LONG-TERM THERMISTOR STABILITY AT AN ELEVATED TEMPERATURE

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Interchangeable thermistors are now available for use at elevated temperatures. These new Negative Temperature Coefficient (NTC) thermistors are available as a result of discoveries, invention and process development. Extensive studies of long-term stability have been completed and the results confirm that these new thermistors have greatly improved stability over old designs.

BASIC CONCEPTS

The name thermistor is derived from the words THERMAL and RESISTOR. Thermistor as a description of a temperature sensing device, can De defined principally as a Negative Temperature Coefficient device of sintered aggregates of metallic oxide crystals.

A thermistor with a Negative Temperature Coefficient (NTC) will show a decrease in resistance with a temperature increase. The NTC has units of ohms/degree C. NTC = Delta R/Delta T.

Thermistors offer sensitivity to extremely small temperature changes. One typical thermistor type changes nearly 501: ohms/degree C at 40 degrees C.

Thermistors can be selected to match the impedance requirements of instruments already installed in your plant.

Repeatability of measurement in a range of .001 degree C is easily achievable. Long-term repeatability of .005 degree C is equally achievable.

Thermistor sensitivity is not constant throughout the thermistor’s range. Absolute resistance sensitivity/degree is not linear throughout the thermistor’s range.

Caution is required during assembly of measurement assemblies to assure that calibration/interchangeability does not change as a result of the assembly process.
Thermistors generally have low thermal conductivity so they do not handle high power as well as pure metal systems (1).

MANUFACTURING PROCESS

A brief description of the manufacturing process will provide some insight into the factors which control the performance of the finished product.

The materials in a thermistor are precise combinations of the oxides of Nickel, Manganese, Copper and Iron. Other “inert” additions have the affect of “diluting” the resistivity and/or affecting bonding. These and other “black art” additions control contact bonding, sintering and, to some extent, stability. The activity of these additions tends to be empirical and is not easily sortable.

In most cases, the intimate mixing of the components is carried out in a ball mill. Milling increases material surface area by reducing particle size. This is important for a successful sintering operation. The material is then pressed into a disc of precise thickness and diameter.

Sintering is a 1000 to 1300 degrees C heat treating process in which the oxides combined chemically to form a new crystalline ceramic material which exhibits semiconducting electrical properties. The crystal structure is that of a spinel. A spinel is classified as a mixed valency semiconductor which depends on its defect structure for resistivity characteristics.

The defect structure is established during sintering and is dependent not only on the mix ingredients, but is also highly dependent on sinter temperature, atmosphere, contaminants and cooling rates.

Electrical contacts must be applied to the disc. A conductive material is applied and fired on. Some materials are applied before sintering and cured during the sintering process. Some materials are applied after sintering and are cured in a separate firing cycle. Lead wires are then attached, normally by soldering. If the thermistor will be subjected to temperatures above the solder melt point, other lead bonding methods can be used.

RESISTANCE/TEMPERATURE RELATIONSHIP

Three definitions are needed here:

1. Accuracy: The extent to which the result of a measurement approaches the true value of a calculated value or a constant of nature.

2. Precision: The quality of being exactly stated.

3. Uncertainty: The estimated amount by which the result of a measurement may depart from the true value of a constant of nature or an interpolation between the constants of nature.

Thermistor accuracy is entirely dependent on the accuracy and precision of the calibration system used. The precision of the measurement statement depends greatly on the method of interpolation between reference points on a temperature scale. An empirical expression which describes the resistance vs. temperature relationship for NTC thermistors is called the Steinhart and Hart equation. This is usually found explicit in T.

$$1/T = a + b\,(1nR) + c\,(1nR)^3$$

where T = Kelvin temperature; R = resistance in ohms; a, b, c are found by making measurements at 3 temperatures and solving simultaneously.

$1/T1 = a + b\ (1nR1) + c\ (1nR1)^3$

$1/T2 = a + b\ (1nR2) + c\ (1nR2)^3$

$1/T3 = a + b\ (1nR3) + c\ (1nR3)^3$

LONG-TERM STABILITY

Long-term stability of thermistors and sources of drift have been extensively studied. Stability reported for this presentation will be discussed as the R/T relationship of the systen. The leads, contacts and bulk materials are treated as one. Examination of these components will assist in understanding the overall result.

Bulk effects in oxidic thermistors are a function of current carriers and depend consequently on the defect structure. When a thermistor is removed from the sinter temperature, it typically cools at a rate too fast to establish phase equilibrium at room temperature. As a result, the thermistor is inherently unstable, as is steel for example, after quenching. The rate for establishment of a new equilibrium condition is slow.

Atmospheric contaminants will, by absorption, change the resistivity of the system. The ultimate solution to contamination is, of course, encapsulation. Operating in various oxygen tensions does not appear to affect stability in any measurable way.

Bulk stability is, in part, due to structure conditions in tile spinels. Lattice change after sintering will lead to instability that is roughly proportional to the time exposed to an elevated temperature. Those conditions occur during annealing, firing of silver contacts and when coating with encapsulants.

Crude defects, such as macrocracks, edge and radial cracks, nonhomogeneous density and internal stress patterns, all have a direct relation to resistivity. Many of these defects are amplified, sometimes to the point of catastrophic failure by temperature cycling. It has been demonstrated that sorting on the basis of electrical noise will, given the right conditions (contacts, etc.), identify those units likely to fail.

Unfortunately, the solutions developed for single problems cannot usually be transferred system to system and, at times, are self-defeating. For example: a certain sinter method can produce a very dense part. The smooth surface resulting from high density makes metallization very difficult.

CONTACT EFFECTS

Experience over many years by many investigators, users and manufacturers has led to the conclusion that the single host common cause of gross thermistor instability is contact degradation, regardless of type or method.

The production of good and long-term moderately stable contacts is difficult. Electromigration, lead attachment and contact material are the three suspected sources of contact instability.

Electromigration can result from any contact shape when the system presents a voltage gradient in the plane of the contact. Tris phenomenon can result in silver migration between the two surfaces of a thermistor. Since perfectly uniform contacts are not to be expected, and since current density will vary, the areas with high current density will exhibit more rapid migration and, therefore, the sensor will display progressively more uneven performance. While under DC measurement potentials, this migration is not important. The phenomena are, however, significant for oxide thermistors used in voltage regulation. Reversible migration is demonstrated where polarity was reversed.

Fired contacts subject the thermistor to multiple mechanical temperature coefficients. That is, the glaze itself, the bulk of the thermistor, and the nonhomogeneity of the silver glaze mix. Since the disc may already be stressed, the addition of a fired contact may produce additional stress. That additional stress may produce microcracks which enlarge progressively when the disc is thermally cycled.

These microcracks will, on occasion, demonstrate this failure mode catastrophically. That is, the microfissure produces a subsequent break across the body of the device, or the contact actually lifts away from the disc surface.

Soldered or welded leads, usually tinned copper, face another hurdle in maintaining high stability, both ohmic and mechanical. Silver alloys with tin during lead attachment and AgSn is formed. The electronic component industry has long recognized the poor adhesion characteristics of this intermetallic compound. Many special solders have been developed to reduce this problem.

Other sources of contact degradation include moisture and absorbed chemically active materials. Migration and grain growth in thin contact sections will also produce drift at elevated temperatures.

Silver whisker formation has been observed in high temperature life tests. Bead thermistors, with their inherently intimate bulk lead contact, show instability caused by temperature coefficient differences in the materials used. This effect is reduced when stressed with direct glass coating.

Data about radiation effects on oxide thermistors is sparse. Data available indicates no shifts which were attributable to moderate levels of neutron or gamma irradiation.

Non-ohmic effects will frequently appear in high resistance elements which have a history of exposure to water vapor and, in most instances, the effects are reversible.

This same phenomenon has been noted in gasses which are easily ionizable (2).

SIGNIFICANT DEVELOPMENTS IN INTERCHANGEABLE THERMISTOR STABILTY

INTRODUCTION

Two discoveries concerning NTC thermistors will require reevaluation of the concept of the behavior of NTC thermistors. These two discoveries are:

DISCOVERY #1

A thermistor's drift was thought to be equivalent to a constant percent change of its resistance. Since the devices show a non-linear resistance vs. temperature characteristic, their error due to drift, expressed as a temperature error, was just assumed to be a variable of temperature.

More than twenty years ago, YSI in conjunction with the National Bureau of Standards began to study the long-term stability of thermistors (3). The results suggest that at least some thermistors drifted more nearly thermometrically than as a percent of their resistance. A thermistor that showed a long-term drift of 0.05 degree C when measured at 70 degrees C showed the same 0.05 degree C drift when measured at 0 degree C.

A later study (4) conducted by NBS with the cooperation of several other thermistor manufacturers appeared to confirm that disc thermistors were drifting somewhat thermometrically. The data from glass bead thermistors was not accurate enough to support or dispute the proposition.

YSI began to collect at the same time substantial data on its own thermistors to prove or disprove the proposition. The results of this show that thermistors manufactured by YSI in their bare form, with epoxy or with glass coatings clearly age thermometrically (5).

DISCOVERY #2

With experiments done over an extended period of time, YSI has discounted a widely held hypothesis. This hypothesis was that disc NTC thermistors drifted more severely than glass bead thermistors due to a phenomenon of oxygen transport through their plastic or other non-hermetic coatings. Disc thermistors were mounted in a highly evacuated glass tubing with their wire leads brought out through hermetic seals. Suspended from their leads, the thermistors were otherwise loose within the tubing; that is, they were under no mechanical restraint from glass. Their drift, with time and temperature, was neither more nor less than their epoxy coated controls. The results of this experiment also suggest that conformal glass encapsulation exercises a mechanical restraining force on the thermistor body thus preventing, or greatly reducing, its ability to change microscopic structural dimensions with time. Further study will be needed to validate the new hypothesis. However, the work suggests the prior hypothesis of an oxygen transport phenomenon into or out of the thermistor body surrounded by an oxygen porous encapsulant to be in error (6).

LONG-TERM AGING STUDY

An extensive study has been done to compare aging characteristics of thermistors with two encapsulating materials. The results show that dramatic stability improvements can be made by changing the encapsulation material. The results also show that the improvements are seen regardless of the bulk materials making up the disc itself.

EXPERIMENTAL METHOD

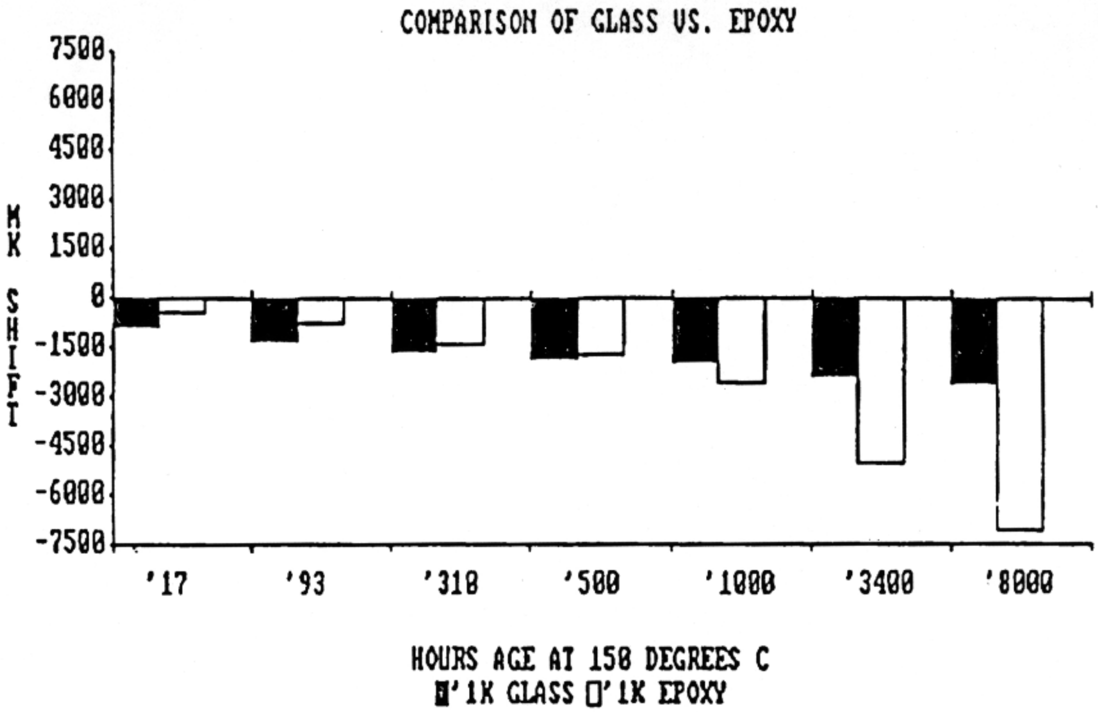
Thermistor groups were selected to study the effect of encapsulation material or aging phenomenon on thermistors of different mix types. A mix type is defined by the oxide materials, proportion and the process steps used to form the thermistor disc. Twenty thermistors were randomly selected from each of four different production approved mix lots. Ten were encapsulated with standard epoxy after lead attachment and ten were encapsulated in glass after lead attachment.

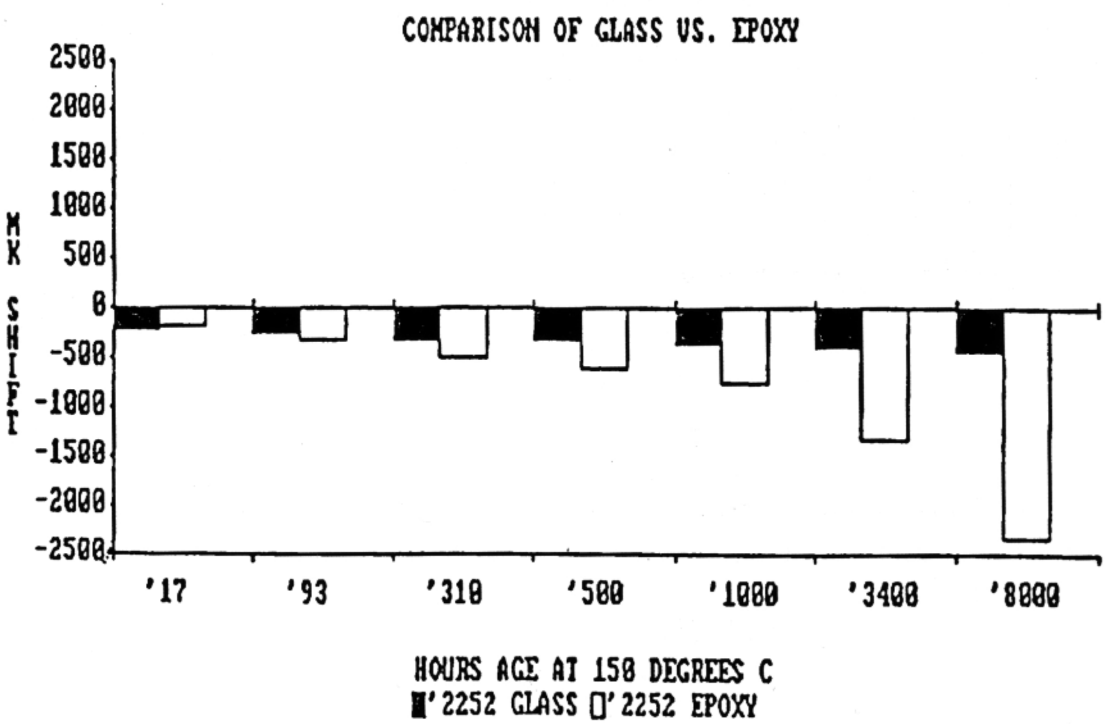
Thermistors of different mix types do not age at the same rate. This becomes obvious when the results are studied.

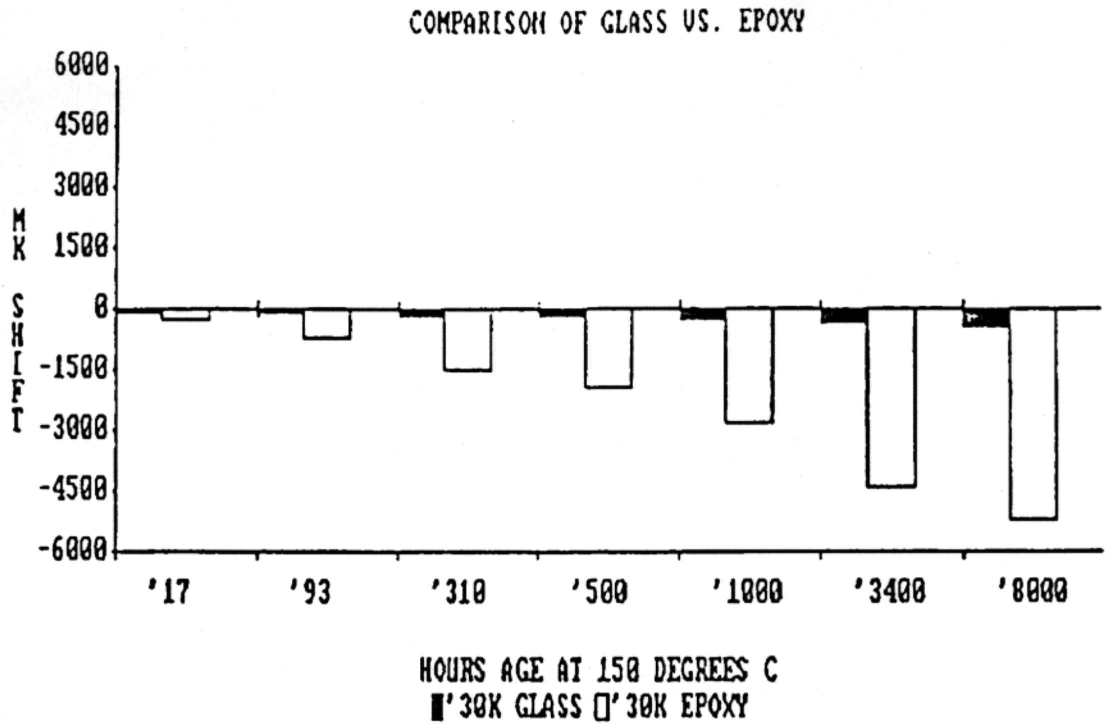
These thermistors were aged at 150 degree C. This is above the recommended temperature for some of the thermistor types studied. The thermistor types are identified by nominal resistance at 25 degrees C.

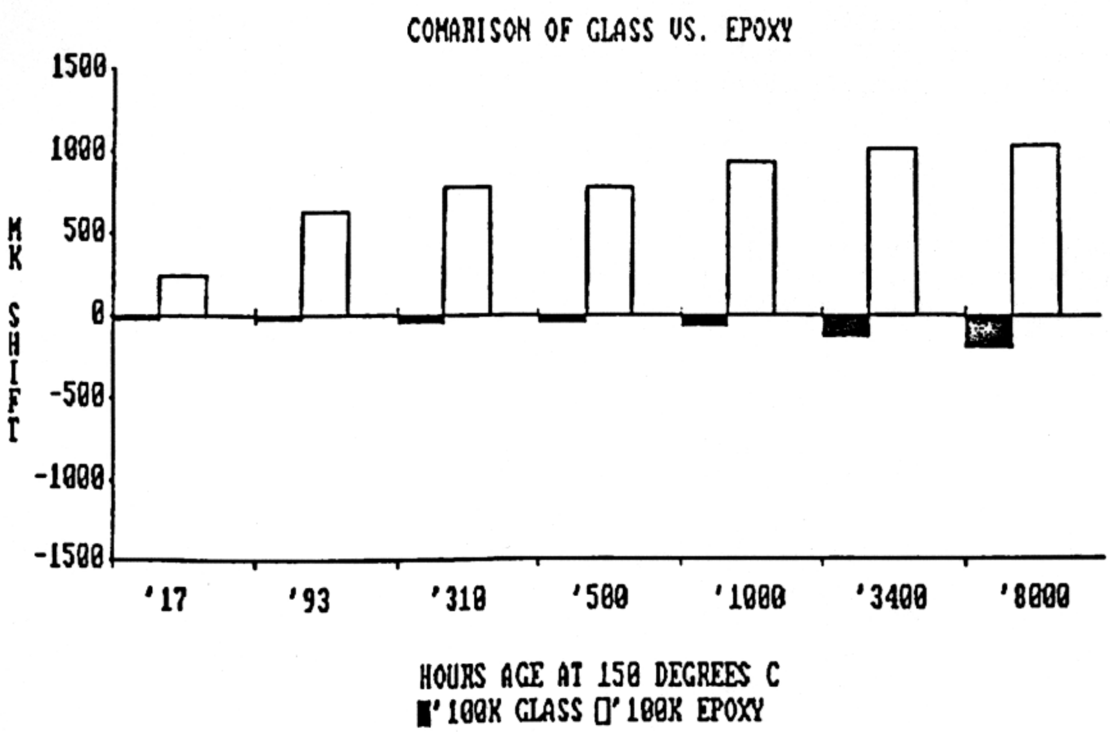
PRESENTATION OF LONG-TERM AGING DATA

The COMPARISON OF GLASS VS. EPOXY bar charts show the amount of drift for the thermistors after a number of hours at elevated temperature. One mK is equal to .001 degree C.


COMPARISON OF GLASS VS. EPOXY
7500
6000
4500
3000
1500
0
-1500
-3000
-4500
-6000
-7500
MK SHIFT
'17
'93
'310
'500
'1000
'3400
'8000
HOURS AGE AT 150 DEGREES C
'1K GLASS
'1K EPOXY


COMPARISON OF GLASS VS. EPOXY
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
MK SHIFT
'17
'93
'310
'500
'1000
'3400
'8000
HOURS AGE AT 150 DEGREES C
'2252 GLASS
'2252 EPOXY


COMPARISON OF GLASS VS. EPOXY
6000
4500
3000
1500
0
-1500
-3000
-4500
-6000
MK SHIFT
'17
'93
'310
'500
'1000
'3400
'8000
HOURS AGE AT 150 DEGREES C
'30K GLASS
'30K EPOXY


COMARISON OF GLASS VS. EPOXY
1500
1000
500
0
-500
-1000
-1500
MK SHIFT
'17
'93
'310
'500
'1000
'3400
'8000
HOURS AGE AT 150 DEGREES C
'100K GLASS
'100K EPOXY

It is clear from these results that the glass encapsulation greatly improves drift characteristics for interchangeable thermistors at elevated temperatures.

Two advantages arise from this stability at high temperatures provided by glass encapsulation.

1. Thermistor interchangeability is assured after long exposure at elevated temperature. This is a quality usually found only at lower temperatures using epoxy encapsulation.

2. A second advantage is that aging occurs at a predictable rate. This means that an instrument designer and a system user can compensate for aging in their work. Aging of thermistors tends to follow a poorer curve of the form:

$$y = -x^a b$$

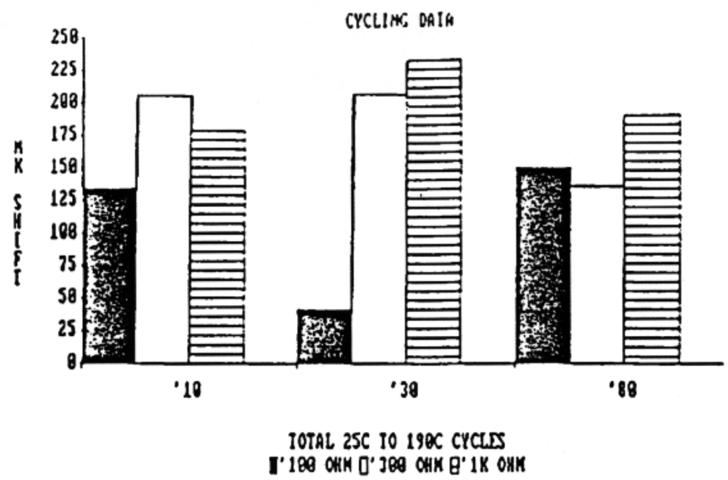
y = shift mK
x = hours aging
a, b = coefficients found by curve fitting methods (7)

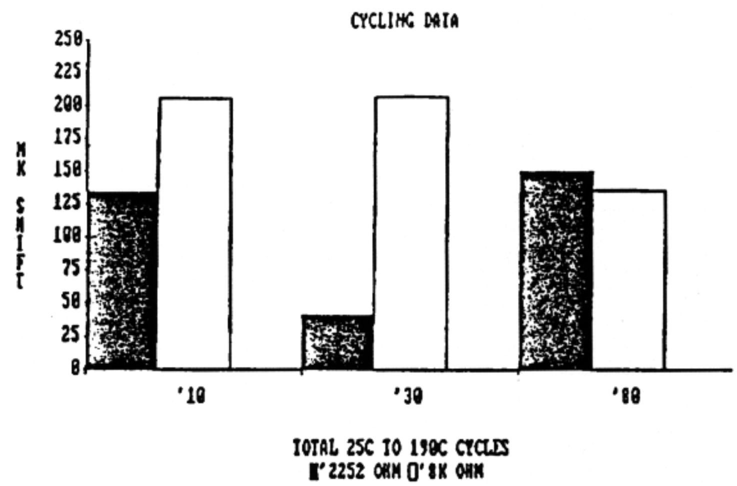
THERMISTOR CYCLING STUDY

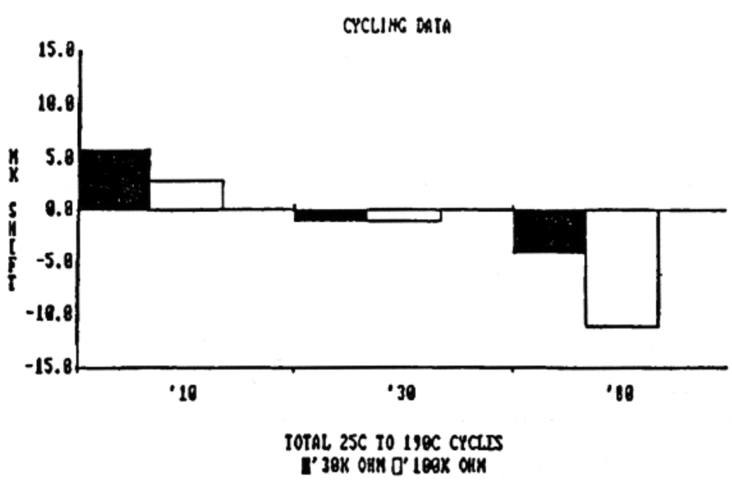
Another study was done to further study aging characteristics of glass coated thermistors. This study was designed to simulate actual usage by the industrial customer. Thermistors from several mix types were chosen randomly for this study. Cycling was done. A cycle consisted of 11 minutes at room temperature and 11 minutes at an elevated temperature. Two groups were studied. Each group consisted of five pieces from each mix type studied. One was cycled to 190 degrees C and the other cycled to 240 degrees C. Measurements were taken initially, after 10, 30 and 80 total cycles.

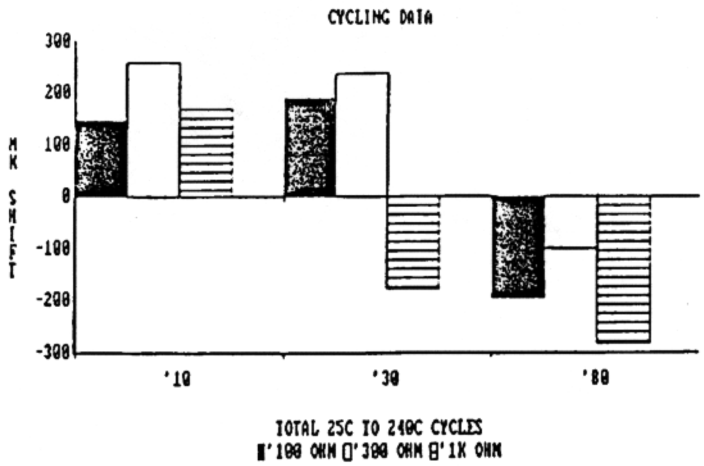
PRESENTATION OF CYCLING DATA

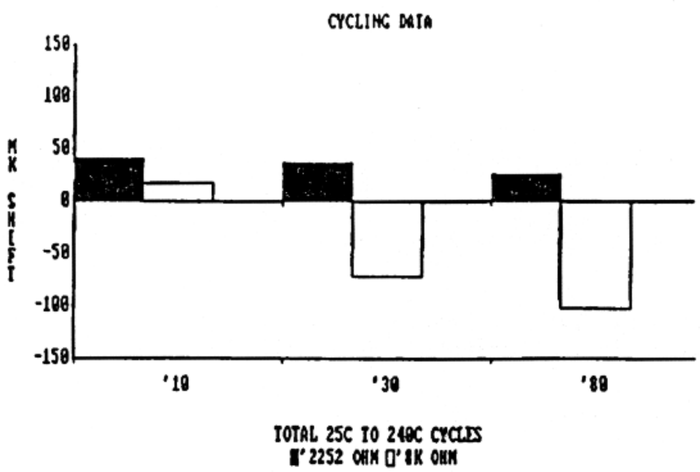
The CYCLE DATA bar charts show the amount of drift after 10, 30 and 80 cycles. Thermistors from similar mix types are presented together to allow comparison.

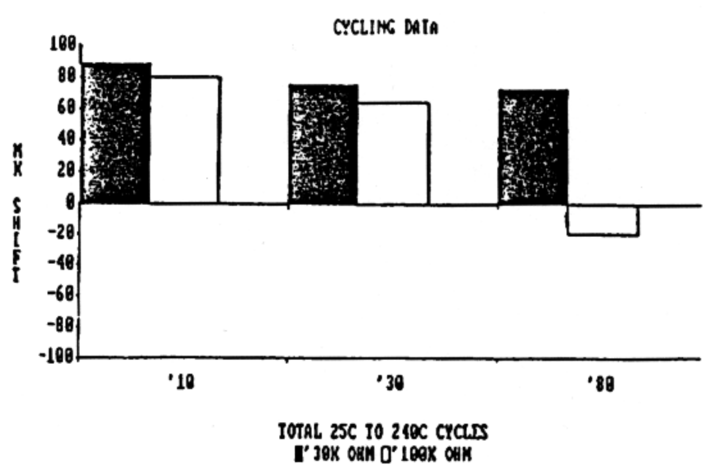

CYCLING DATA
250
225
200
175
150
125
100
75
50
25
0
MK SHIFT
'10
'30
'80
TOTAL 25C TO 190C CYCLES
■'100 OHM □'300 OHM ⊟'1K OHM


CYCLING DATA
250
225
200
175
150
125
100
75
50
25
0
MK SHIFT
'10
'30
'80
TOTAL 25C TO 190C CYCLES
■'2252 OHM □'8K OHM


CYCLING DATA
15.0
10.0
5.0
0.0
-5.0
-10.0
-15.0
MK SHIFT
'10
'30
'80
TOTAL 25C TO 190C CYCLES
■'30K OHM □'100K OHM







Temperature Product Group
2670 Indian Ripple Road
Dayton, Ohio45440-3605 USA
www.meas-spec.com

The results show no catastrophic failure. The small sample size may account for the variable behavior implied by the data.

CONCLUSION

The results of these studies show that glass encapsulation adds high temperature interchangeability, predictability, and stability to the long list of thermistor qualities.

REFERENCES

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(2) Flora, N., "Basic Concepts of Thermistors for Thermometry."

(3) Copies of the condensed results of this study are available from YSI.

(4) Wood, S.D., Magnum, B.W., Fillen, J.J., Tillet, S.B., Journal of Research, National Bureau of Standards, Vol. 83, Issue 3, May-June, 1978, p. 247-263.

(5) Zurbuchen, J.M., Case, D.A., "Temperature, Its Measurement and Control in Science and Industry," American Institute of Physics, New York, Vol. 5, 1982, p. 889-896.

(6) Flora, N., "Significnnt Developments in Interchangeable Thermistor Stability."

(7) LaMers, T.H., Zurbuchen, J.M., Trolander, H.W., "Temperature, Its Measurement and Control in Science and Industry," American Institute of Physics, New York, Vol. 5, 1982, p. 865-873.