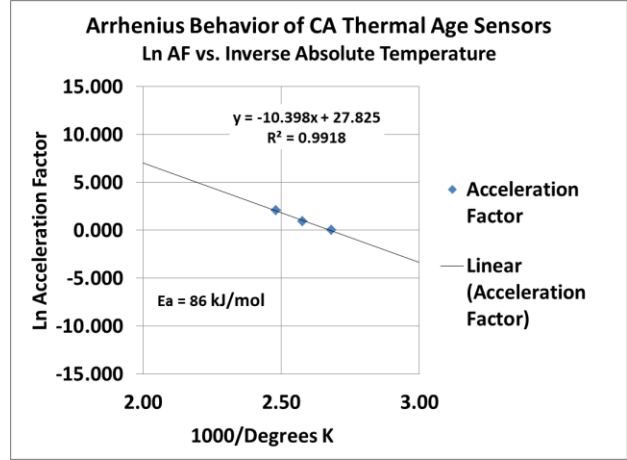


Figure 5: Arrhenius plot of natural logarithm of the acceleration factors and inverse absolute temperatures of Table 1.

The high linearity of the data as shown in Figure 5 demonstrates the excellent Arrhenius behavior of resistance of the thermal age sensor over the temperature ranges of this data. Arrhenius calculation of the activation energy of thermal age sensor resistance under the test conditions of the thermal aging yielded 86 kJ/mol.

Ideally, a thermal age sensor responds only to the integrated time and temperature of its environment. In practice, sensor resistance is also affected by measurement temperature, humidity, applied voltage, mechanical shock and other factors. For example, thermal age sensors show both temperature and humidity coefficients of resistivity. These coefficients can be measured and compensated for if necessary, by ambient temperature and humidity measurements. Temperature compensation for many matrixes does not require compensation unless measured under extreme thermal conditions. Humidity effects can be eliminated by hermetic sealing of the sensor package. Applied voltage and mechanical shock sensitivities are typically very low and normally do not require compensation.

Below is a photograph of a packaged thermal age tag having the thermal properties described above. Multi-meter probe connectors allow measurement of thermal age sensor resistance with an ohmmeter or multi-meter. Use of an epoxy container for the tag provides hermetic sealing and mechanical protection for use in industrial applications such as electrical equipment and structures.



Figure 6: Photograph of a packaged thermal age tag having a CA matrix.

3. TARGET MATERIAL PROPERTY ANALYSIS

The empirical correlation models of this approach utilize Arrhenius analysis of a selected target material property with aging time at multiple temperatures. The material property is normally selected to provide an indication of remaining usable life of the material or product.

The approach is similar to that of the Arrhenius analysis of thermal age sensor resistance. Ideally, the selected material property follows Arrhenius behavior during thermal degradation. An example of a selected property of a generic product or material comprising polymers during thermal degradation is shown in Figure 7 below.

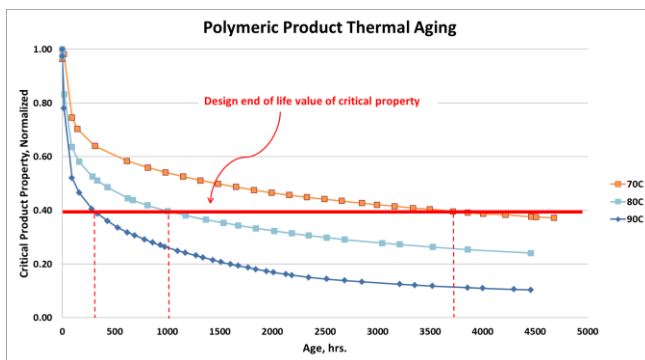


Figure 7: Characteristic degradation of a selected property of a product undergoing thermal degradation.

The rate of degradation of the property depends on the temperature environment with the rate typically being faster for higher temperatures. If a design threshold value of this property is established, as indicated by the red line of Figure 7, the design thermal life at any temperature or the current percentage of remaining life for a partially aged product may be determined.

The selected property for analysis ideally provides a reasonable “marker” for projecting target material end-of-

life conditions. This property data may be chemical properties, or they may be mechanical properties, physical properties or even biological properties as long as the property generally follows a repeatable temperature-dependent rate such as those properties displaying consistent Arrhenius behavior.

Product and material degradation are complex processes involving multiple chemical reactions including crosslinking, chain scission and oxidation reactions, physical processes such as volatile fraction loss, and in some cases biological or nuclear reactions. However, the thermal response of many products and components will show reasonable Arrhenius response over a limited temperature range when other environmental conditions are controlled or properties selected where other environmental stressors are of limited influence.

The selected material property data should be taken at multiple temperature aging conditions where other environmental factors such as humidity, gaseous environments or hermetically sealed conditions of the material approximate operational conditions as closely as possible. This data may be available from material or product manufacturers, industry or trade organizations, or in some cases available from the literature. Where the multiple temperature test data under relevant conditions is not available, trials may be necessary to provide this data.

An example of a material chemical property aging is shown below for degree of polymerization (DP) measurements made on kraft paper transformer insulation thermally aged in dried, degassed transformer oil (Lundgaard, Hansen, Linhjell, & Painter, 2004). Reduction of DP of the kraft insulation over time results in loss of mechanical properties of the insulation and the ability of the transformer to withstand mechanical, thermal and electrical stresses resulting from surges, overloads and other transient conditions the equipment is subject to. Although DP of kraft insulation is a very complex degradation process affected by a number of environmental stressors such as moisture and oxygen, loss of DP can be predicted for sealed conditions at different temperatures over extended aging periods as demonstrated by the authors.

Time temperature superposition analysis of the multi-temperature target material property data such as that of Figure 8 is used to determine Arrhenius behavior. The 90C/110C and 130C data is used in this analysis so that 70C data can be used for approach verification as described in section 4.

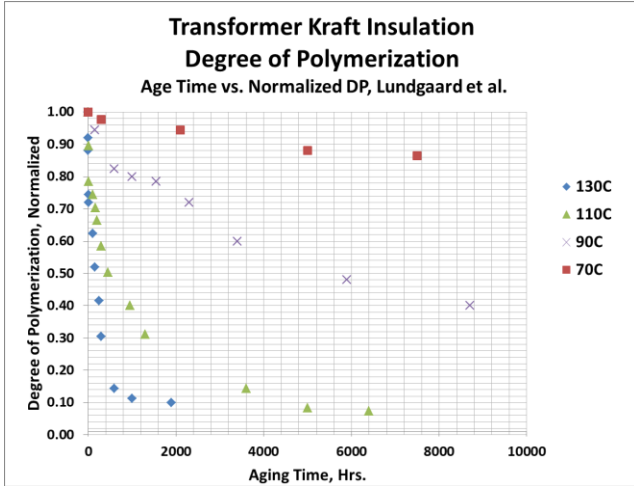


Figure 8: Degree of Polymerization of kraft paper transformer insulation in oil and aged at 130C, 110C, 90C and 70C (Lundgaard et al., 2004).

Figure 9 below shows the TTS analysis of the DP aging data of Figure 8.

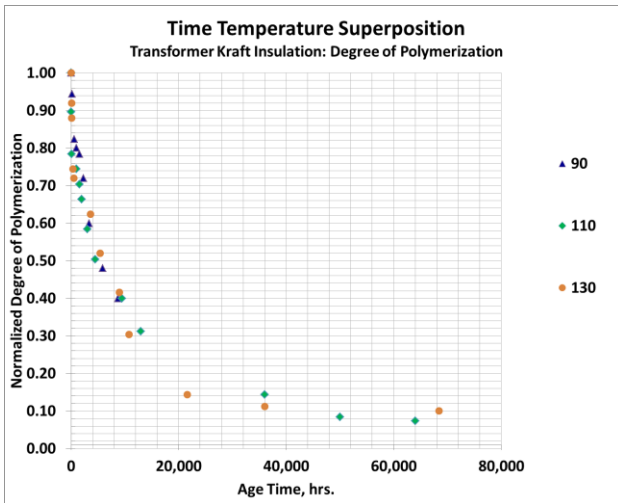


Figure 9: Time temperature superposition of transformer insulation DP data of the previous figure.

Table 2 shows the acceleration factors determined in the TTS of Figure 9.

Table 2: Acceleration factors determined from the TTS analysis of transformer insulation DP.

TEMPERATURE (C)	ACCELERATION FACTOR
90	1.0
110	10
130	36

Since acceleration factors are a measurement of the reaction rate of DP response at a given temperature, they can be used to evaluate the Arrhenius behavior of DP to temperature. Figure 10 below is a graph of the natural logarithm of the acceleration factors vs. the inverse absolute temperatures of the data of Table 2. The good linearity of the data in this graph suggests good Arrhenius behavior of DP degradation over time within the temperature range of the data.

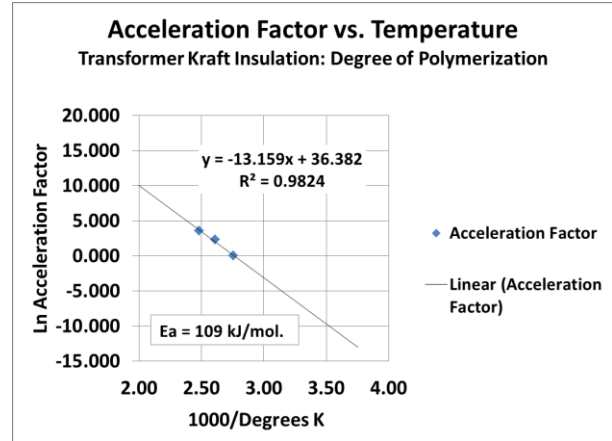


Figure 10: Plot of Ln of the acceleration factors vs. inverse absolute temperature of Table 2.

Arrhenius calculation of the activation energy of DP degradation under the test conditions of the Lundgaard et al. data yielded 109 kJ/mol.

4. EMPIRICAL CORRELATION MODELS

Empirical models are used to correlate thermal age sensor resistance with properties of target materials, products or components for which aging data is available. Two methods that are used in this approach are direct correlation of thermal age sensor resistance and thermal age data, and Arrhenius modeling of property data. The Arrhenius modeling approach of thermal age sensor data provides the effective temperature (T_{EFF}) over the total calendar time.

Empirical correlation models provide a means for projecting approximate target material/product condition without embedment of the thermal age sensor or tags in the material or sealed environment of a product. However, empirical modeling requires multiple temperature aging data taken under environmental conditions as similar as possible to product conditions for reasonable accuracy. And empirical models will not forecast material or product property degradation due to product defects. Both models require analysis for Arrhenius behavior of the target material degradation process in order to provide reasonable confidence in the correlation.

4.1. Direct Correlation Model

A direct correlation model is the simplest approach and requires only sensor resistance as an input to predict the current property of the target material once the model algorithm has been developed for a target material.

Direct correlation models can be made by numerical approaches or by plotting thermal age sensor resistance and the selected material property at the same age time and temperature. Unless thermal age sensors and target material are co-aged, this will normally require adjustment of sensor resistance to the target material product data age time by use of acceleration factors of the sensor determined from target aging temperatures. An example of a direct correlation of CA thermal age sensor to the transformer DP data of Figure 8 is shown below.

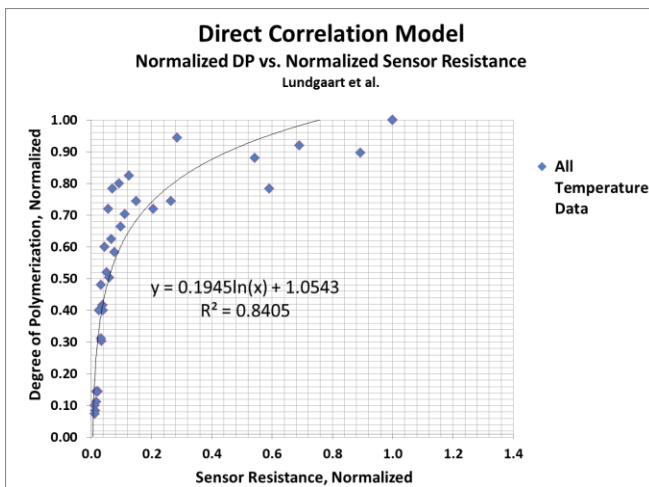


Figure 11: Direct correlation model of normalized sensor resistance to normalized degree of polymerization.

4.2. Arrhenius Model

A second approach utilizes a sensor acceleration factor determined by the calendar time for which the sensor has been associated with the product (assumed to be the total age time if the sensor has been associated with the target material since production) divided by the time required for the sensor to reach that value at the lowest calibration temperature. For the example here, the age time for the 100C curve of Figure 3 (the base or lowest test temperature) would be used for a CA sensor associated with a target material.

Figure 5 can be used to determine the effective temperature T_{EFF} of the sensor. T_{EFF} is defined as that temperature, which if held constant for the calendar time of the sensor reading, provides the same resistance change as the actual (variable or complex) thermal history of the sensor. If the assumption is made that T_{EFF} of the target material is the same as T_{EFF} of the sensor, current target condition may be

projected by determining the target AF from Figure 10 and applying it to the base temperature (90C) data of Figure 8.

Figure 12 below shows projected DP vs. experimental data at 70C using Figure 8 data (70C) outside of that used in development of the model. This approach provides a first level of model verification requiring extrapolation of target aging data.

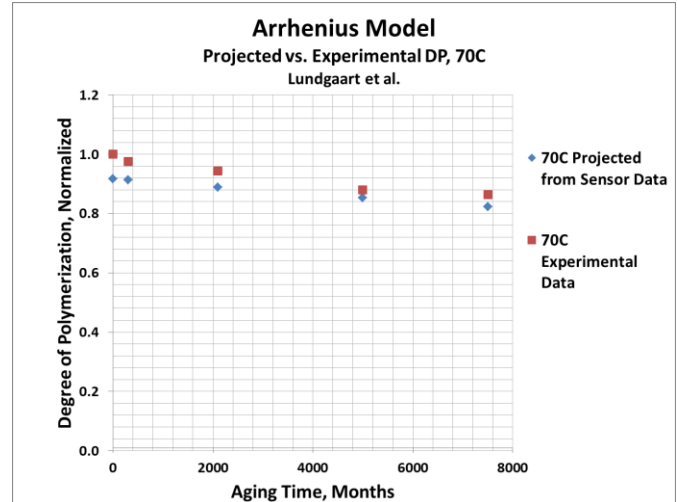


Figure 12: Projected vs. experimental DP for 70C aging using Arrhenius modeling.

Supervised learning models, such as support vector machine (SVM) approaches may be employed to provide improved accuracy of correlations and projections.

5. UNIVERSAL THERMAL AGE TAG

In constant temperature aging conditions, matching of the activation energies of thermal age sensors and the target material is not an issue. For example, thermal age sensors of any E_a , co-aged with a target material will project the same thermal life of the target material. However, in real-world conditions, this is not the case since thermal aging is highly non-linear with temperature. Use of a time-average temperature will always project longer target material life than actual life since aging at temperatures above the mean proceed at a rate higher than the compensation of slower aging below the mean.

A significant limitation to the direct correlation and Arrhenius approach when using a single thermal age sensor is that reasonable projection agreement with experimental data across a variable (real world) temperature range requires good agreement of the E_a of the thermal age sensor and the effective E_a of the property data of the target material or component. Errors increase with the difference in E_a of the sensor and material property E_a , and the magnitude of temperature variation. Development of

thermal age sensors that provide good agreement with the activation energy of all degradation properties of all materials and components of interest represents a very significant development effort.

One approach which eliminates the need for a large number of sensors for many different materials and/or properties is utilization of two thermal age sensors with different E_a in a single thermal age tag. A modeling approach which projects the T_{EFF} at any activation energy in a complex thermal environment means that a single tag that is associated with one or more materials or components provides the resistance data required to project current properties of any of the materials or components in that environment for which adequate thermal age data is available.

This approach utilizes the sensor resistance of each sensor, representing integrated time-temperature at the E_a of the sensor and calendar time to determine T_{EFF} for each sensor as described in 4.2. An empirical relationship of T_{EFF} at each sensor E_a is established to allow projection of T_{EFF} at the E_a of a selected material property.

An example is shown in the following figures utilizing three thermal age sensors of different E_a aged under constant temperature conditions (Figure 13) and three thermal age sensors of the same E_a aged under a sequential two-temperature aging profile (Figure 14). The constant temperature conditions are representative of laboratory oven aging as described previously. The sequential aging of Figure 14 sensors was 50% time aging at 57C, followed by 50% time aging at 65C. T_{EFF} determined by the method described previously is shown for each sensor, and time average temperature (T_{AVE}) is shown for the two temperature aging.

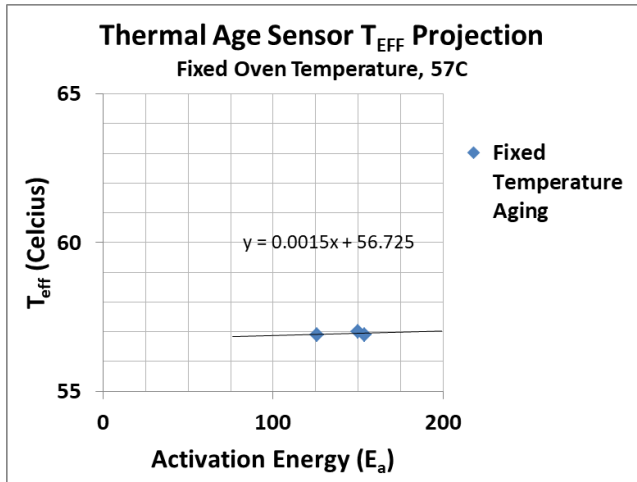


Figure 13: T_{EFF} as a function of thermal age sensor E_a under fixed (constant) temperature conditions. Note relative independence of E_a on T_{EFF} .

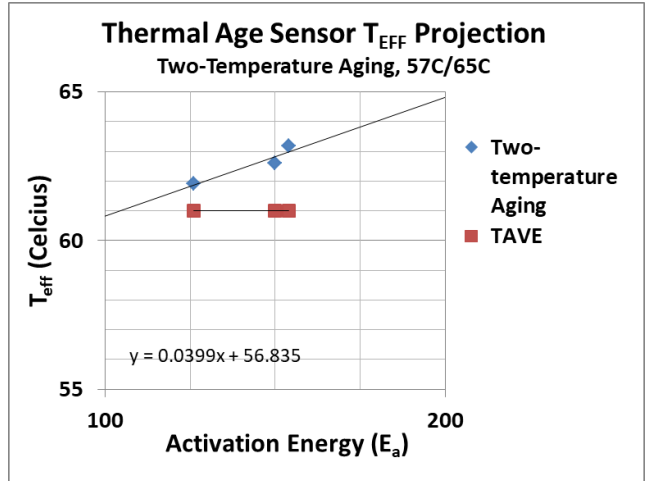


Figure 14: T_{EFF} as a function of thermal age sensor E_a under two-temperature aging conditions. Note high dependence of E_a on T_{EFF} .

The relative insensitivity of E_a in the fixed temperature aging of Figure 13 is expected. The high dependence of E_a on T_{EFF} in Figure 14 is also expected, since aging is highly non-linear, resulting in significant aging during the higher temperature time portion as compared to aging at a constant temperature. The results of this show that T_{EFF} is higher for higher E_a , and higher than the average temperature T_{AVE} .

Use of a single tag with multiple sensors having different E_a allows determination of T_{EFF} for a wide range of processes or materials for which aging data is available for correlation. Selection of thermal age sensors with a significant difference in E_a allows interpolation of T_{EFF} projection.

A photograph of encapsulated single and dual sensor thermal age tags are shown in the Figure 15 below.



Figure 15: Photograph of encapsulated single sensor (left) and double-sensor (right) thermal age tags.

6. APPLICATIONS OF THE APPROACH

Simplicity, low cost, small size and elimination of the requirement for complex data management and battery replacement issues associated with data loggers are the motivating factors for application of thermal age tags in

applications where shelf life, fixed replacement and “run-to-failure” methods are insufficient. They offer significant cost reductions resulting from reduced unscheduled downtime for rapidly aged equipment, and reduced premature replacements where equipment is replaced on a fixed replacement time scenario.

Thermal age tags have potential applications in virtually any industry or market segment where improvements over simple shelf life or fixed replacement time systems are needed. For example, the tag of Figure 6, bonded to the case of an electric motor, generator or transformer can be used to predict thermal aging of winding insulation by correlating sensor resistance to NEMA life ratings (corrected for case/winding temperature drops). Or, a thermal age tags on building roof systems provides a simple indicator that the system is nearing end-of-life based on its actual thermal exposure. Other applications include projection of remaining life of foods and pharmaceutical products, medical devices, wire and cable insulation, structural components, industrial and consumer rubber products, and propellants.



Figure 16: Measuring a thermal age tag attached to an electrical motor at a municipal water facility. The tag projects remaining winding insulation thermal life.

The passive nature of thermal age tags lends well to passive Radio Frequency Identification (RFID) tag approaches where a thermal age sensor is utilized in a passive RFID tag to both track a product and predict remaining thermal life. An example of a passive RFID tag is shown in the photographs of Figure 17 below.

Additional tag capabilities can be expanded with additional sensor capabilities including chemical sensors and shock/vibration sensors. Polymer Aging Concepts has shown feasibility of a passive thermal/humidity age tag capable of predicting material properties under both variable thermal and variable humidity conditions.

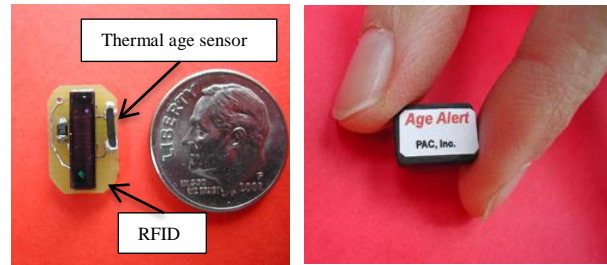


Figure 17: Passive RFID with thermal age sensor (left) and encapsulated tag (right)

7. CONCLUSIONS

Thermal age sensors offer a simple, low-cost approach to identify prematurely aged materials and components and to extend the shelf life of materials and components which are optimally transported and stored.

Empirical modeling approaches can be employed that correlate the resistance of the thermal age sensor (representing the integrated time-temperature of the tag environment) to current target material or product condition. Accurate correlation requires multiple target material property data at multiple temperatures and property threshold data for “Red light/Green light capability. These empirical approaches will not detect product degradation due to product manufacturing defects.

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BIOGRAPHIES

Ken Watkins, President, Polymer Aging Concepts, was born in Cloquet, Minnesota on April 20, 1948. He received his BSME degree from Georgia Institute of Technology in 1970. He served active duty in the US Navy 1970 – 1975 including submarine qualification and serving as a Naval Nuclear Power School Prototype instructor. His engineering experience included civilian nuclear power plant maintenance, pulp and paper project engineering and sales. He is the founder of Polymer Aging Concepts, Inc. and operated a prototype laboratory from 2003 – 2017, completing over \$4M in thermal age sensor research and development projects for the US Department of Energy and the US Department of Defense. He currently provides consultation on thermal age sensor design and fabrication, empirical modeling and applications. His interests include photography, reading and sailing. He is a retired Captain in the US Navy Reserve.

