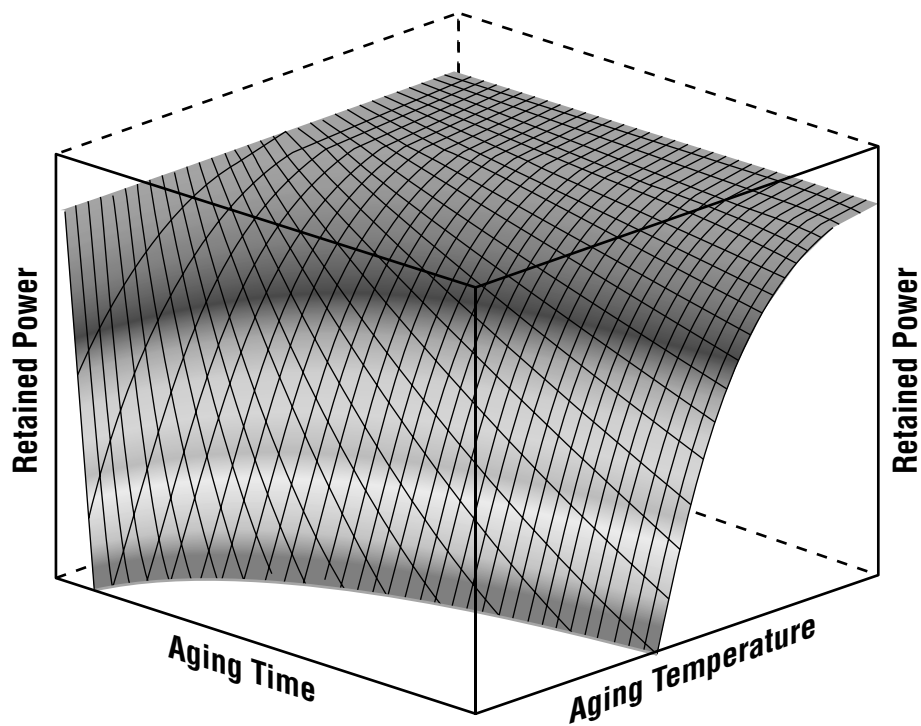


3D Arrhenius Plot



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Introduction

Conductive polymers are finding continued success in electric heating devices, especially when formulated to have a positive temperature coefficient of resistivity (PTC-R). A familiar form of such devices is that of a heating cable, shown in Figure 1. In this version of a conductive polymer heating device, two copper wires serve as parallel electrodes. Between the two electrodes is the conductive polymer heating element, which conducts electricity when a voltage potential exists between the electrodes. The heat generated as a result of current flowing through the resistive element (the conductive polymer segment) is conveniently expressed as “watts per foot” of heating cable.

An important characteristic of heating cables and other devices based on PTC-R conductive polymers is that as the surrounding temperature increases they limit their heat generation. This means that the devices will not overheat themselves as a result of their own power generation.

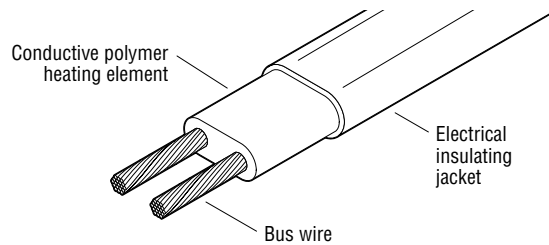


Fig. 1. Typical construction of a basic self-regulating heating-cable device

Figures 2 and 3, respectively, show the resistivity-versus-temperature and power-output-versus-temperature characteristics of PTC-R heating cables. Because the power output decreases markedly with increasing temperature, these heating cables are often described as “self-regulating.”

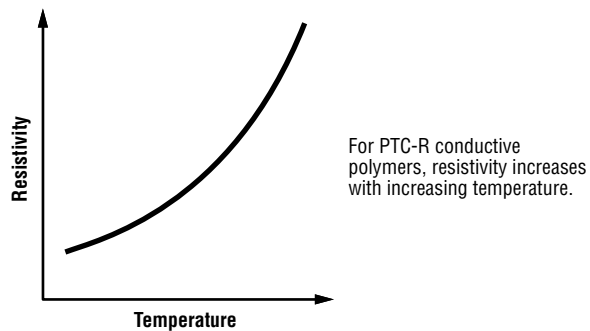


Fig. 2. Resistivity versus temperature

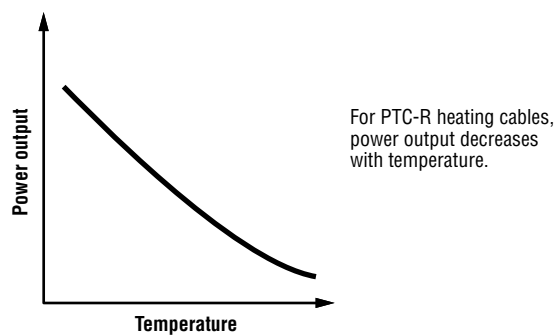


Fig. 3. Power output versus temperature

Self-regulating heating cables are widely used in many industries. Because the heating cables often are critical to successful operation and to smooth process start-up or changeover, and because the cost and inconvenience of repairing or replacing heating materials that have failed can be significant, long-term reliability and functionality of such devices is an important consideration.

Conventional polymeric material evaluation techniques are applicable to PTC-R heating cables if the special nature of the heating cable construction and modes of operation are allowed for in the evaluation program and in the interpretation of results. This paper discusses those special aspects of self-regulating polymeric heating cables and a new approach to estimating heating cable life. This includes determination of heating cable operating temperature and a three-dimensional approach to conducting the Arrhenius predictions.

General Life-Projection Techniques

Public standards that present approaches for obtaining estimates of long-term performance at operating temperatures have existed for some time. These are presented in several publications from standards bodies, including UL746B, IEC216, and IEEE Standards 1, 98, and 99.

The procedures are based on the fact that chemical reactions for polymeric materials occur faster as the temperature is increased. The evaluation procedures call for exposure of product samples to temperatures above the normal operating temperature. Several different elevated temperatures are usually employed, selected to cause material property changes over times ranging from as little as 100 hours to 10,000 or more hours.

One or more material properties are monitored during the accelerated aging program. In many cases the selected property will relate directly to an actual performance attribute of the product. For example, when testing a polymer whose use requires it to maintain some degree of flexibility, the monitoring of tensile elongation may be appropriate during the aging program. If the oxidative aging of the product directly affects the parameter of interest, this technique may well be appropriate. It is the existence of this effect, or relationship between oxidative aging (a chemical reaction) and the property that allows the use of the Arrhenius equation to estimate long-term behavior at lower temperatures.

Figure 4 shows representative plots that could result from the measurement of elongation after various exposure times at five different temperatures using these time-honored techniques. There is a wealth of information that links retention of this property (elongation retention) with oxidative aging of the material. In this example a failure criterion of 50% retention of the original elongation was selected. The "failure" line in Figure 4 shows the actual time during which this occurred for the aged samples. A typical plot will contain many data points for each temperature. To make the presentation of the technique clear, only the mean "curve" for each temperature is shown in Figure 4.

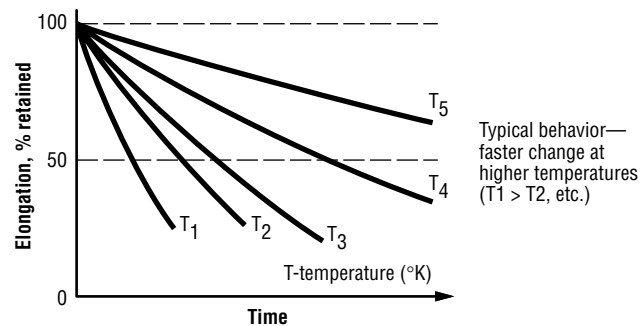


Fig. 4. Tensile elongation versus time and temperature

The next step is to establish the impact of temperature on the rate of change for the property of concern. The goal is to estimate the long-term behavior of the property at lower temperatures. In the example, the selected failure criterion is “50% retention of elongation.” The elongation failure points (see Figure 4) for higher temperatures (T_1 through T_4) may be used to estimate the “time to failure” for a lower temperature (T_5). For many materials a property is a function of the temperature the material is exposed to, as well as the duration of the exposure. This type of aging may be described as the temperature dependence of the rate of a chemical reaction. The Arrhenius equation can be used to characterize this behavior.

The Arrhenius equation for a chemical reaction is given by:

$$K = A \exp(-E/RT) \quad (1)$$

Where:

K = Specific reaction rate

A = Constant

E = Activation energy of the reaction

R = Gas constant

T = Absolute temperature

Because the goal is to estimate “life” or “time to failure,” equation 1 is algebraically modified to the form shown in equation 2. Equation 2 can be simplified to its basic components, or equation 3.

$$\text{Log (Life)} = \text{Constant} + (1 / 2.303) * (E / RT) \quad (2)$$

or

$$\text{Log (Life)} = a + b / T \quad (3)$$

It can be seen that equation 3 has a linear algebraic form. Experimental data can be plotted as log (life) versus the reciprocal of the absolute aging temperature.

In Figure 5 the time to failure is plotted versus $1/\text{temperature}$ in K. The plot should appear linear for T_1 through T_4 if this is a reaction-rate-based property change. Then, extending the linear plot out to the temperature of interest, T_5 , one can estimate the time to failure.

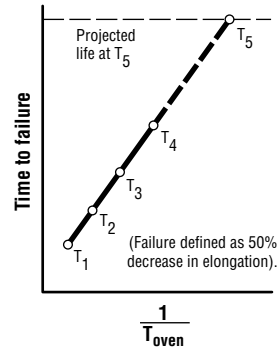


Fig. 5. Arrhenius graph example, tensile elongation

This same classic technique can be used for evaluating the expected life of self-regulating heating cables. Modern statistical approaches have increased the precision and certainty of projections made using the Arrhenius equation. There are, however, a number of failure modes that are not due to temperature-dependent (or oxidative) aging of the product. Before discussing how the Arrhenius estimation technique can be used, a review of these additional failure modes is in order. Many of these additional failure modes produce nonuniform heating in the cable, and are unacceptable for use in Arrhenius estimates. Using samples that exhibit one or more of these additional failure modes in an Arrhenius estimation will yield invalid life predictions.

Early failure modes

Even when the materials selected for use in making a self-regulating heating cable are appropriate, early operating failure can result if individual processing steps are inadequate. This may result in product with localized internal high heating-element temperatures. These localized high temperatures may be quantified by using an infrared temperature sensor to determine the surface temperature of the heating element through an open window in the thermal insulation, as shown in Figure 6. Using this technique, a sample of the product is attached to a constant-temperature substrate, such as a metal pipe. Close-fitting pipe insulation is then installed. A very small window in the insulation is created. The window should be only as large as required to allow use of an infrared temperature sensor, as shown.

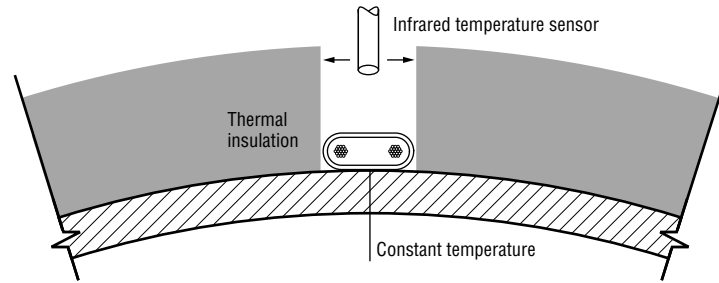


Fig. 6. Test to determine the heating cable-element temperature uniformity

With the heating cable energized and the substrate held at a constant temperature, the thermal profile may be characterized. By moving the infrared temperature probe from side to side, the uniformity across the heating element is characterized. A temperature profile is then produced. These profiles help detect whether manufactured product exhibits any of the early failure modes discussed below. Sophisticated electrical tests can also be conducted to find some of these early failure modes.

Two sources for such high localized temperatures are nonuniform resistivity and electrical contact resistance at the bus-wire-to-polymer interface.

Nonuniform resistivity of the polymer matrix can result from inadequate mixing of the conductive carbon black into the polymer, as well as from other sources. The resulting resistivity profile would be nonuniform, as shown in Figure 7. When energized, the temperature at the higher resistivity points would be higher since proportionately more heat is being generated at these locations. This is due primarily to a higher voltage drop across that location in the heating cable. Figure 7 shows the resistance and temperature profiles that could result from nonuniform mixing of the polymeric heating-element material during processing.

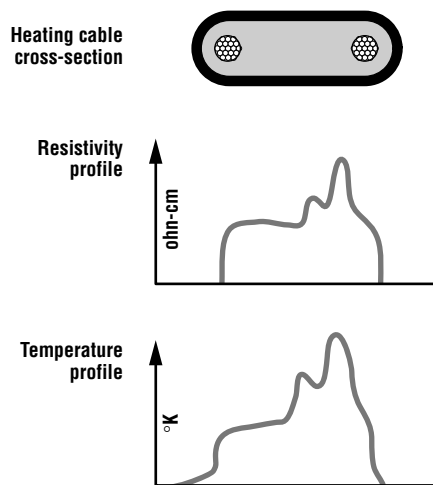


Fig. 7. Effect of nonuniform resistivity on internal temperature

Temperature nonuniformity results when electrical contact resistance exists at the bus-wire-to-polymer interface. All of the electrical current passes through this interface. If correct processing techniques are not used, the resistance around the bus wires can be relatively high. The resulting localized high temperatures (see Figure 8) will cause an accelerated degradation at these points. The elevated power is, as before, created by higher voltage drop across this high-resistance region.

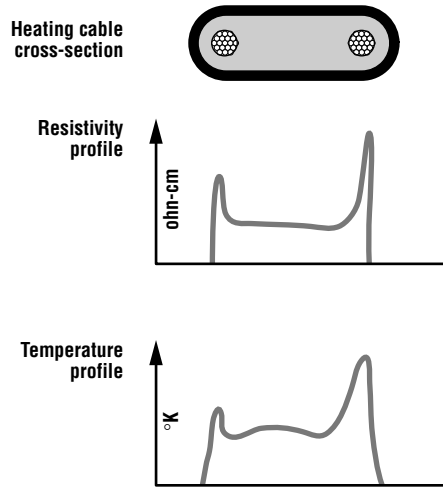


Fig. 8. Effect of electrical contact resistance at the conductive polymer-electrode interface

While the previous two potential early-failure modes stem from self-generated high temperatures Figure 9 dramatizes the higher temperatures that result from poor heat transfer. Note also that for conductive polymer PTC-R heating cables, the power output will be reduced if the heating element itself is at a higher temperature. This can result in lower-than-required power output initially and faster degradation due to the higher heating-element temperature.

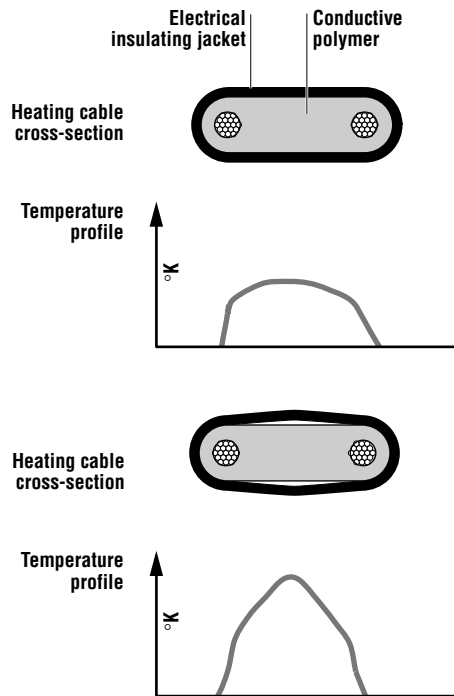


Fig. 9. Effect of poor heat transfer on temperature profile

Arrhenius techniques for estimating self-regulating heating cable life

Product used in aging studies must be randomly selected from a manufacturer's inventory. Product with characteristics as discussed above will have early-failure-mode symptoms. These indicate that design and manufacturing quality are poor; such early failures invalidate the use of Arrhenius techniques for life projections.

Because it is necessary to relate changes in the measured property to the actual polymer aging temperature, it is necessary to know, with a high degree of reliability, the heating-element temperature. Therefore, aging of heating cable products in ovens must be done without energizing the heating cable. Measuring the temperature of energized heating cables in aging ovens is not practical for two reasons: (1) the operating temperature of energized heating cables continually changes as the power output drops with aging, and (2) the logistics of handling large numbers of samples and monitoring the heating-element temperature of each sample make this test nearly cost-prohibitive. However, because energized heating cables operate at a higher temperature than the pipe or substrate, characterization of the operating heating-element temperature is required. In addition, from the customer viewpoint, the product's temperature rating is best stated as the temperature to be maintained, not the temperature of the heating device itself. One can determine the operating temperature of product, and characterize this as a function of power output. This characterization of the heating-element temperature can be accurately determined by using exemplar samples.

To characterize the heating-element temperature, samples can be installed as shown in Figure 10. A heating cable is carefully instrumented with 36 AWG or smaller thermocouples affixed under the electrical insulating jacket on each side of the cable. The thermocouples are in direct contact with the surface of the polymeric heating element and are identified as T_{surface1} and T_{surface2} . The heating cable is then installed on a heat sink—such as a metal pipe or other metal substrate—that can be controlled at a constant temperature. The installation is then insulated, the pipe or substrate is set to the maximum use temperature recommended by the manufacturer, and the heating cable is energized. Once equilibrium is reached, the temperatures of the top and bottom of the heating element are recorded. This test is performed on product selected at varying power output levels. Typically, the required range of power outputs extends from the highest power levels to the lowest for product made with the same polymer matrix and of the same physical construction.

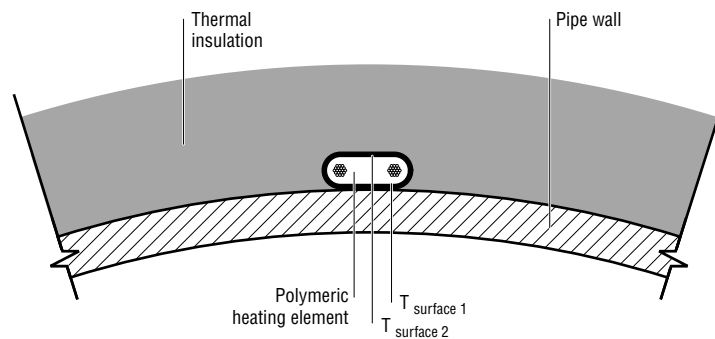


Fig. 10. Heating cable installed and instrumented for heating-element temperature determination

Figure 11 shows typical results from characterizing the operating temperature of a heating cable. It can be seen that the heating-element surface temperature, $T_{\text{surface}2}$, facing away from the pipe is substantially warmer than $T_{\text{surface}1}$, on the side of the heating element facing the pipe. In practice, a number of different use temperatures may be tested by varying the controlled pipe or substrate temperature, creating a family of curves for a product. Further discussion on how to use this information will be presented later.

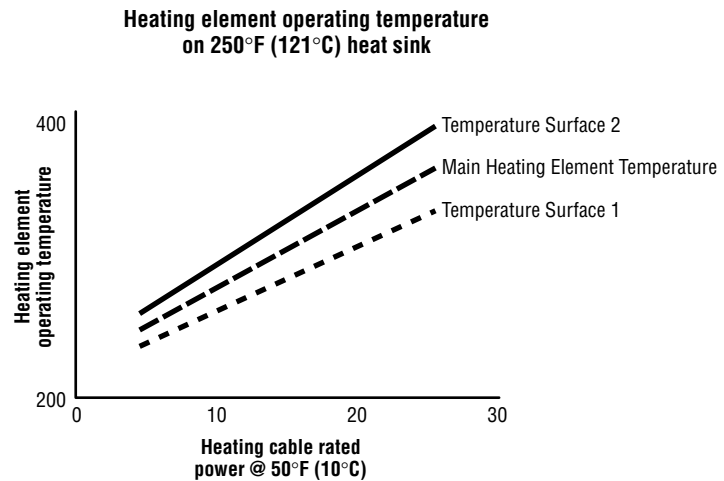


Fig. 11. Heating-element temperature (typical) versus heat-sink temperature

In establishing a test plan for accelerated aging, a minimum of four test temperatures is required; five temperatures are preferred. Steps between each temperature must be 25°F (14°C) or greater. To achieve any significant aging, all temperatures must be above the designed maximum use temperature.

The maximum aging temperature may be limited as well. Phase changes in the polymers and chemical reaction thresholds that may be exceeded by the maximum aging temperature must be considered. Using temperatures above this level implies that the test itself will be modifying the product, and other failure modes not expected in field operation may be introduced.

For each product being examined, no fewer than eight samples are selected for the highest aging temperature. This allows high confidence levels for the most rapidly aging samples. For each subsequent lower temperature, the sample count at that level increases by eight. The increasing numbers of samples at lower temperatures provide a larger amount of data to characterize behavior at those lower temperatures. A typical sample count per temperature is as follows:

Highest aging temperature	8
Next lowest aging temperature	16
Next lowest aging temperature	24
Next lowest aging temperature	32
Lowest aging temperature	48

Samples are removed periodically from the aging ovens, and their power output is measured when affixed to a metal pipe or other metal substrate maintained at 50°F (10°C). Every measurement produces a data point of retained power, and all data points are used in the final Arrhenius regression. For a typical aging experiment each sample may be read up to 10 times. For the above-described sample size, up to 1,280 data points would be included in the regression data set.

The general form of the equation for Arrhenius regression in three dimensions is:¹

$$P_n = 10^a (a - t \cdot b \cdot \exp(-c/K))$$

P_n	= Normalized retained power (% retained/100)
a	= A constant characteristic of the product
$b \cdot \exp(-c/K)$	= The reaction rate of the degradation process
t	= Time
c	= Activation energy for the reaction / Boltzmann's constant

¹The equation is a form of the Arrhenius equation. Further detailed discussion of its derivation can be found in *Accelerated Testing* by Wayne Nelson, ISBN 0-471-52277-5, pages 524-530.

The regression is then performed with suitable three-dimensional regression software. A typical three-dimensional output is shown in Figure 12.

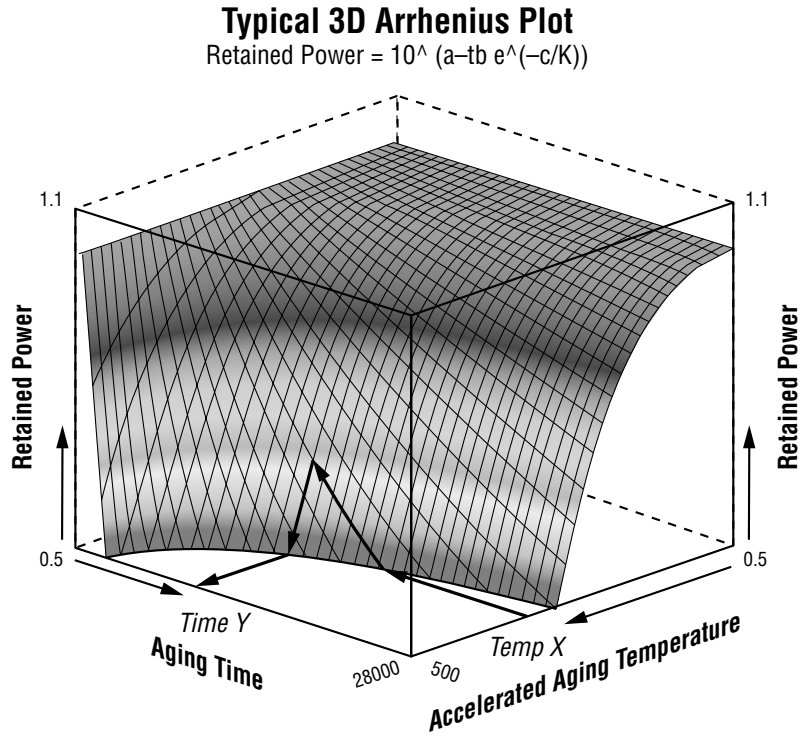


Fig. 12. Typical three-dimensional Arrhenius plot

The customer is often interested in the estimated operating life of a product for a given pipe temperature. To make a conservative estimate, one may assume the heating cable is energized 100% of the time. Any time in a nonenergized state would extend the life estimate considerably. Another conservative assumption is to use the maximum heating-element temperature in Figure 11, or $T_{\text{surface}2}$. However, using the average heating-element temperature will also produce a reasonable estimate. Once a heating-element temperature is selected, to determine the estimated product life (time Y) for that operating condition one enters the 3D Arrhenius curve (as shown in Figure 12) at that temperature (temp X), moves up to the defined failure criteria, and then out to the time axis of the projection.

One can also create a more “traditional” two-dimensional life chart for the specific temperature of interest. The temperature X “plane” can be created, and corresponding Power and Time information selected and displayed. Such a plot at a proposed design limit temperature is shown in Figure 13. This approach could be useful in selecting a heating cable whose initial power is higher than needed and whose decreased power is sufficient to ensure a useful life at the temperature of interest.

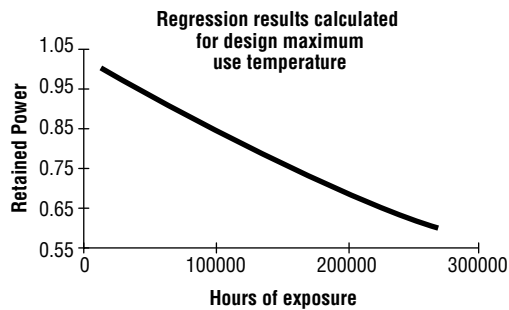


Fig. 13. Regression results calculated for design maximum use temperature

Another way to use the three-dimensional Arrhenius information is to select an operating life—for example, 10 years (87,660 hours)—and determine the maximum use temperature for a system in which a 25% decrease in power is allowed. See Figure 14 for this example.

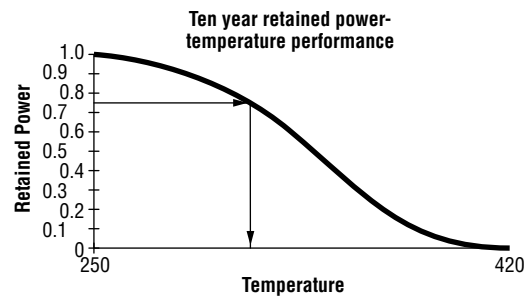


Fig. 14. Ten-year retained-power temperature performance curve

There are numerous ways to improve the estimate for specific applications with additional mathematical processing. The duty cycle of a product in an application can be considered by determining the aging temperature in both conditions and calculating the estimated life by weighting the results based on duty cycle. One can also explicitly account for the lowering of the aging temperature as the heating element ages with time. As the power drops during the installed life of a product, the heating-element temperature is also lower. This tends to extend the estimated life of the product.

Conclusion

This paper has presented a new statistical approach to utilizing the data from aging studies. It gives the manufacturer of polymeric heating cables the ability to more accurately estimate the performance of products for customers. The manufacturer can quickly respond to customer inquiries about performance when the heating cable will be operating outside normal use conditions. The power of three-dimensional Arrhenius regressions lies in the ability to use data points directly in the final regression, which are not exactly at—or are only estimates of—a single failure criteria. One can now quickly explore alternate failure criteria and use conditions without re-analyzing the experimental data.

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