

Evaluation of ethylene–propylene rubber O-rings for incoming quality control ^a

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Abstract

Analytical methods and control charting were used to provide a means of monitoring the composition and glass transition temperature of ethylene–propylene rubber O-rings.

INTRODUCTION

S&C Electric Company manufactures products for the electrical power transmission industry. One of our products contains high pressure gases sealed mechanically with an O-ring. This O-ring used in our switchgear is made from ethylene–propylene rubber (EPR). It is filled with carbon black and zinc oxide. The material composition and the inherent physical properties of this EPR elastomer are critical to the end use performance of these O-ring seals.

The purpose of chemical testing is to ascertain if the O-rings in the shipment conform to the specified composition before they are accepted and individually tested for sealing. The chemical tests have been designed to monitor the composition of the ethylene–propylene rubber and the low temperature glass transition temperature. The EPR data are evaluated using control charts to determine if other more selective and involved experiments are necessary.

EXPERIMENTAL METHODS

The chemical testing is performed within four working days of receiving a shipment of O-rings. The composition is qualitatively surveyed using pyrolysis infrared spectroscopy. Soxhlet extraction and thermal analysis provide

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quantitative analysis of the EPR O-rings. These numerical values are entered into a control chart format for easy evaluation of the data. The analytical tests are straightforward and have been performed by five different operators over a three year period.

Three O-rings were removed at random from every shipment received from the supplier and then analyzed. The total quantity of O-rings received in each shipment varied.

Infrared spectral analysis

A 10 mg sample was placed onto the ribbon of the Barnes Engineering PY-2 pyrolysis unit. The pyrolyzate volatiles were condensed onto a cesium iodide crystal. The IR spectrum was obtained using the Nicolet Model 20SXB Fourier transform IR spectrometer.

Soxhlet extraction

This extraction is consistent with ASTM Method D-297. Each O-ring was cut into eight 2 mm × 4 mm × 40 mm sections. Approximately 15 g of these sections was placed inside a macro-soxhlet thimble. The macro-soxhlet apparatus was assembled and 200 ml of dichloromethane was added as solvent. Dichloromethane was chosen for its ability to solubilize most plasticizers and oils from the EPR material without causing it major deterioration. The soxhlet extraction was carried out by refluxing the dichloromethane for 6 h. After completion the thimble was retrieved and allowed to dry under ambient conditions of 22°C and 42% relative humidity for 3 days before reweighing. The percentage residue is calculated from eqn. (1).

$$\% \text{ Residue} = \frac{(\text{final dry sample mass} - \text{empty thimble mass})}{(\text{original sample mass} - \text{empty thimble mass})} \times 100 \quad (1)$$

The refluxing solvent is retained for further analysis if necessary, depending on the acceptance of the shipment. If the shipment is suspect, the dichloromethane-soluble components may be analyzed by gas chromatography.

Thermal analysis

The thermal data were obtained using the DuPont 1090 programmer and its allied software and modules. The DuPont 951 thermogravimetric analyzer (TGA) was used to obtain mass loss data in a dry nitrogen purge until 700°C. The percent mass loss was calculated between 200 and 550°C for samples ranging in mass between 35 and 45 mg. At 700°C the purge was switched to air until 1000°C when the heating run finished. The samples ranged in mass between 35 and 45 mg. The mass loss between 200 and 550°C was calculated and entered into the control chart.

The Model 912 differential scanning calorimeter (DSC) was used after being calibrated using both deionized water and indium as standards. The nitrogen purge gas was dried using a molecular sieve trap and an oxygen trap. The O-rings were clipped into 2 mm × 2 mm × 2 mm flat-sided cubes. Each cube was placed into an open aluminum sample pan. The DSC was programmed to heat from -100°C to 50°C at a rate of 10°C min⁻¹. The glass transition temperature (T_g) was determined between -70°C and -10°C using the DuPont software. Both the T_g onset and T_g midpoint temperature values were calculated for each sample using the software.

Statistical analysis

The quantitative data were tabulated and entered into SQCPack, a software program obtained from PQ System, Dayton, Ohio. This SQCPack is a statistical process control program designed to provide control chart analysis of data. The statistical calculations used in SQCPack are in agreement with those reported by ASTM in STP 15D [1].

Control charting is an iterative process. It is intended to identify trends in the data. The quantitative data entered into SQCPack were first entered as individual datum for each O-ring sample. Initially, twelve different O-rings were analyzed and their data for percent soxhlet residue, TGA mass loss (200–550°C) and T_g onset, were entered as reference historical data into the SQCPack data base. Initial historical control limits were charted and out-of-control tests were generated using these twelve samples. The limits were arbitrarily calculated using the mean plus or minus 2.0 times the standard deviations (s.d.) where s.d. is defined as

$$\text{s.d.} = \sqrt{\frac{(\bar{x} - x_i)^2}{n - 1}} \quad (2)$$

where x_i is an individual sample value, \bar{x} is the arithmetic mean and n is the number of individuals. The variance within one TGA experiment was less than that for all the TGA data. The historical 2 s.d. limits of individual O-ring samples were used to establish the control chart. After two years of data collection, the O-ring data were reorganized into groups of three representing the sampling. So, after the 51 O-rings or 17 different shipments were received and analyzed, the data were recalculated. A new mean and 2 σ control limits were determined.

The intent of using the control chart was to identify trends in the data. The choice of 2 σ control limits were arbitrary and conservative. Data for samples falling outside the control limits required further inspection or perhaps a resampling of the shipment for repeated analysis.

RESULTS AND DISCUSSION

The incoming samples are qualitatively evaluated using IR spectroscopy to confirm the presence of EPR. The pyrolyzate spectrum shown in Fig. 1 is

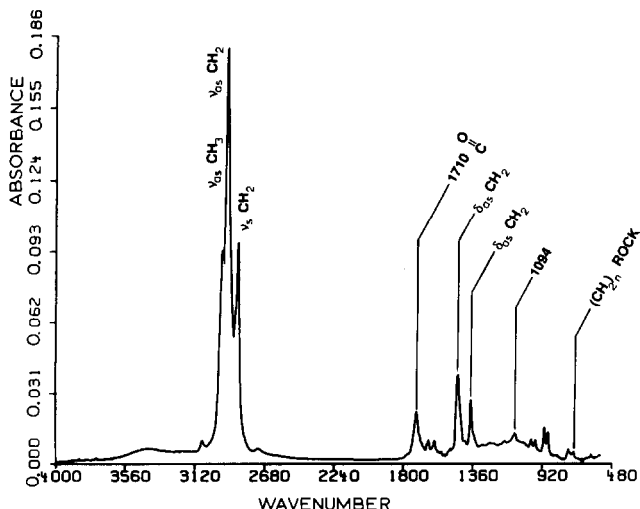


Fig. 1. Pyrolyzate IR spectrum for O-ring 84.

characteristic of the molecular repeating unit of EPR $(-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-)_2$. The band assignments [2] are shown in the figure. The pyrolysis conditions are rigorous and the vacuum generated in the pyrolysis chamber is moderate at best. Consequently, some oxygen may be introduced into the pyrolyzed vapor. As a result, there is a small band present at 1710 cm^{-1} usually assigned to a ketone carbonyl located in a saturated hydrocarbon. The band at 1094 cm^{-1} may be due to the C-C-C bending associated with an aliphatic hydrocarbon.

The quantitative data are summarized in Table 1 for formula A which is the expected O-ring material. The first entry is for the mean values for the twelve historical samples used to establish limits for specifying the O-rings. The second mean value for formula A is the overall data for 30 shipments of three O-rings each. These data clearly define the EPR composition using the methods described above.

The soxhlet extraction data are plotted by SQCPack in a frequency distribution chart shown in Fig. 2. SQCPack software treats every datum as an individual. The plot contains the number of observations on the y -axis versus the percent residue value on the x -axis. So, each block represents the number of observations having that range of residue values. The mean represents 26 observations between 96.145% and 95.625%. These data are normally distributed about the overall mean of 95.82%. The control limits are at 2σ and the SQCPack calculations are in the margin. These SQCPack constants confirm that the soxhlet data are normally distributed.

The thermogravimetric mass loss curve is shown in Fig. 3 for two different O-rings. The curve for O-ring 84 uses the right-hand axis which is shifted for clarity. The actual mass losses are within the mean plus the

TABLE 1
Summary of means

	Number of samples		Soxhlet residue (%)	TGA mass loss 200–550 °C (%)	DSC T_g (°C)
Formula A					
Historical	12	Mean	95.72	69.69	-54.5
		s.d.	0.85	1.65	0.6
Shipments	30	Mean	95.82	69.74	-56.6
		s.d.	0.98	1.28	1.2
Single O-ring	9	Mean		69.33	
		s.d.		0.79	
Formula B					
	3	Mean	96.57	53.43	-54.2
		s.d.	0.95	0.36	0.8
Formula C					
	3	Mean	95.68	69.23	-53.3
		s.d.	0.17	0.18	0.3

control limits. The TGA curves are similar. Neither TGA curve contains a mass loss associated with the loss of plasticizer or oil. The first mass loss begins above 200 °C. The carbon black filler is oxidized in air above 700 °C. The residual ash at 950 °C has been assayed as zinc oxide.

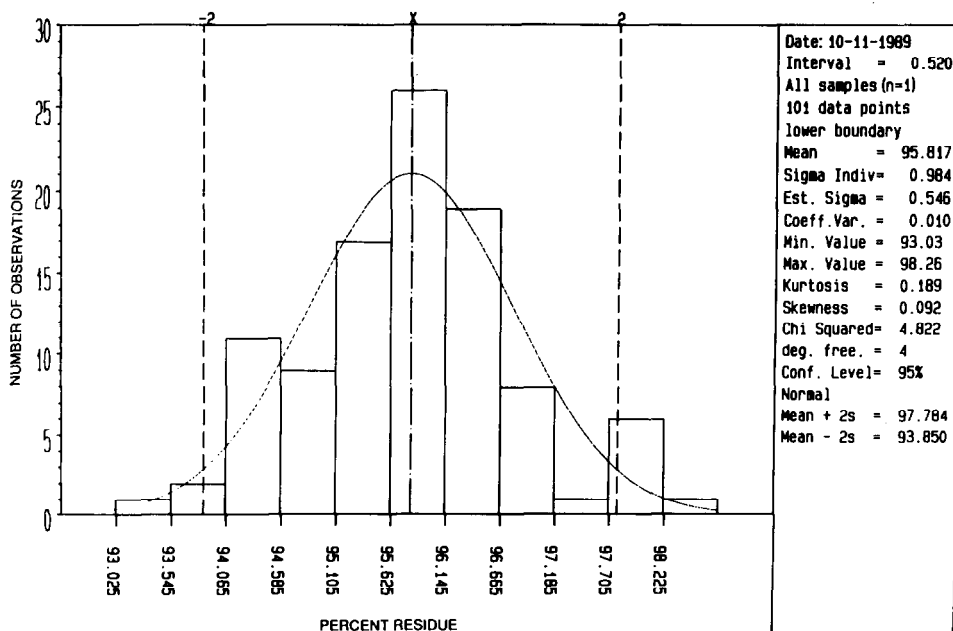


Fig. 2. CH_2Cl_2 soxhlet extraction data for O-rings.

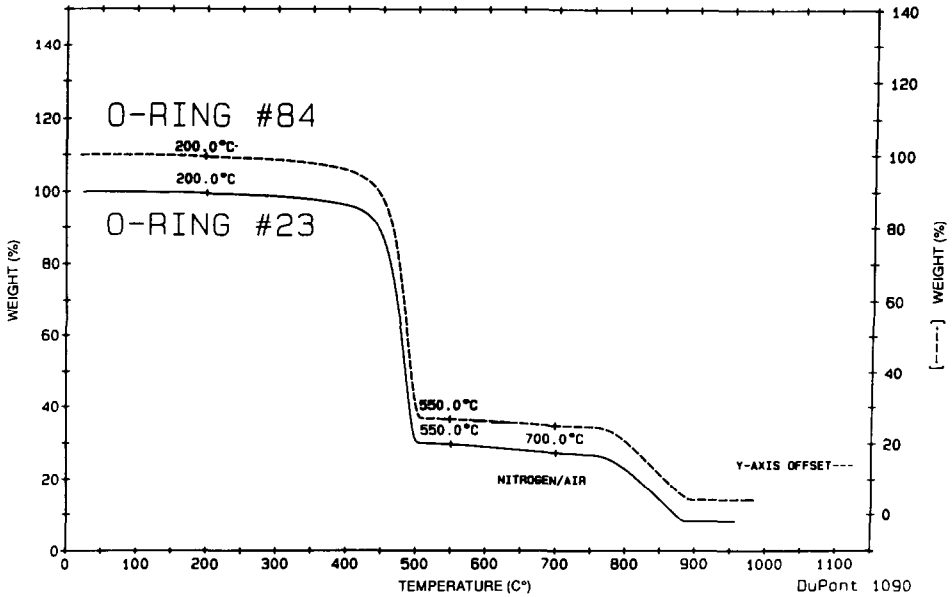


Fig. 3. TGA mass loss curves for two different O-rings.

In a nitrogen purge atmosphere, the largest mass loss occurs between 200 and 550°C. This represents the volatilization range for the ethylene-propylene base polymer [3]. The actual mass loss values are shown graphically

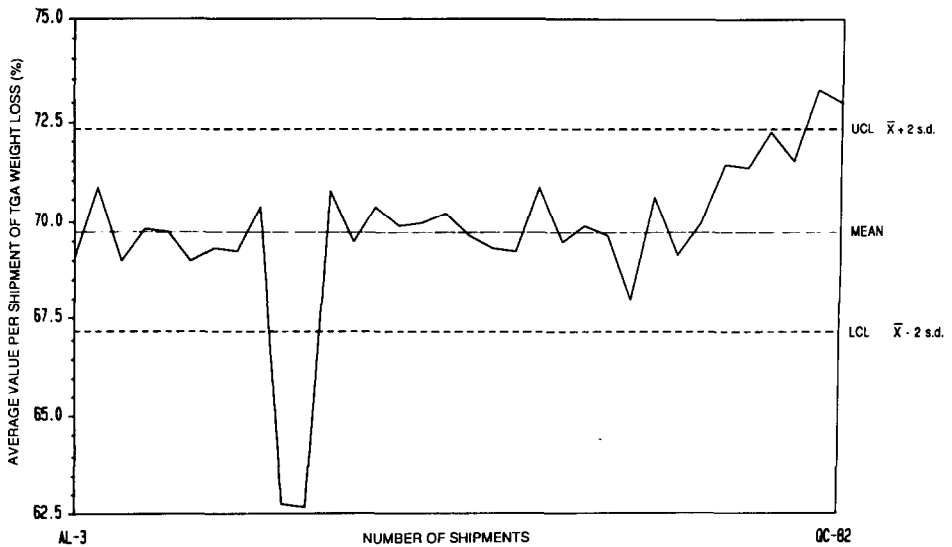


Fig. 4. TGA mass loss (%) in the temperature range 200–550°C for various shipments of \bar{x} chart values using 2σ (individuals), based on AL-3 to QC-82 are as follows: LCL, 67.18%; mean, 69.738%; UCL = 72.296.

TABLE 2
Split samples

O-Ring no.	S&C	Supplier
TGA mass loss 200–500 °C (%)		
5 In-limits	70.4	67.6
6 In-limits	70.8	67.6
9 Out-of-limits	66.2	64.0
10 Out-of-limits	66.1	62.0
DSC T_g onset (°C)		
31A	-55.3	-54
31B	-52.8	-54
32C	-55.4	-54
32D	-56.2	-55
33E	-54.7	-55
33F	-54.6	-55

in Fig. 4 in an \bar{x} chart. The mean TGA mass loss was $69.74 \pm 1.28\%$ and the control chart is also shown in Fig. 4. The solid line connects the mean value for each shipment. There are two shipments with means of 62.6% which are plotted as points below the lower limit and were out of control.

Since these two shipments gave low mass loss values, the shipments were resampled. A process of comparing our data with the supplier's data began.

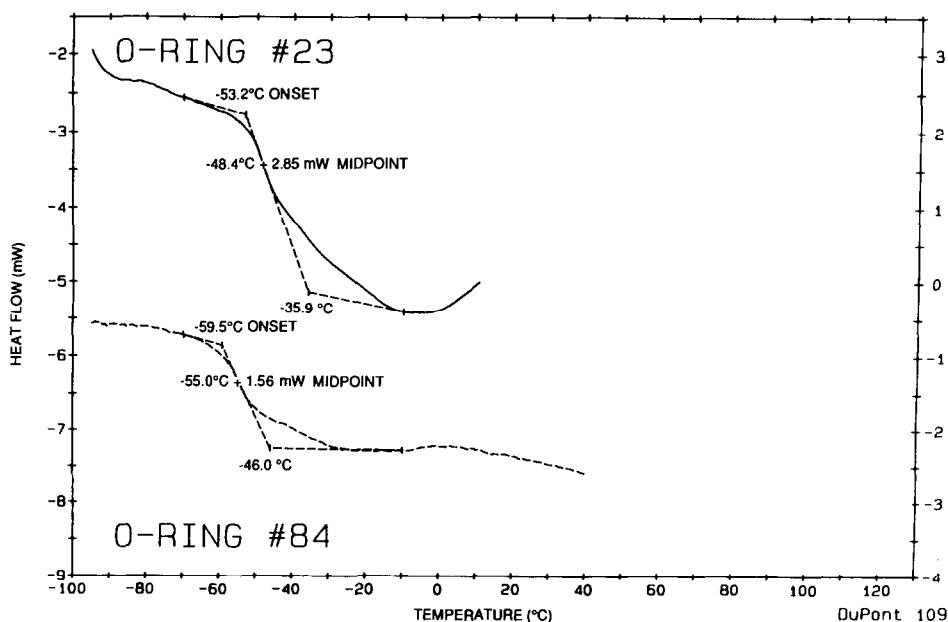


Fig. 5. DSC data for two different O-rings.

Four O-rings were cut in half and each half was analyzed. These split samples represent two samples in-limits and two suspect O-rings. The TGA data are shown in Table 2 for both laboratories using identical methodology. Although the exact values do not replicate between laboratories, the trend in these data is consistent. By splitting samples and sharing the results, the two laboratories improved communication and began to build credibility.

The twelve historical O-ring samples gave a mean of $69.69 \pm 1.65\%$ for the TGA mass loss due to volatilization. One historical O-ring was then analyzed nine additional times. The mean was $69.33 \pm 0.79\%$. This one O-ring had a variance (s.d.²) of 0.63% compared to the larger variance of 2.71% for the twelve historical O-rings. By comparing these values for the variance, it appeared that the TGA method had less variance within one sample that observed for twelve different samples from one shipment. This was expected.

The DSC glass transition temperature for EPR is very important in the operation of these elastomers since the retention of sealing properties is critical for performance of our switchgear. Therefore, the T_g midpoint temperature range was specified to be lower than -55°C . In Fig. 5, O-ring 84 has a T_g midpoint at -55.0°C which meets this requirement. O-Ring 23 has a T_g midpoint at -48.4°C which is too high for the specification. These two O-rings had equivalent TGA mass losses, so one technique would not be sufficient to demonstrate a difference.

The SQCPack control chart for the T_g onset results is shown in Figs. 6 and 7. The control chart has the mean of six heating runs represented in each

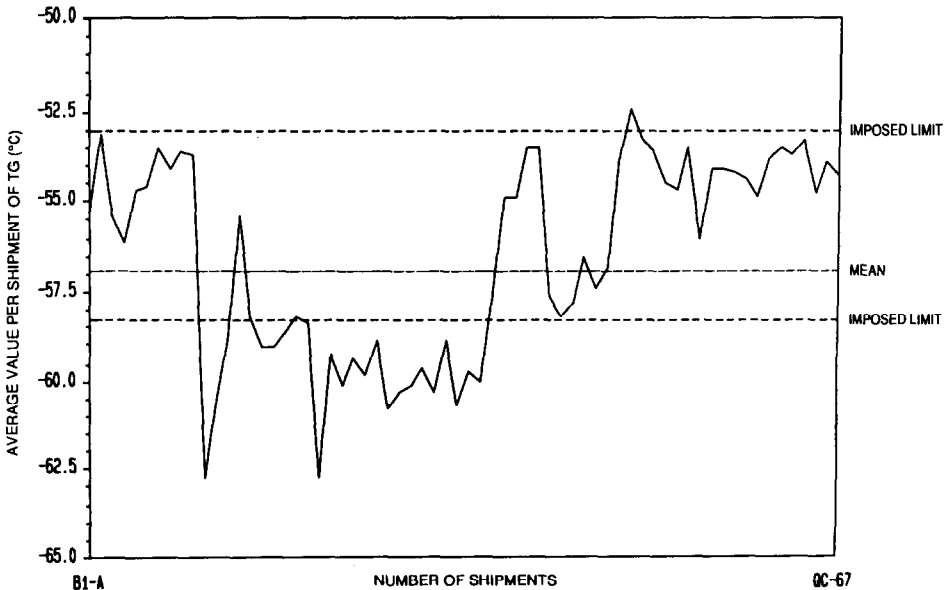


Fig. 6. T_g onset determined by DSC on O-rings. The \bar{x} chart values obtained using historical limits, based on B1-A to QC-31 are as follows: LCL, -58.24% ; mean, -56.89 ; UCL, -53 .

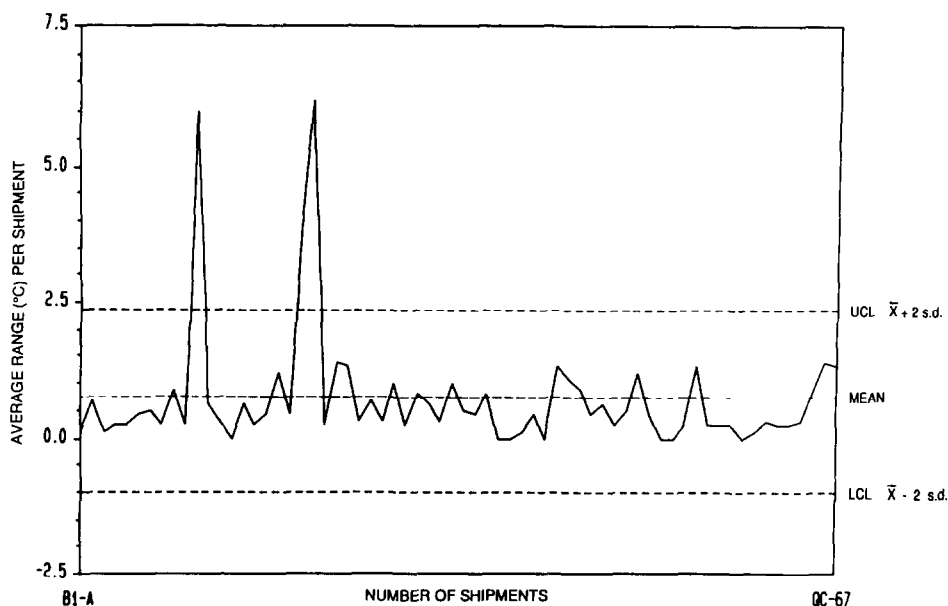


Fig. 7. T_g onset determined by DSC on O-rings. Range chart obtained using historical limits, based on B1-A to QC-31: LCL, -1 ; mean, 0.72 ; UCL, 2.34 .

plotted point. The T_g onset values are used as an acceptance criteria for the incoming O-rings. When O-ring 23 was received and found to be out of the limits, a resampling was done. The shipment was analyzed again and the split samples were taken and shared with the supplier. The T_g results for splitting the samples are also shown in Table 2. Although identical DSC methods were employed, the values reported were a few degrees different. During this second split sample experiment with the supplier, it was determined that the supplier used the T_g onset temperatures. The T_g onset temperature was lower than the T_g midpoint temperature. So, the control chart data were redone to include the T_g onset values only instead of the T_g midpoint values.

The T_g onset temperature upper control limit was set at -53°C as shown as the upper dashed line in Fig. 6. The data are plotted and the mean is shown in the figure. The lower control limit was arbitrarily set independently of the data. Figure 7 represents the range between the individual datum and the \bar{x} value. There were only two shipments where this range exceeded 5°C .

Data for two other O-ring compositions are given in Table 1. These EPR formulas B and C were not selected for our application even though the glass transition temperatures were below -50°C . The incoming TGA mean values for formula B are outside the range for the formula A historical samples. Therefore, it is easy to distinguish formula B from formula A by the TGA data. It is more difficult to distinguish formula C from formula A.

Formula C is so similar to formula A that the incoming criteria do not rule out the use of this formula in our seals. In actuality, the ethylene-propylene portion used in formula C came from a different supplier and was compounded into the A formula by the O-ring producer.

CONCLUSIONS

Some thirty different shipments of the EPR O-rings were subjected to incoming chemical testing. The analytical methods and the control charting using SQCPack software for the data provided a means for monitoring the composition and glass transition temperature. When shipments gave results out-of-control, further testing using split samples between the supplier and our company were analyzed and used to resolve any discrepancies.

ACKNOWLEDGMENT

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