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See Proposed Change To Tech Specs.

SUBJECT: Forwards response to NRC request for addl info on slave relay test frequency relaxation LAR 94-11,dtd 941114.Encl addl info does not affect conclusions of SE & no significant determination performed for LAR 94-11.

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December 7, 1995

PG&E Letter DCL-95-268

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Docket No. 50-275, OL-DPR-80
Docket No. 50-323, OL-DPR-82
Diablo Canyon Units 1 and 2
Response to NRC Request for Additional Information on Slave Relay Test Frequency Relaxation Amendment (LAR 94-11, dated November 14, 1994)

Gentlemen:

PG&E Letter DCL-95-254, dated November 14, 1994, submitted License Amendment Request (LAR) 94-11. LAR 94-11 proposed a revision to the Diablo Canyon Power Plant (DCPP) Technical Specifications (TS) to relax the slave relay test frequency from quarterly to refueling frequency. The LAR submittal included WCAP-13878 (proprietary), "Reliability Assessment of Potter & Brumfield MDR Series Relays," June 1994. PG&E is the lead plant for the Westinghouse Owners Group for this TS change.

NRC letter dated April 27, 1995, identified six questions regarding WCAP-13878 and the reliability of Potter & Brumfield MDR relays used at DCPP. In addition, a 10CFR Part 21 report was submitted by San Onofre Nuclear Generating Station on July 21, 1995, on MDR relays with potentially damaged contact arms. The applicability of this problem and its potential effects on slave relay reliability was evaluated and is discussed in this submittal. PG&E's responses and supporting attachments are enclosed.

The enclosed additional information does not affect the conclusions of the safety evaluation or the no significant hazards consideration determination performed for LAR 94-11.

Sincerely,

Greg Rueger

Gregory M. Rueger

18CRA

A001

cc: Edgar Bailey, DHS
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Michael D. Tschiltz
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Diablo Distribution

Enclosure
Attachments

RESPONSE TO NRC REQUEST FOR ADDITIONAL INFORMATION ON SLAVE RELAY TEST FREQUENCY RELAXATION AMENDMENT (LAR 94-11, DATED NOVEMBER 14, 1994)

NRC Question 1: De-energized Relays

With regard to relay failures, Information Notice (IN) 92-04, dated January 6, 1992, page 2, under the discussion section, third paragraph, states that, "...Failures may occur regardless of current or power, the use of ac or dc power or normally energized or de-energized." Also the report S93-06 from the Office for Analysis and Evaluation of Operation Data (AEOD), page 49, section 4.1.2, paragraph 1, states that, "Most of the MDR relay failures occurred in normally energized relays, while 30 percent occurred in normally de-energized relays, which may have been energized during shutdown conditions."

The Westinghouse topical report WCAP-13878, "Reliability Assessment of Potter & Brumfield [P&B] MDR Series Relays", does not address failures of normally de-energized P&B MDR relays. Therefore, in order for the staff to determine acceptability of the normally de-energized MDR relays, we request that you discuss the root cause for all these failures identified with these relays.

PG&E Response

The failure data for Potter & Brumfield motor driven relays (MDRs) was analyzed for those relays specifically used as slave relays in the Solid State Protection System (SSPS) at Westinghouse Owners Group (WOG) plants and for all MDR relay failures in the industry as reported in AEOD Report S93-06, Appendix C.

The analysis that follows applies to WOG plants that have complied with the recommendations for MDR slave relay replacement and whose SSPS is exposed to environmental conditions similar to those experienced at Diablo Canyon Power Plant (DCPP) and Farley Nuclear Plant. The recommendations are provided in WCAP-13878, sections 8.4.1 through 8.4.5. Each plant should provide a site specific response confirming 1) the similarity of models of MDR relays used, 2) energization state of SSPS relays, 3) SSPS ambient conditions, 4) status of relay replacement based on the WCAP recommendations, 5) contact loading review, and 6) procurement program review for those MDR relays which are proposed for surveillance extension.

SSPS Configuration

The standard Westinghouse SSPS uses normally de-energized slave relays for all Technical Specification (TS) required functions. In general, only two of the 40 or more MDR relays are normally energized at power. In addition, a small number of relays may be energized during shutdown. At DCPP, only two of the 40 relays installed in each of the SSPS output bays are normally energized at power, and neither relay performs a TS function. No DCPP TS slave relays are normally energized during outages since the SSPS is removed from service then. Additional information on SSPS configuration is provided in PG&E's response to NRC Question #6.

SSPS Slave Relay Failure Data

WCAP-13878, section 9.0, addresses the failures of P&B MDR relays used as slave relays in the Westinghouse SSPS. As noted in Table 9-3 on page 156, 1,158 MDR relays installed in Westinghouse plants with the SSPS have experienced a combined failure rate of 7.9E-05 failures/demand.

WCAP Table 9-4 on page 157 and Section 9.2 present and discuss six MDR relay failures. Of the 1,158 slave relays reported on by 16 nuclear plants with SSPS, six failure events were reported. Two of the six failure events are not relevant to normally de-energized slave relay failures; one caused by offgassing in a normally energized relay and one caused by valve limit switch failure, not slave relay failure.

The remaining four failures involved normally de-energized slave relays. Two of the failures were determined to be infant mortalities caused by open coils in 1989 at South Texas. One failure root cause was contact fusing due to overloading caused by inadequate circuit design in 1989 at Beaver Valley. One failure was attributed to a latching slave relay after a single containment spray pump was found running after a reactor trip and safety injection at DCPP Unit 2. The 1985 LER (85-007-00) concluded that after thorough testing and investigation, the exact cause of the pump start could not be determined. Since one possible cause was mechanical failure of the relay, the relay was replaced.

The small number of failures of normally de-energized SSPS slave relays, and the absence of failures since 1991 despite enhanced reporting mechanisms, are indicative of satisfactory service of the normally de-energized P&B MDR relays.

AEOD Report S93-06 Failure Data

PG&E and Westinghouse completed an evaluation of the MDR relay failures reported in AEOD Report S93-06, Appendix C, "P&B MDR Relay Failure Data."

The table in Appendix C of the report was copied and expanded to add two additional columns: 1) the relay size, and 2) notations on the cause of the failure and implications for SSPS slave relays. In addition, missing coil wattage ratings were added and rated coil voltages were corrected in some cases where the relays were incorrectly identified. The revised AEOD table is enclosed as Attachment 1, "Table 1: Expanded Appendix C of AEOD Report S93-06." Blocks where information was added or changed from the original table are indicated by bold type, with the original information, if any, shown in parentheses.

The final column in the table provides table notations. These notations indicate features of the relay, circumstances of usage, or failure modes that differentiate the relay from the small, de-energized, ac coil relays used at DCPP and other WOG plants as SSPS slave relays. Failure events involving relays of significantly different construction or usage than SSPS slave relays are shaded. A discussion of the table notations and their relevance to slave relay reliability follows.

Notation 1: (M) Medium MDR Relays

Latching and non-latching MDR relays are furnished in two sizes: small and medium. There are significant differences between the two sizes' physical and electrical characteristics such that many failure modes are either restricted to or much more likely to occur in medium relays.

Physically, the medium relay is 1.57" wider than the small relay at the base, and up to 1.87" taller than the small relay when each is configured with its maximum contact decks. The two sizes utilize the same switch ring (contact) sections, but the medium relays are provided with up to twice as many contact decks as the small relays. Physically larger coils, stators, and shading coils are used to permit the medium relays to reliably switch against the larger contact spring forces resulting from the additional decks. The larger components generate additional rotational force to make and maintain contact closure.

Failures due to shading coil detachment are limited to medium size relays due to design differences. Shading coil configurations are addressed in detail in PG&E's response to Question #3.

The coil wattage column of Table 1 indicates that the medium MDR relay coils dissipate between 12 and 30.8 watts, and that small MDR relays dissipate between 5.5 and 20.6 watts. Due to the lower power requirements and lower associated heat dissipation, small ac relays experience slower material degradation than medium relays for those aging mechanisms related to heating.

DCPP uses small models 4102 and 4103 relays as SSPS slave relays. The 4102 relays are physically the same as the 4120 relays used in the SSPS at other WOG plants. Due to the differences in relay components' sizes and design, power requirements, and heat dissipation, failures associated with medium relays are not relevant to SSPS slave relay reliability.

Notation 2: (DC) dc Coil Relays

SSPS slave relays are all small 115 to120 Vac coil relays in latching and non-latching configurations. Small ac relays experience fewer problems than small dc relays because the coils draw less power and because the coils are physically smaller.

DCPP's small ac latching (model 4102) and non-latching (model 4103) relays with two contact decks have power requirements of 5.5 and 6.5 watts respectively. Small 125 Vdc latching and non-latching relays with two contact decks require 20.6 and 10.3 watts, respectively. The difference in power requirements directly affects the amount of heat dissipated, so that the small ac relays experience a smaller temperature rise than dc relays. Consequently, the energized small ac relays experience slower material degradation for those aging mechanisms related to heating.

Inspection of relays removed from DCPP and disassembled and correspondence from P&B confirmed that small ac relays have physically smaller coils than similar configuration dc relays. Manufacturing defects related to oversize coils interfering with the fit of the top end bell are unlikely to affect the ac relays because of the coil size difference.

Since the Westinghouse SSPS uses low power requirement, physically smaller coil ac coil relays, failures of dc coil relays are not relevant to the reliability of the SSPS slave relays.

Notation 3: (V) Varnish Offgassing

The primary failure mechanism for pre-1986 small and medium MDR relays is coil varnish offgassing and recondensing on bearing surfaces inside the relay, resulting in the relay failing to operate on demand. Elevated relay temperature is the dominant factor in the rate of offgassing experienced in older MDR relays. Most older MDR relays that operate sluggishly, slowly, or are stuck in either the energized or de-energized position failed due to varnish offgassing. In 1986, P&B changed the coil coating material from polyester-based varnish to non-offgassing epoxy resin, eliminating this failure mechanism.

Between 1986 and 1990, P&B made additional substitutions to remove all materials which offgassed hydrochloric acid or chloride vapors and all materials subject to corrosive attack by those vapors. Residues from these vapors and signs of corrosion had been noted in some of the varnish offgas failed relays. See WCAP-13878, Section 5.4, for a discussion of the materials changed in the relays.

The rate of coil varnish offgassing is dependent on the temperature in the relay motor housing. Elevated temperatures caused by coil self-heating directly affect the energized relay and may affect other relays mounted nearby. There is very little offgas deposition in a relay with a varnished coil maintained at ambient room temperature over a long period of time. However, there may be heavy offgassing to the point of relay failure in either an energized relay or a relay mounted in a hot environment.

WCAP-13878 concludes that older MDR relays with polyester-based varnished coils, which are either normally energized or periodically energized for significant periods of time, are subject to coil varnish offgassing failure. In sections 8.4.1 through 8.4.5, the WCAP provides recommendations for replacement of older relays based on the month and year of manufacture and service usage (energization period). Relays which are energized each refueling outage but are normally de-energized during power operation were defined as 20 percent duty cycle relays. The 20 percent duty cycle relays have specific replacement recommendations based on the year of manufacture.

DCPP has complied with the recommendations provided in WCAP-13878 sections 8.4.1 through 8.4.5. All normally energized SSPS MDR relays were replaced with relays made after May 1990 prior to the issuance of WCAP-13878. DCPP has no 20 percent duty cycle relays because the SSPS is removed from service during refueling outages.

WOG plants which have completed normally energized and 20 percent duty cycle relay replacements as recommended by WCAP-13878, and maintain the original normally de-energized MDR relays at a mild ambient temperature, are not subject to the varnish offgassing failure mechanism.

Notation 4: (MD) Manufacturing Defects

The dominant failure mode for older MDR relays is coil varnish offgassing in energized relays, resulting in relay failure to operate, as discussed in Notation #3. Manufacturing defects (1990-1995) have been noted by the NRC, NSSS vendors, and other nuclear plants, including San Onofre Nuclear Generating Station (SONGS). These defects do not affect the SSPS slave relays installed as original equipment in the 1970s and early 1980s. Many of the identified

defects are associated with medium size or dc coil relays, and do not affect the small ac coil relays used in the SSPS. Analysis indicates that identified manufacturing defects generate relay failures before installation or early in life for energized MDR relays.

At DCPP, energized replacement relays have provided acceptable service for over 2.5 years in both units, indicating they were not affected by manufacturing defects. Manufacturing defects and PG&E's commercial grade dedication program are further discussed in response to NRC Question #2 on page 9 of this submittal.

Notation 5: (CL) Contact Loading

Failures related to improper contact loading (low-level, overload, and series or parallel contacts) are related to actuation circuit design. DCPP has completed loading studies for SSPS slave relay contacts to ensure that all of the contacts are used within their capabilities. No improper slave relay contact loading has occurred at DCPP. Consequently, this failure mode is not applicable . Contact loading is further discussed in response to NRC Question #4 on page 13 of this submittal.

Notation 6: (OV) Coil Over-voltage Application

Overvoltage conditions are most likely to be associated with dc coil MDR relays. Two overvoltage conditions are of particular note.

The first condition is the utilization of 24 and 28 Vdc coil relays in 36 Vdc circuits in normally energized applications in plant reactor protection systems (RPS) furnished by a different vendor. The overvoltage condition resulted in higher power dissipation in the relay and a higher rate of varnish offgassing. These relays were the first to reach end-of-life and expose this failure mechanism.

The second overvoltage condition is the routine dc power supply voltage elevation used to ensure sufficient battery capability. The result of the elevated voltage on energized dc relays is additional internal and external heat dissipation, increasing the offgassing rate inside the relay and raising the internal cabinet temperature for nearby relays. For example, River Bend calculated internal relay temperatures using a finite element model for relays energized at 120 Vac and 125 Vdc as 127°F and 149°F, respectively (AEOD S93-06, page 13).

In contrast, the vital instrument ac power system that supplies the SSPS slave relays at DCPP is maintained at a nominal output voltage of 120 Vac at all times.

Since the relays are not exposed to high coil voltages, they do not experience accelerated offgassing when energized.

Notation 7: (NE) Normally Energized

Many MDR relays are used in close-packed energized applications in reactor protection and safeguards systems in other NSSS vendor designs. Due to the self-heating and relay-to-relay heating effects that accompany normally energized usage, these relays experience accelerated aging. Failure modes associated with normally energized usage include varnish offgassing and the manufacturing defects of over-size coil binding, coils opening, and tramp epoxy sticking.

DCPP uses normally de-energized small MDR models as SSPS slave relays for all TS applications. Due to the difference in heat dissipation, failures associated with normally energized relays are not relevant to normally de-energized SSPS slave relay reliability.

Summary of AEOD S93-06 Appendix C Review

Table 1 indicates that of the 120 failures listed in the AEOD report, 95 may be eliminated as not applicable to DCPP SSPS slave relays because the failed relays were either medium sized or had dc coils.

Twenty-five failures occurred in small 115-120 Vac coil relays. Of these failures, 19 occurred in normally energized relays: 11 due to slow operation indicative of offgassing, 1 burnt out coil, 2 stuck contact and 1 corroded contact failures, 1 noisy relay (replaced prior to failure), 1 end cover binding, and 2 uncategorized failures. A majority of the categorized failures are not applicable to the normally de-energized usage found in the SSPS. Failures due to offgassing, burnt out coils, noisy relays and end cover binding are associated with energized usage. Stuck contacts may be caused by either offgassing or contact overloading, neither of which is applicable to the TS slave relays used in the DCPP SSPS. The corroded contact is most indicative of contact overloading and is also not applicable. The two uncategorized failures cannot be addressed due to insufficient information.

Six of the 120 failures noted in the AEOD report involved small, de-energized, 120 Vac coil relays. These six failures are shown in Table 2, on the next page.

Table 2 AEOD Report Failures of De-Energized 120 Vac Coil MDR Relays				
Failure	**Model**	**In-Service to Failure Dates**	**NSSS**	**Failure Mechanism**
1	134-1	3/80 to 6/86	CE	mechanical binding
2	134-1	1/85 to 5/85	B&W	contacts stuck
3	4094	1/85 to 7/85	GE	intermittent operation
4	4094	1/85 to 7/85	GE	intermittent operation
5	4121-1	6/78 to 10/87	W	relay operated slowly
6	4134-1	4/86 to 9/90	GE	burnt out coil

Based on the in-service dates, the six failures involved polyester-based varnish coil relays, since P&B did not change to epoxy-dipped coils until mid-1986.

Failure 1 due to mechanical binding and failure 5 due to slow operation were potentially caused by varnish offgassing. Insufficient information is given to determine factors which may have influenced these failures, such as location in cabinets with high ambient temperatures or significant energization periods during plant shutdown (i.e. 20 percent duty cycle).

Failures 2, 3, and 4 are cases of infant mortality in 1985. There is insufficient information presented to allow determination of relevance of these three failures. The most likely causes of these failures are manufacturing defects or failures due to problems generated elsewhere in the electrical circuit and incorrectly attributed to the relay. Manufacturing defects are commonly associated with incidents of infant mortality, since a new relay used in an application within the design specifications of the relay would not be expected to fail at the beginning of life.

Failure 6 may be the result of a random manufacturing defect resulting in a burnt out coil within the relay. Insufficient information is provided to determine whether this relay may have been energized for significant periods of time during shutdown.

Failure History Summary

The six failures presented in Table 2 and the five failures noted in WCAP-13878 together represent the best available data on failures associated with small ac coil de-energized MDR relays. Of the eleven known relay replacements reported as failures, five were infant mortality events, three were potentially related to varnish offgassing, one was replaced after a reactor trip although no failure was documented, one was induced by a design weakness allowing contacts to be overloaded, and one was due to a burnt open coil. It is notable that the most recent failure in either table was in 1991, with the great majority of

the failures occurring 8-10 years ago. Procurement programs, reporting practices, and industry communication have improved markedly since that time.

A review of these failures indicates that two actions will provide substantial protection against MDR relay failure. First, only relays which have been procured via thorough commercial grade dedication and testing activities should be installed. Second, relays susceptible to varnish offgassing should be replaced pursuant to the recommendations presented in WCAP-13878.

PG&E and the WOG believe the failure history presented in the WCAP together with a review of the applicable failures from the AEOD report represent a satisfactory performance history for small, normally de-energized, ac coil MDR relays used in a suitable design application.

<u>NRC Question 2: Refurbished P&B MDR Relays</u>

IN 90-57 and Supplement 1 alerted licensees to refurbished MDR relays which were found to be materially and functionally substandard and may not have operated as required. However, WCAP-13878, page 43, last paragraph, considers the MDR relays that have been refurbished in substandard fashion to be beyond the scope of this report.

Your submittal does not discuss whether DCPP has any refurbished MDR relays and whether your program for commercial grade equipment certification is adequate to detect the problems identified by the information notices. Please provide this information.

<u>PG&E Response</u>

IN 90-57 concerned a particular company and individual that willfully misrepresented and sold refurbished, substandard MDR relays. On receipt of the notice, PG&E verified that no receipts were on record from the associated companies for any type of materials. Additionally, PG&E inspected every MDR relay in the DCPP warehouse using the criteria of the information notice. All relays on site were determined to be acceptable. Finally, PG&E reviewed maintenance records to identify any MDR relays installed in the plant which were procured commercial grade. Three installed relays were identified, and verified to have passed sufficient dedication criteria and testing to assure their acceptability.

Manufacturing defects occurring since May 1990 include shading coil detachment (medium ac relays only), tramp epoxy deposition (all models

experiencing rework), oversize coils causing relays to bind (dc coil relays), incorrectly wrapped coils (all models), deficient springs (all relays have been identified), and bent contact arms (reworked models).

In addition to the problem reports noted in AEOD Report S93-06, on July 21, 1995, San Onofre Nuclear Generating Station (SONGS) issued a 10CFR Part 21 report concerning relays that were returned to SONGS with bent contact arms following P&B rework. Some of the reworked relays experienced subsequent failures during commercial grade dedication activities. Past reports have identified other instances of new MDR relays failing commercial grade dedication activities.

PG&E has completed evaluating the SONGS Part 21 report along with other industry experience reports regarding MDR relays. As a result of the evaluations, DCPP has put into place an enhanced commercial grade dedication process to prevent substandard or refurbished relays from being installed in the plant. All existing MDR relay warehouse stocks were placed on hold during the evaluation period, and will be re-inspected using the new enhanced criteria.

Elements of the DCPP commercial grade dedication program for safety related ac coil MDR relays follow. The dedication program may be changed from time to time based on new information, in accordance with the plant replacement parts equivalency evaluation program.

1. No DCPP MDR relays will be sent out for rework. No relays will be accepted if rework or refurbishment is known to have been performed.

2. Each relay will receive either a detailed source inspection during the assembly process or verification of operability via additional testing.

    a) The source inspection requirements include 100 percent sample size worksmanship verification of contact arm assembly, black light inspection, coil tape wrapping overlap at edges and corners, and coil dimensions. These inspections will eliminate the failure modes of bent contact arms, tramp epoxy sticking, coil failure due to insufficient wrapping, and oversize coils.

    or,

    b) In lieu of source inspection, non-destructive testing may be performed on receipt. A sample population of the relays will be baked at a temperature and time sufficient to permit coil cold flow relaxation and tramp epoxy setup to occur. Then, relay response time testing and 100 percent contact operation verification will be performed.

In addition to the above source inspection or non-destructive testing, each MDR relay will receive the following inspections on receipt:

3. Each MDR relay will receive visual inspection to verify configuration and manufacture date;

4. Each MDR relay will receive electrical testing consisting of verification of pickup and dropout voltages and coil resistance, dielectric withstand voltage testing, and contact voltage drop, current carrying, and current interrupting capacity testing;

5. Each MDR relay must be accompanied by a certificate from the manufacturer stating black light examinations have been performed on the relay prior to assembly, to prevent tramp epoxy problems. Although P&B does not furnish MDR relays as safety grade components, requiring this extra inspection should help assure that satisfactory relays are received.

PG&E believes this testing program will ensure that substandard MDR relays will be detected on receipt and not installed in the plant.

<u>NRC Question 3: Pre-1992 MDR ac Relays</u>

AEOD Report S-93-06, page 48, section 4.1.1, item 3, states that, "Failure of the ac MDR relays to reset was caused by the detachment and wedging of a copper (sic) shedding coil between the rotor and the stator because the epoxy attaching the shading coil to the stator cracked due to temperature-induced expansion and stretch (MDR relays made prior to 1/92)." Also, page 51, first full paragraph, states that, "The many contributors to MDR relay failures result in an unpredictable failure history that makes it unlikely that a scheduled surveillance testing, preventive maintenance, or replacement program can be effectively applied to pre-1990 MDR dc relays or pre-1992 MDR ac relays."

WCAP-13878 does not discuss any basis for accepting pre-1992 ac MDR relays. Therefore if these relays are used at DCPP, provide your basis for their acceptability.

<u>PG&E Response</u>

Shading Coils

Shading coils are copper rings mounted on the relay stator pole pieces of ac coil relays that delay the change of the magnetic field in the stator, tending to

prevent chatter and reduce hum. Relays with dc coils do not have shading coils. Small and medium sized ac coil MDR relays have different designs of shading coils.

The small ac coil MDR relay shading coil design utilizes an insulated wire inserted in two keyhole shaped slots in the stator face with the wire ends twisted to form a mechanical connection and then soldered together at the bottom of the stator. The wire is physically restrained by the configuration of the slots, the mechanical twist connection, and the solder joint. Epoxy is not used to restrain the shading coil. WCAP-13878, Figure 4-5a on page 23, shows a small relay's motor cavity and shading coils.

The medium ac coil MDR relay originally used a formed ring of copper installed over the end of the stator and resting in an open slot on the stator. The ring is secured with beads of epoxy at the top and bottom of the stator pole. The copper rings are susceptible to temperature-induced expansion when the relays are energized. P&B used the same polyester-based varnish as was used on the coils to attach the copper shading rings to the stator. The original polyester-based varnish remained flexible when the copper shading ring expanded, and held the ring in place. The epoxy which replaced the coil varnish was susceptible to cracking under excess copper ring expansion.

To eliminate this problem, P&B replaced the copper ring in medium size ac coil relays with a ring made of beryllium-copper. The beryllium-copper is a harder material and does not deform or stretch as much as copper, so the shading rings are sufficiently restrained by the epoxy beads.

DCPP slave relays are small ac coil MDR relays which are not susceptible to this shading coil failure since they do not use the copper ring shading coil design. Medium sized MDR relays are not used to perform safety related functions at DCPP.

Pre-1992 ac MDR Relays

PG&E and Westinghouse have reviewed the various failure incidents reported for MDR relays. As discussed in the response to Question 1, the majority of the failures noted in AEOD Report S93-06 have occurred in energized, dc coil, or medium sized relays. Many of the failures were associated with excessive heating due to exceeding the rated voltage or mounting the relays in isolation cans. When small MDR relays are used in normally de-energized applications in mild environments, few failures occur.

The majority of the slave relays for both Unit 1 and 2 were manufactured in 1975 or 1976, and installed in the SSPS at DCPP in 1976. Since that time, the relays

have demonstrated highly reliable performance. There have been no confirmed slave relay failures during testing or required actuations since DCPP started power operation in 1985.

Nine SSPS MDR relays at DCPP have been replaced. One Unit 2 slave relay was replaced in 1985 after a reactor trip when the cause of an ESF actuation could not be determined (LER 85-007-00). Since one possible cause was mechanical relay failure, the relay was replaced. No actuation problems or sticking were noted when the removed relay was tested on the bench. The relay was disposed of after bench testing, and no record of disassembly inspection exists. Eight (two per SSPS train) energized SSPS relays were replaced with new MDR relays as part of PG&E's response to IN 92-04. None of the eight relays performed TS functions. All eight relays were disassembled and inspected for the presence of offgas material or other readily visible problems. Four of the eight relays were from the same lots as the original slave relays. The other four relays were installed in the mid-1980's as part of a design modification. As discussed in LAR 94-11, the good material condition of the eight energized slave relays was judged to bound the remaining normally de-energized slave relay population.

Based on past performance and the defects found in new MDR relays, PG&E does not believe that replacing the older, de-energized MDR relays with new relays will increase safety or the reliability of SSPS performance. The maintenance activities associated with unwiring and replacing the relays on a programmatic basis would introduce the potential for wiring errors, inadvertent ESF equipment operation, infant mortality failures, and require extensive testing. The satisfactory performance of the de-energized slave relays in this application does not warrant replacement of the relays.

In summary, the pre-1992, de-energized, small, ac coil SSPS MDR relays are not subject to the excessive failures identified in the AEOD report. The installed DCPP slave relays have given years of satisfactory service, and are not implicated by the 1992 problem reports or current industry concerns with the quality of new MDR relays.

NRC Question 4: Misapplication of Relay Contacts

AEOD Report S93-06, page 49, discusses application problems and states that:

1. *Increased contact resistance was caused by misapplication of MDR relays in switching low level loads that permit contact resistance to build up.*

2. *Intermittent contact continuity was caused by contact erosion in direct current application where there is a substantial difference between the ac and dc current ratings of the relay contacts and inductive loads not included in the circuit design.*

3. *Contact failure was caused by paralleling sets of relay contacts to switch loads greater than a single set can handle when lack of simultaneous contact opening results in one contact taking all the loads.*

The NRC staff has also issued IN 92-19 regarding this problem and WCAP-13878, page 44, section 6.5, states that this is beyond the scope of this report. Identify corrective actions you have taken to address this problem.

PG&E Response

In 1991, in response to an operational experience report concerning MDR relay contact failure at Beaver Valley, PG&E completed a loading study covering each contact on every SSPS slave relay for Unit 1. The loading study recorded the manufacturer, model, and device ratings of each actuation device (solenoid or relay) operated by each slave relay contact. Unit 2 SSPS design and loads are similar to Unit 1, and were not reviewed. All slave relay contact loading was found to be acceptable.

In 1992, PG&E expanded the study to include other safety related relays and to specifically consider low-level loading. Again, all slave relay contact loading was found to be acceptable. Finally, in 1995, the loading study was reviewed to incorporate plant modifications completed since 1992. All contact loading was found to be acceptable.

Changes in circuit loading which could affect slave relay contact loading are reviewed in the design process. The design modification electrical review process includes direction to review the effect of changes in control circuit loading on the ratings of contacts in the circuit.

Discussion of the three specific NRC concerns identified in Question #4 follows.

Low-Level Loading

In the loading studies, four slave relays per train were identified that switch low-level loads. In the study, low-level loads were defined as loads less than 20 mA. This cutoff is consistent with the concerns raised in the IN, Attachment B, where low-level loads were discussed using an example of 10 mA.

In each of the four relays, the contacts used to switch low-level loads provide multiplexed ESF annunciation to the main control room. None of the low-level load contacts provide safety-related functions; consequently, low-level loading is not a concern for DCPP slave relay circuitry.

Single Contact Overloading

In the loading studies, all slave relay single contacts were evaluated for overload, for both ac and dc contact applications. Contact derating required for inductive loads was considered in determining the acceptability of the loading.

All DCPP slave relay single contact ac and dc loads are within the continuous current carrying and switching capabilities of the slave relay contacts. Additionally, a review of slave relay surveillance history found no intermittent contact failures indicative of contact erosion. Since all single contact loads are acceptable and adequate guidance is provided in the design modification process, single contact overloading is not a concern for DCPP slave relay circuitry.

Contact Pair Overloading

DCPP does not use parallel contacts on slave relays to increase the contact continuous current and break ratings. However, in several cases, two contacts in series are used to increase dc contact current make and break capability. The two contacts in series act to increase contact separation, which increases both the maximum dc voltage and current that can be controlled. Series contacts are subject to some of the same concerns as parallel contacts, since independent contacts may not operate at exactly the same time. If one contact opens or closes earlier than the other, most of the arcing will still occur on one contact.

The series contact usage for slave relays performing TS required functions can be broken into three applications: 1) to provide blocking signals to 4KV switchgear breaker closing coils, 2) to energize Electroswitch relays for bus

transfer, and 3) to energize various loads which are within a single contact rating.

The blocking signal contact application is used in two relays per train in engineered safety feature (ESF) pump control schemes to open the autotransfer closure circuit if a safety injection signal is received. Opening the autotransfer circuit permits the safety injection loading sequence to be followed instead of the standard bus autotransfer loading sequence. The slave relay is actuated by a safety injection signal and opens its series contacts within 12 to 15 milliseconds of actuation. The first affected load will not receive an autotransfer start signal for at least 4 seconds (minimum time setting for component cooling water pumps, see TS Table 4.8-2b). Consequently, the slave relay contacts open under no load conditions and are not subject to circuit breaker closing coil loading.

The second contact application is used in one relay per train in the vital 4KV bus autotransfer control circuit to initiate a bus transfer to startup power. The slave relay is actuated by a safety injection signal and closes its series contacts to energize an autotransfer trip relay. The Electroswitch trip relay is self-clearing, and de-energizes its trip coil within 20 milliseconds. The Electroswitch relay coil loads are within the short term current carrying rating of single slave relay contacts. The actuation contacts are further protected by a contact protector around the Electroswitch trip coil. Because of the self-clearing design of the trip relay, the slave relay contacts neither break nor carry excessive current.

The third series contact application is used in a small number of relays to actuate equipment that has design loading below the contact ratings for single contacts. Past design changes may have reduced the circuit loading to single contact range, accounting for the presence of series contact design in applications which do not require it. For these circuits, there are no design loading concerns.

Slave relay surveillance history was reviewed, and no instances of contact failure or intermittent actuation in series contact applications were found.

DCPP does not use parallel contacts to increase contact current carrying capacity. Series contacts are used in applications where increased load break capability may be required. Evaluation of the slave relay circuits where series contacts are used indicates that the MDR relay contacts are used within their design capabilities. Consequently, neither parallel or series contact applications are a concern for DCPP slave relay circuitry.

NRC Question 5: Relays Manufactured in 1992

AEOD Report S93-06, pages 48 and 49, states that:

4. *Prevention of relay actuation was caused by chlorine induced stress corrosion cracking of rotor return springs, permitting a broken spring part to lodge between the rotor and stator (applicable to 172 relays manufactured in 1992).*

5. *Binding of the rotor at 137 degrees Fahrenheit was caused by insufficient end-play of the shaft due to an oversized coil, over shimming, and tolerance stackups (MDR relays made in 1992).*

6. *Rotor response time may be slowed at lower temperatures, such as 40 degrees Fahrenheit, caused by uncured epoxy on the stator interfering with rotor movement (MDR relays made in 1992).*

WCAP-13878 and your submittal does not discuss the basis for acceptability of these relays made in 1992. If these relays are used at DCPP, provide your basis for their acceptability.

PG&E Response

Rotor Return Springs

According to the Asea Brown Boveri (ABB) 10CFR Part 21 report, LD-93-003, this problem was limited to 172 relays with one lot of return springs made from improperly manufactured or passivated wire. PG&E does not use any of the various models of relays (170-1, 7032, 7033, and 7034) identified in the report. All of the identified models are medium sized MDR relays. This problem is not applicable to the small ac coil relays used in the SSPS.

Binding Caused by Insufficient End-Play of Shaft or Oversize Coils

According to the ABB 10CFR Part 21 report, LD-93-177, this problem occurred in 1992, in medium sized relays furnished to Waterford. The relays identified in the part 21 are medium models 7032, 7033, and 7034 with date codes between 9239 and 9349. P&B identified an error in the manufacturing process where the coil size was gauged to the wrong specification resulting in coils which were too large, which in turn, resulted in insufficient end-play of the shaft. PG&E does not use these models of medium sized relays.

Root cause evaluation work performed at San Onofre indicates that this failure mode applies to both small and medium dc coil relays. Coils of dc relays are significantly larger than ac relay coils for any given relay size. Oversized dc coils can impede installation of the top and bottom endbells, requiring additional rotor spacers. Once the relay is heated for a period of time, the coil epoxy or varnish cold flows away from the end bell pressure points, allowing the end bell to move and exert additional force on the rotor causing the rotor to bind.

The original SSPS MDR relays were produced as safety-related parts approximately 20 years ago. If these relays were susceptible to the end bell binding failure mechanism, failure would have been evident, since cold flow would have occurred during this period. The eight non-TS, energized ac SSPS relays replaced for IN 92-04 have been in service over 2.5 years with no indication of relay binding or failure to operate. Laboratory testing performed at San Onofre indicates that essentially all coil relaxation affecting end bell tolerances occurs within the first week of energization. Therefore, end bell binding failure is not an expected failure mechanism for DCPP SSPS relays.

Tramp Epoxy

Tramp epoxy, defined as epoxy deposited in undesired locations, was found in reworked relays undergoing commercial grade dedication at ABB as documented in CE Tech Note No. 92-05. Tramp epoxy sufficient to impede rotor movement was found on the stator and rotor faces and the stator body. Uncured epoxy and tramp epoxy have also been found in medium sized ac and dc MDR relays undergoing commercial dedication at San Onofre.

Tramp epoxy problems previously occurred in 1989 at Palo Verde, as documented in AEOD Report S-93-06, section 3.2, page 8. At Palo Verde, several reworked relays failed in their first week of energization due to complete lack of rotation on de-energizing the coils. Epoxy was found on the stator faces and mating rotor surface. It was believed that epoxy had been inadvertently deposited during the relay manufacturing process.

DCPP does not use the relay models implicated in the reported events. The only medium sized relays used at DCPP are used as a normally de-energized test relays, and have no safety function. However, PG&E recognizes that this failure mode may apply to other MDR relays, and has enhanced the commercial grade process to ensure that safety related MDR relays are not affected by this failure mechanism.

NRC Question 6: Aging

Your submittal and WCAP-13878 proposes a 30-year life for normally energized MDR relays. This determination is based on the use of the Arrhenius Methodology. The staff needs the following information on the input data used with the Arrhenius methodology in order to assess the acceptability of these relays:

1. *For the ambient temperature data collected at Farley describe:*

   a. *How the data were taken, e.g., forced ventilation vs. natural circulation, cabinet door open vs. closed, and how long the cabinet door was open before the measurements were taken.*

   b. *How many relays were energized and duration of energization prior to measurement.*

2. *Temperature rise is assumed to be 58 degrees centigrade. Provide the basis for assuming this temperature rise since the MDR relays used at Westinghouse plants are designed to facilitate close spacing for mounting in cabinets that may result in higher temperature rise than the vendor prediction.*

3. *Table 8.24a for normally energized relays based on the 58 degrees centigrade ambient condition (Farley data) predicts the life of relays to be less than 30 years. However, WCAP-13878 proposes 30-year life for the MDR relays. Provide justification for this discrepancy.*

4. *Tables 8.4, 8.4a and 8.19 list higher service life for 100 percent duty cycles vs. 20 percent duty cycle. Justify or correct the discrepancies.*

5. *Tables 8.4, 8.4a and 8.4b indicate life of Neoprene rubber based on elongation (60 percent retention), while Tables 8.5, 8.5a and 8.5b indicate life for Neoprene rubber based on elongation (100 percent retention) for 65 degrees centigrade, 58 degrees centigrade, and 25 degrees centigrade temperature rise respectively. However, the life for 100 percent retention is listed as more than for 60 percent retention. Provide justification or correct the discrepancies.*

PG&E Response

6.1.a. Farley Temperature Data

The temperature data were recorded with three thermistor-based data logger units installed in and around the Farley SSPS output bays. The units were installed for a period of approximately fourteen months, for the period May 11, 1992, through July 26, 1993, and recorded actual air temperatures inside and outside the cabinet at 20 minute intervals.

Two temperature data loggers were installed in the cabinet, with one being located adjacent to a normally energized relay (worst case) and the other measuring internal cabinet ambient air temperature in the upper section of the cabinet. Additionally, one data logger was mounted external to the cabinet to record ambient air temperature.

The Farley SSPS was operated normally, with both trains in service and cabinet doors maintained closed at all times, unless surveillance activities required that they be opened. During the majority of this time the plant was in Mode 1.

The monitored conditions reflected temperature fluctuations corresponding to ambient room temperatures, nominal seasonal and day/night temperatures, and the position of the cabinet doors (open vs. closed). The data provides a record of the times when the cabinet doors were opened as evidence by an abrupt drop in internal recorded temperatures. The data characterize the cabinet temperature rise that should be expected in a typical SSPS output cabinet during normal plant operation.

The Farley temperature data is summarized in WCAP-13878 Table 8-3, on page 103. The table presents the data as grouped in data files, with each file covering approximately 6 weeks. Comparison of the ambient temperature data with the node 1 and node 2 data quantify the temperature rise expected inside the SSPS output bay.

The temperature rise experienced at the worst case location (node 1) compared to the external ambient temperature was consistent throughout the test period. Temperature ranges for the Farley SSPS output cabinet were:

Nominal	3°F rise	worst case vs. external
Typical Range	1 to 4°F rise	" "
Maximum	8°F rise	one time, maximum difference between worst case and ambient as determined from a review of the raw data

6.1.b. Energized Relays: Farley vs. DCPP Configuration

The Farley SSPS is located in the main control room area, and consists of two redundant trains of the standard three bay Westinghouse SSPS. In accordance with standard system design, the SSPS has no forced ventilation and is not equipped with cabinet blowers or ventilating fans. Natural circulation heat removal is provided through louvers on the front and back cabinet doors.

Farley has two normally energized slave relays in the output cabinet during Mode 1 operation, and as many as six energized during shutdown periods. Farley's slave relays are AR type relays. According to Westinghouse work completed on AR type relays, energized AR relays dissipate 14 watts of power and have a rated temperature rise of 30°C.

The DCPP SSPS trains are of the same standard three bay Westinghouse design as the Farley SSPS. The two trains share a small room located next to the main control room. SSPS room ventilation is provided by the safety related control room ventilation system, and is maintained in the same temperature range as the control room, year-around.

Temperatures in the DCPP SSPS are comparable to Farley. WCAP-13878, Table 8-3 on page 103, indicates that the Farley ambient room temperature ranged from 70.9°F to 83.9°F over the entire data period. Although DCPP does not have comparable records, SSPS room temperature data was recorded twice on random occasions during the preparation of this response. On June 23, 1995, DCPP Unit 1 SSPS room was 69°F and Unit 2 was 76°F, as measured by the TS-required engineered safety features (ESF) room temperature monitoring system. On November 22, 1995, Unit 1 SSPS room was 68.8°F and Unit 2 SSPS room was 75.3°F, by the same system. The room sensors are located outside of the cabinets near the ceiling. Control room temperatures are normally maintained in the range of 65 - 80°F by the operators to provide a comfortable working environment.

Similar to Farley, during normal power operations, DCPP has only two non-latching, non-TS relays energized in the SSPS. The energized small, non-latching MDR slave relays dissipate 6.5 watts each, substantially less than the Farley AR relays. Therefore, the heating effect provided by these two relays is bounded by the cabinet heating effects recorded at Farley.

During refueling outages and cold shutdowns, DCPP removes both the logic and output cabinets of the SSPS from service. Only the 15 Vdc test voltage is available to the slave relay coils, and this voltage is insufficient to actuate any of the relays. Consequently, DCPP does not have any 20 percent-duty cycle slave relays energized for the duration of refueling outages or cold shutdowns.

DCPP and Farley SSPS installations are sufficiently similar that the Farley temperature data is indicative of the normal cabinet temperature rise that would be experienced at DCPP.

6.2. Relay Spacing and Temperature Rise

Relay Spacing

Although the MDR relays used at DCPP are closely packed in their mounting arrangement, only two relays per train are normally energized. One of the energized slave relays is located in the bottom right corner of the cabinet, and the other relay is located near the left center of the cabinet. The heat generated by these two relays is removed by natural convection, and does not substantially affect the relays located nearby. Consequently, the temperature rise for individual MDR relays in the cabinet is not affected by the close pack mounting arrangement.

DCPP Relay Temperature Rise Testing

Relay temperature rise testing was completed at DCPP in January 1994. Additional temperature measurements of the energized ac coil slave relays in Unit 1 were taken in July 1995.

In 1994, two ac coil relays were tested, one small model 4121-1 latching relay with no date code (same configuration as the model 4102 slave relays), and one small model 4103 non-latching relay manufactured in December 1976. The second relay is from the same batch as many of the installed slave relays at DCPP. The relays were energized at 120V ac on the test bench in a horizontal orientation similar to that used in the SSPS, and relay temperatures were allowed to stabilize. Temperatures were measured using a calibrated contact pyrometer at various external points on the relay motor and switch sections.

Initially, the energized relays were placed in a cardboard box to eliminate air currents (no air flow) and allow the relays to self-heat to a point of equilibrium. Closed box temperature was measured at 91.2°F, and then the box was briefly opened to measure the temperature on the external relay locations. Then the energized relays were removed from the box and allowed to reach equilibrium again for the ambient room air temperature tests, where the relays were exposed to normal room air currents. The ambient room air temperature was measured at 76°F.

The highest temperatures on both relays were measured at the top center of the stator laminations. This position would be expected to be the hottest on the

relay, since the stator laminations contain the energized relay coils. Table 3 presents the temperatures measured at top center for each of the conditions, and the temperature rise over closed box conditions in both °F and °C.

Table 3: DCPP MDR Relay Temperature Rise Data

Model	Temp. °F (box at 91.2°F)	Temp. °F (room at 76°F)	Max. Temperature Rise (closed box at 91.2°F)	
			Δ °F	Δ °C
4121-1 latching ac no date code	119.7 °F	111.5 °F	28.5 °F	15.8 °C
4103 non-latching ac date code 7652	148.3 °F	139.6 °F	57.1 °F	31.7 °C

In July 1995, confirmatory temperature measurements were acquired during power operation. The four normally energized Unit 1 SSPS slave relays were measured (two per train). A contact pyrometer was used to measure the temperature at the warmest point found in the 1994 testing, the top center of the stator laminations. All four relays were model 4103-1 non-latching small ac coil relays manufactured in August 1992. Ambient room temperature measured outside the relay cabinets was 76°F. The four temperatures at the stator laminations ranged from 115°F to 118.9°F. This temperature rise corresponds to a range of 21.7°C to 23.8°C. All readings were taken expeditiously to preclude cabinet cooldown while the doors were open.

WCAP-13878 Temperature Rise Data

The manufacturer states a maximum temperature rise of 65°C bounds the MDR model series. This is a conservative maximum based on testing of the medium MDR relays. Medium relays have larger coils and higher coil power dissipation than small relays for most relay configurations. P&B has data demonstrating a peak temperature rise of 58°C for a medium MDR relay with dc coil when energized continuously "for a significant time." This temperature rise is substantially greater than would be expected for the lower coil wattage small MDR ac relays, based on the testing and measurements performed at DCPP.

As noted above, PG&E performed temperature rise testing on two small ac MDR relays, and measured a maximum temperature rise of <u>58°F</u> (33°C if each temperature is rounded up) for relays energized in a box with no air flow. It was intended that this temperature data be used for calculations presented in WCAP-13878. Inadvertently, because of the similarity in numbers, the <u>58°C</u> temperature associated with medium MDR relays was used in calculations. Therefore, most calculations in WCAP-13878, Chapter 8, are very conservative.

Additional temperature measurements were made in July 1995 on the four normally energized MDR relays in Unit 1 SSPS. The maximum temperature rise was 23.8°C. These readings place the energized SSPS relays within the 25°C data columns of WCAP-13878.

In summary:

- So few relays are normally energized that close spacing is not a factor under normal operating conditions.
- Temperature rise experienced by the SSPS slave relays is less than or equal to 33°C, not 58°C.
- Temperature rise data used in the aging assessment calculations is very conservative since it was calculated using the 58°C term in error, instead of 33°C. In addition, the energized relays are actually experiencing less than 25°C temperature rise.

6.3. Table 8.24a Results vs. Thirty Year MDR Life

WCAP-13878, Tables 8-24, 8-24a, and 8-24b, provide the results of Arrhenius calculations performed on the basis of Westinghouse Long-Term Component Aging Program test data. The purpose of the long-term program was to verify that the relays would not experience common mode failure due to age-related, temperature-induced degradation if they were subjected to a design basis seismic event. The program completed accelerated aging of the relays for one year at 130°C (234°F) prior to performing seismic testing on the relays. The relays passed the seismic testing.

The long-term program assumed a 0.5 eV activation energy. This is more conservative than the lowest activation energy presented in Table 8-1 of WCAP-13878 for any component in the relay. Employing a low value of activation energy in deriving the accelerated aging parameters causes all materials having a higher activation energy to be over-aged with respect to the simulated conditions, providing conservatism. The long-term program data does not reflect consideration of the failure modes and effects analysis or the out-gassing phenomenon.

The Tables 8-24 data calculations provide a backfit of the long-term data down to temperatures corresponding to the Farley SSPS room ambient and maximum temperatures. The data indicate that MDR relays of the three duty cycles, experiencing the temperature rises given in table notation 1 of each table, would not fail due to material degradation if they experienced a design basis seismic event.

The service life estimates presented in Tables 8-24 would be most applicable to relays manufactured after May of 1990, which are not subject to accelerated offgassing failures, due to significant improvements in materials of construction. Normally de-energized MDR relays of all vintages should have a useful life greatly in excess of the plant design life (40 years).

Energized 100 percent or 20 percent duty cycle MDR relays of pre-1989 vintage are unlikely to reach the service lives estimated in Table 8-24a (58°C rise) or 8-24b (25°C rise) of WCAP-13878, due to the varnish offgassing degradation mechanism. The calculated Arrhenius service lives in the tables range from 5.12 to 25.7 years for 58°C and 25°C rise, respectively, for a 100 percent duty cycle relay at the maximum cabinet temperature measured at Farley of 86.5°F.

As discussed previously in response 6.2 of this submittal, the expected relay temperature rise in the SSPS is less than 33°C. Additional Arrhenius calculations were completed by Westinghouse for all of the materials using a 33°C temperature rise. Although the lifetimes were extended slightly over those for a 58°C temperature rise, the recommendations on replacement times in WCAP-13878, Section 8.4, were unchanged.

In summary, the Tables 8-24 data are not directly applicable to SSPS MDR relay lifetimes. The data were based on more conservative activation energies than those applicable to the most limiting materials in the relay. The tables provide a confirmatory assessment for the recommended lifetimes found in WCAP-13878.

6.4 Tables 8.4, 8.4a, 8.19 Service Lives

The data are consistent in these tables. The service lives for 20 percent duty relays are longer than the 100 percent duty relays in each table. These tables use negative exponents for the 100 percent duty relays in every case.

6.5 Neoprene Rubber

WCAP-13878 section 8.3.1.1, page 78, contains an error. The two groups of tables (8-4, 8-4a, 8-4b, and 8-5, 8-5a, 8-5b) are identified with incorrect elongation criteria. Tables 8-4, 8-4a, and 8-4b should be identified with 60 percent elongation at low temperatures. Tables 8-5, 8-5a, and 8-5b should be identified with 100 percent elongation criteria at high temperatures. The tables themselves, on pages 104-109, are correct. The WCAP will be corrected in a future revision.

Neoprene rubber was used in the lead wire grommets of the MDR relay coil assembly, as shown in WCAP-13878 Figure 4-6, on page 25. Neoprene was

replaced by polyetherimide in June 1989, to eliminate chloride compound offgassing. The grommets protect the incoming coil wires from abrasion if the relay is exposed to shock or vibration. Physical degradation (loss of elasticity or hardening) or complete removal of the grommets has no direct consequence to the relay, and will not affect relay operation. The degradation of Neoprene is only significant because it is eventually accompanied by the release of chlorine and hydrochloric acid, which can be predatory to other materials in the relays.

WCAP-13878, Sections 8.1.2.1 and 8.3.1.1, discuss age-related degradation of Neoprene and evolution of chlorides and hydrochloric acid. There are at least two mechanisms involved in the degradation of Neoprene rubber. The first mechanism is anti-oxidant dissipation and the second mechanism is oxidation of Neoprene, releasing chlorides and hydrochloric acid. A study performed at Westinghouse showed that the rate of degradation for Neoprene rubbers differs with temperature. Only one of these two degradation mechanisms will be dominant at a given temperature and age. Therefore, more than one activation energy could be determined dependent on the temperature conditions used for testing. Attachment 2 provides details of work performed by Westinghouse, which characterizes the low temperature dissipation of Neoprene anti-oxidant compounds.

The differences in lifetimes apparent in Table family 8.4 (60 percent elongation) and Table family 8.5 (100 percent elongation) are due to the different tests the tables are based on. The test cited in Tables 8.4 was run at "cool" temperature: 40°C, for 40,000 hours, using an activation energy of 0.84eV (associated with dissipation of the anti-oxidant). The acceptance criteria for this test was retention of 60 percent of the material's original elongation property. The test cited in Tables 8.5 was run at a "hot" temperature: 120°C, for 800 hours, using an activation energy of 1.3eV (associated with oxidation of the Neoprene) and an acceptance criteria of 100 percent retention of the material's original elongation property.

Since the Neoprene rubber grommets are of little importance to MDR relays not exposed to shock and vibration, Arrhenius-based estimates of Neoprene life only serve to provide an approximation of when the release of chlorine or hydrochloric acid should be expected to begin. The estimates also indicate whether the release is abrupt and completed in short time, or very slow, resulting in minimal, ineffective concentrations of the predatory species occurring over a number of years. There are two degradation cases to be considered; first, normally energized and 20 percent duty cycle relays, which will experience accelerated Neoprene aging, and second, normally de-energized relays, with very slow degradation.

For energized relays, the Neoprene anti-oxidant will quickly dissipate and the offgassing should occur over a relatively short time. This creates a localized environment internal to the relay, with high chlorine and/or HCl concentrations at relatively high temperature. There is cause for concern that the presence of chlorine/HCl will initiate or expedite the degradation of other relay component materials. Components which may be affected by chlorine/HCl are discussed in Section 8.3.1.1 of WCAP-13878 on pages 79-80.

Since neoprene has not been used in MDR relays since 1989, older energized relays would have already experienced both anti-oxidant dissipation and hydrochloric acid offgassing. Since DCPP replaced all pre-1990 energized MDR relays in safety related service, there is no further concern with hydrochloric acid offgassing in energized relays.

For de-energized relays, the degradation occurs much more slowly. The Neoprene anti-oxidant is depleted slowly and the release of chlorine/HCl, when it begins, produces very little predatory species at any one time. This, coupled with the absence of the relay temperature rise, neither causes nor expedites the degradation of other relay materials. Consequently, the normally de-energized SSPS slave relays are not likely to experience Neoprene out-gassing related failure modes.

Additionally, chlorides were found on the broken rotor springs noted in response to Question #3. However, in that instance, the chlorides were noted to most probably have been left during an incomplete passivation process, and are mentioned here only for completeness. Rotor springs removed from DCPP relays, which had been in energized service for over ten years, showed no appreciable signs of corrosion or weakness.

TABLE 1:

EXPANDED APPENDIX C of AEOD REPORT S93-06

TABLE 1: EXPANDED APPENDIX C of AEOD REPORT S93-06

NOTATIONS:

Two or more notes apply in many failure events. For example, Notes M, DC, V, and OV are cited in the cases of medium, dc coil relays applied in an over-voltage conditions conducive to varnish offgassing. Each of these factors contributes to reducing both relay life and reliability; none apply in the case of the SSPS slave relays.

Failure events involving relays of significantly different construction or usage than SSPS slave relays are shaded.

Where data was missing or clearly erroneous in the AEOD report, additional data is supplied. Blocks where information was added or changed from the original table are indicated by bold, italicized type. The original information, if any, is shown in parentheses.

N1	(M)	Medium-size MDR relay
N2	(DC)	dc coil relay
N3	(V)	Possible varnish offgassing failure
N4	(MD)	Manufacturing defects
N5	(CL)	Contact loading
N6	(OV)	Over-voltage application
N7	(NE)	Normally Energized

** Insufficient Information.

Table 1: Expanded Appendix C of AEOD Report S93-06

P&B MOR Relay Failure Data

Model No. (MDR-)	Coil Rated Volts	Coil Watts	*Coil Size*	E/D	Failure/ Inservice Date(s)	Fail Time (Yr)	NSSS	System	Results of Failure	Relay Failure Mechanism	*NOTES*
131-1	120V ac	7.1	*S*	E	27-AUG-85/ 19-DEC-79	5.7	CE	CS	BKUP PRZR HTRS DIDN'T SHUT OFF	RELAY BURNT OUT	*NE*
134-1	115V ac	6.5	*S*	E	22-JUN-87/ 16-JUN-74	13.0	W	MS	S/G BLOWDOWN ISO VLV CLOSED - ST	CONTACTS STICKING	*NE, possible V or CL*
134-1	115V ac	6.5	*S*	D	20-JUN-86/ 26-MAR-80	6.2	CE	LPSI	LPSI VALVE DIDN'T OPEN - ST	MECHANICAL BINDING	***possible V FAILURE 1***
134-1	115V ac	6.5	*S*	D	17-MAY-85/ 01-JAN-85	0.5	B&W	ESFAS	EFW ISOL VALVE DIDN'T OPEN - ST	CONTACTS STUCK	***possible V or CL FAILURE 2***
136-1	*28 Vdc (36 Vdc)*	*10.3*	*S*	E	04-JAN-93/ 27-MAY-85	7.5	CE	ESFAS	EFW FLOW CONTROL VLV INOP - ST	OPEN SET OF CONTACTS	*DC, NE, OV (36 Vdc), V*
136-1	28 Vdc	10.3	*S*	E	06-SEP-92/ 01-APR-84	8.4	CE	ESFAS	AFW CONT ISO VALVE TO S/G INOP	OVERSIZED COIL STUCK SHAFT	*DC, NE, MD, OV (36 Vdc)*
136-1	28V dc	10.3	*S*	E	20-NOV-87/ 26-MAR-80	7.6	CE	ESFAS	"B" EFW VLV TO "A" S/G INOP - ST	OXIDE FIM ON CONTACTS	*DC, NE, CL, OV (36 V dc)*
136-1	28V dc	10.3	*S*	E	20-NOV-87/ 26-MAR-80	7.7	CE	ESFAS	"A" EFW VALVE TO S/G INOP - ST	CONTACT FAILURE, BUT TESTED OK	*DC, NE, **, OV (36 V dc)*
136-1	28V dc	10.3	*S*	E	11-AUG-87/ 01-JAN-84	3.8	CE	ESFAS	EFW PUMP DIS VALVE TO S/G INOP	DEFECTIVE CONTACTS	*DC, NE, **, OV (36 V dc)*
136-1	28V dc	10.3	*S*	E	30-JUL-85/ 26-MAR-80	5.3	CE	ESFAS	1 ESFAS DIDN'T RESET POST RXTRIP	RELAY STUCK	*DC, NE, V, OV (36Vdc)*
136-1	28V dc	10.3	*S*	E	13-JAN-84/ 26-MAR-80	3.7	CE	ESFAS	EFV DIS ISO VALVE INOP - ST	MECHANICAL BINDING	*DC, NE, V, OV (36 Vdc)*
137-8	125V dc	10.3	*S*	E	28-DEC-92/ 01-NOV-90	2.2	CE	ELECT	EDG DIDN'T PICK UP LOAD ON GRID	STICKING CONTACTS DIDN'T OPEN	*DC, NE, possible V,CL or MD*
137-8	125V dc	10.3	*S*	E	04-JUL-90/ 19-MAY-89	1.1	CE	CIS	S/G SAMPLE VLV DIDN'T STAY OPEN	CONTACTS DID NOT PICK UP	*DC, NE, possible V or MD*

Table 1: Expanded Appendix C of AEOD Report S93-06

P&B MOR Relay Failure Data

Model No. (MDR-)	Coil Rated Volts	Coil Watts	*Coil Size*	E/D	Failure/ Inservice Date(s)	Fail Time (Yr)	NSSS	System	Results of Failure	Relay Failure Mechanism	*NOTES*
137-8	125V dc	10.3	*S*	E	01-MAY-89/ 24-SEP-85	3.6	CE	CS	CSP ISOLATION VALVE INOP - ST	CONTACTS STUCK INTERMITTENLY	*DC, NE, possible V*
137-8	120V dc	9.5	*S*	E	16-NOV-88/ 08-AUG-83	5.3	CE	ELECT	EDG VOLTAGE REGULATOR INOP	STUCK IN ENERGIZED STATE	*DC, NE, possible V*
137-8	125V dc	10.3	*S*	D	17-JUN-88/ 01-APR-84	4.2	CE	ELECT	EDG CONTROL SYSTEM - PM	RELAY DID NOT RESPOND PROPERLY	*DC, ** *
137-8	125V dc	10.3	*S*	D	16-JUN-88/ 01-APR-84	4.2	CE	ELECT	EDG CONTROL SYSTEM - PM	RELAY DID NOT RESPOND PROPERLY	*DC, ** *
137-8	125V dc	10.3	*S*	D	15-JUN-88/ 01-APR-84	4.2	CE	ELECT	EDG CONTROL SYSTEM - PM	RELAY DID NOT RESPOND PROPERLY	*DC, ** *
137-8	125V dc	10.3	*S*	D	15-JUN-88/ 01-APR-84	4.2	CE	ELECT	EDG START RELAY FOUND BAD - PM	RELAY DID NOT RESPOND PROPERLY	*DC, ** *
137-8	128 Vdc	10.3	*S*	D	13-JUN-88/ 01-APR-84	4.2	CE	ELECT	D/G VOLT. REG ADJUSTMENT PROB	2 CONTACTS WOULDN'T CLOSE	*DC, possible V*
137-8	120V dc	9.5	S	D	13-JUN-88/ 01-APR-84	4.2	CE	ELECT	EDG VOLT. REG. RELAY INOP	2 CONTACTS INOP WITHOUT TAPPING	*DC, possible V*
137-8	120V dc	9.5	S	E	09-MAY-88/ 01-APR-84	4.1	CE	ELECT	EDG PROT. RELAY INOP - PM	DID NOT MEET MANF. SPECS	*DC, NE, ** *
137-8	120V dc	9.5	*S*	D	15-OCT-87/ 01-APR-84	3.5	CE	ELECT	EDG CONTROL SYSTEM - PM	WOULD NOT RESPOND PROPERLY	*DC, ** *
137-8	125V dc	10.3	*S*	D	10-SEP-87/ 08-AUG-83	4.1	CE	ELECT	EDG CONTROLS - PM	RELAY OUT OF TOLERANCE	*DC, ** *
137-8	*125V dc* (28 Vdc)	*10.3*	S	D	20-MAY-87/ 01-APR-87	0.1	CE	ELECT	"B" EDG VOLT REG LIGHT INOP	FAILED RELAY - END OF LIFE	*DC, ** *
137-8	115V dc	9.5	*S*	D	13-JAN-87/ 01-APR-84	2.7	CE	ELECT	EDG TROUBLE ALARM DIDN'T RESET	UNKNOWN	*DC, ** *

Table 1: Expanded Appendix C of AEOD Report S93-06

P&B MOR Relay Failure Data

Model No. (MDR-)	Coil Rated Volts	Coil Watts	*Coil Size*	E/D	Failure/ Inservice Date(s)	Fail Time (Yr)	NSSS	System	Results of Failure	Relay Failure Mechanism	*NOTES*
137-8	125V dc	10.3	*S*	E	21-AUG-85/ 10-MAR-84	1.4	CE	ELECT	EDG UNDERVOLTAGE ALARM INOP	CONTACTS OPEN	*DC, NE, possible V or MD*
137-8	125V dc	10.3	*S*	D	03-AUG-85/ 26-MAR-80	5.4	CE	COND	COND PP DIDN'T STOP POST RX TRIP	RELAY FAILED	*DC, ***
138-8	125V dc	10.3	*S*	D	21-NOV-92/ 01-NOV-90	2.0	GE	HPCS	HPCS DG OVERSPEED PROT. INOP	RELAY BINDING	*DC,, possible V or MD*
138-8	125V dc	10.3	*S*	D	04-NOV-92/ 01-NOV-90	2.0	GE	ELECT	EDG OVERVOLTAGE RELAY INOP	FAILED TO OP AT SET VOLTAGE	*DC, possible V or MD*
138-8	125V dc	10.3	*S*	D	13-MAR-91/ 17-NOV-86	4.3	W	ELECT	"B" EDG SEQUENCER FAILED - ST	CONTRACTS DIDN'T MAKE - TEST OK	*DC, ***
138-8	125V dc	10.3	*S*	D	25-DEC-89/ 08-AUG-83	6.3	CE	CVCS	ION EXCHANGER BYPASS VALVE INOP	CHATTERED/DIDN'T STAY CLOSED	*DC, possible V or MD*
138-8	125V dc	10.3	*S*	D	09-OCT-89/ 27-MAY-85	4.4	CE	ELECT	EDG CLG WATER PP DIDN'T START - ST	LOAD SEQUENCER CONTACTS STUCK	*DC, possible V or MD*
138-8	125V dc	10.3	*S*	D	17-JUN-88/ 01-APR-84	4.2	CE	ELECT	EDG CONTROL SYSTEM - PM	RELAY DID NOT RESPOND PROPERLY	*DC,***
138-8	125V dc	10.3	*S*	D	17-JUN-88/ 01-APR-84	4.2	CE	ELECT	EDG CONTROL SYSTEM - PM	RELAY DID NOT RESPOND PROPERLY	*DC, ***
138-8	125V dc	10.3	*S*	D	15-JUN-88/ 01-APR-84	4.2	CE	ELECT	EDG CONTROL SYSTEM - PM	RELAY DID NOT RESPOND PROPERLY	*DC,***
138-8	120V dc	9.5	*S*	E	05-MAY-88/ 01-APR-84	4.1	CE	ELECT	EDG PREVENT. MAINT.	RELAY DIDN'T MEET MANF. SPECS.	*DC, NE, ***
138-8	125V dc	10.3	*S*	E	14-JAN-86/ 04-SEP-82	3.3	GE	ELECT	EDG OUTPUT BRKR DIDN'T CLOSE - ST	SOME CONTACTS DID NOT CLOSE (LA SALLE)	*DC, NE, possible V or MD*
138-8	125V dc	10.3	*S*	D	25-NOV-85/ 08-AUG-83	2.3	CE	ELECT	LOSS OF EDG 125VDC CONTROL - ST	END OF LIFE	*DC, ***

Table 1: Expanded Appendix C of AEOD Report S93-06

P&B MOR Relay Failure Data

Model No. (MDR-)	Coil Rated Volts	Coil Watts	*Coil Size*	E/D	Failure/ Inservice Date(s)	Fail Time (Yr)	NSSS	System	Results of Failure	Relay Failure Mechanism	*NOTES*
170-1	*115V ac*	*17.0*	*M*	**	13-JAN-92/	**	CE	RCS	LOST PRZR HIR CONTROL CIRCUIT	ROTOR STUCK WHEN SPRING BROKE	*M, MD*
170-1	115V ac	*17.0*	*M*	E	03-OCT-91/ 17-SEP-89	2.1	CE	RPS	"B" RPS BREAKER KEPT TRIPPING	NORMAL WEAR OUT OF RELAY	*M, NE*
170-1	115V ac	*17.0*	*M*	E	01-OCT-91/ 17-SEP-89	2.1	CE	RPS	MASTER RPS RELAY DIDN'T TRIP - ST	NORMAL WEAROUT OF RELAY	*M, NE*
170-1	115V ac	*17.0*	*M*	E	01-OCT-91/ 17-SEP-89	2.1	CE	RPS	"D" RPS BRKR CONTINUOUS TRIP - ST	MASTER RELAY WOULDN'T ENERGIZE	*M, NE, possible V or MD*
170-1	115V ac	*17.0*	*M*	E	11-JUN-91/ 22-JUN-90	1.0	CE	RPS	"C" RPS FAILED TO RESET - ST	RELAY FAILED TO RESET	*M, NE, possible V or MD*
170-1	*115V ac (12V dc)*	*17.0*	*M*	E	13-AUG-87/ 01-APR-84	3.4	CE	RPS	SPURIOUS TRIP OF RX BREAKERS	FEEDER CABLE HOT	*M, NE, V*
170-1	*115V ac (12V dc)*	*17.0*	*M*	E	22-SEP-86/ 01-APR-84	2.5	CE	RPS	"B" RPS PATH 2 DID NOT TRIP	STUCK IN ENERGIZED STATE	*M, NE, V*
170-1	120 Vac	*17.0*	*M*	E	06-JUN-84/ 25-MAR-80	4.2	GE	RPS	FALSE RPS CHANNEL 2 TRIP	1 OF 3 RELAYS ACTING ABNORMALLY	*M, NE, V, OV*
4094	115V ac	8	*S*	E	15-JAN-88/ 01-MAY-84	3.7	GE	RWCU	RWCU PUMP COULD NOT SHUTDOWN	RELAY STUCK	*NE, V*
4094	115V ac	8	*S*	E	09-FEB-87/ 01-SEP-82	4.3	GE	ESSW	ESSW PUMP FAN DIDN'T SHUTDOWN	RELAY STICKING	*NE, V*
4094	115V ac	8	*S*	E	11-SEP-86/ 01-SEP-82	4.0	GE	ESW	ESW PUMP FAN RUNNING IN AUTO	RELAY CONTACTS STUCK	*NE, V or CL*
4094	115V ac	8	*S*	D	06-JUL-85/ 01-JAN-85	0.5	GE	MS	SRV POSITION INDICATION INOP	INTERMITTENT OPERATION IN - ST	*CL or MD FAILURE 3*
4094	115V ac	8	*S*	D	06-JUL-85/ 01-JAN-85	0.5	GE	MS	SRV POSITION INDICATION INOP	INTERMITTENT OPERATION IN - ST	*CL or MD FAILURE 4*

Table 1: Expanded Appendix C of AEOD Report S93-06

P&B MOR Relay Failure Data

Model No. (MDR-)	Coil Rated Volts	Coil Watts	*Coil Size*	E/D	Failure/ Inservice Date(s)	Fail Time (Yr)	NSSS	System	Results of Failure	Relay Failure Mechanism	*NOTES*
4103-1	118V ac	6.5	*S*	E	15-SEP-89/ 10-OCT-85	3.9	W	RPS	CHRG PP MIN FLOW VALVE OPENED - ST	STUCK IN ENERGIZED POSTION	*NE, V*
4121-1	120V ac	5.5	*S*	D	04-OCT-87/ 06-JUN-78	9.3	W	MS	MSIV DIDN'T SHUT IN TIME	RELAY OPERATED SLOWLY	*V FAILURE 5*
4130-1	120V ac	6.5	*S*	E	01-JUN-92/ 01-OCT-86	6.7	GE	RPS	CH A/RPT A TCV SCRAM RESPONSE> TS	SLOW OPENING CONTACTS	*NE, possible V*
4130-1	120V ac	6.5	*S*	E	01-JUN-92/ 01-OCT-86	6.7	GE	RPS	CH B/RPT A TCV SCRAM RESPONSE> TS	SLOW OPENING CONTACTS	*NE, possible V*
4130-1	120V ac	6.5	*S*	E	16-DEC-87/ 15-JAN-85	2.9	GE	RPS	BACKUP SCRAN VALVE FAILED	RELAY FAILURE	*NE,***
4134-1	120V ac	7.1	*S*	E	09-JAN-93/ 23-JUN-89	3.5	GE	RPS	RPS/MSIV CLOSURE TIME>IS LIMIT	"EXPECTED WEAR"	*NE,***
4134-1	120V ac	7.1	*S*	E	14-JUN-92/ 01-OCT-86	6.8	GE	RPS	CH B/B2 TCV SCRAN RESPONSE> TS	SLOW OPENING CONTACTS	*NE, V*
4134-1	120V ac	7.1	*S*	E	14-JUN-92/ 01-OCT-86	6.8	GE	RPS	CH B/B1 TCV SCRAN RESPONSE> TS	SLOW OPENING CONTACTS	*NE, V*
4134-1	120V ac	7.1	*S*	E	12-JUN-92/ 01-OCT-86	6.8	GE	RPS	CH B/B1 TCV SCRAN RESPONSE> TS	SLOW OPENING CONTACTS	*NE, V*
4134-1	120V ac	7.1	*S*	E	12-JUN-92/ 01-OCT-86	6.8	GE	RPS	CH B/B1 TCV SCRAN RESPONSE> TS	SLOW OPENING CONTACTS	*NE, V*
4134-1	120V ac	7.1	*S*	D	21-SEP-90/ 11-APR-86	4.4	GE	ESV	BACKWASH VALVE DIDN'T CLOSE - ST	BURNED OUT RELAY COIL	*open coil FAILURE 6*
4134-1	120V ac	7.1	*S*	E	15-SEP-88/ 15-JAN-85	3.7	GE	RPS	PREVENTED RPS HALF SCRAM	SMALL END COVER HOLE BOUND SHAFT	*NE, MD*
4135-1	120V ac	7.1	*S*	E	03-AUG-91/ 28-JUN-86	5.1	GE	RPS	"B" APRM RPS TRIP INPUT - PM	EXCESS NOISE: EXPECTED FAILURE	*NE, MD, ***

Table 1: Expanded Appendix C of AEOD Report S93-06

P&B MOR Relay Failure Data

Model No. (MDR-)	Coil Rated Volts	Coil Watts	*Coil Size*	E/D	Failure/ Inservice Date(s)	Fail Time (Yr)	NSSS	System	Results of Failure	Relay Failure Mechanism	*NOTES*
4135-1	120V ac	7.1	*S*	E	13-NOV-89/ 18-FEB-86	3.4	GE	RWCU	RWCU CONT ISO VALVE DIDN'T OPEN	CONTACTS DIDN'T CLOSE-CORROSION	*NE, V*
4135-1	120V ac	7.1	*S*	E	05-APR-88/ 28-JUN-86	1.7	GE	RPS	"D" MAIN STEAM MI RAD TRIP SLOW	DEFECTIVE RESPONSE TIME	*NE, V*
4135-1	120V ac	7.1	*S*	E	02-APR-88/ 28-JUN-86	1.7	GE	RPS	RPS DIV. 2 & 4 RELAY FAILED ST	RELAY OPERATED SLOWLY	*NE, V*
5059	125V dc	10.3	*S*	E	11-JAN-92/ 01-JAN-84	8.0	W	AFW	CHANGED AFW STEAM TO ALT SUPPLY	FAILED TO DE-ENERGIZE POSITION	*DC,V*
5060	125V dc	10.3	*S*	D	03-SEP-85/ 08-AUG-83	2.1	CE	CIS	SAMPLE CONT ISO VALVE INOP - ST	PREMATURE END OF LIFE	*DC,***
5061	125V dc	*10.3 (20.6)*	*S*	D	29-MAY-89/ 24-SEP-85	3.7	CE	HVAC	EDG ROOM EXHST FAN DAMPER INOP	COIL HAD OPEN CIRCUIT	*DC, open coil*
5062	125V dc	10.3	*S*	E	02-NOV-92/ 01-JAN-90	1.8	GE	CAC	ISOLATION VALVE POSITION INOP	RELAY STUCK	*DC, NE, V*
5062	125V dc	10.3	*S*	E	29-SEP-92/ 01-MAY-84	8.4	GE	RCS	RECIRC PUMP 1B WOULDN'T TRIP	RELAY STUCK IN ENERG POSTION	*DC, NE, V*
5062	125V dc	10.3	*S*	E	29-SEP-92/ 01-MAY-84	8.4	GE	RCS	RECIRC PUMP 1A WOULDN'T TRIP	RELAY STUCK IN ENERGIZED STATE	*DC, NE, V*
5062	125V dc	10.3	*S*	E	13-SEP-92/ 01-MAY-84	8.4	GE	CS	NO DIV 1 CONTROL PWR LOSS ALARM	RELAY STUCK IN ENERGIZED STATE	*DC, NE, V*
5062	125V dc	10.3	*S*	D	05-APR-86/ 08-JUN-83	3.8	GE	ELECT	ESW/RHRESW PPS INOP ON EDG - ST	SEQUENCER CONTACTS STUCK OPEN	*DC, V*
5062	125V dc	10.3	*S*	D	15-FEB-84/ 01-SEP-82	2.4	GE	CS	CS PUMP BKR DIDN'T OPEN IN - ST	NOT WORKING PROPERLY	*DC, ***
5076	125V dc	*10.3*	*S*	E	22-MAR-91/ 22-MAY-76	14.8	W	CI	PRT ISO VALVE DIDN'T CLOSE - ST	RELAY FAILED CLOSED	*DC, NE, V*

Table 1: Expanded Appendix C of AEOD Report S93-06

P&B MOR Relay Failure Data

Model No. (MDR-)	Coil Rated Volts	Coil Watts	*Coil Size*	E/D	Failure/ Inservice Date(s)	Fail Time (Yr)	NSSS	System	Results of Failure	Relay Failure Mechanism	*NOTES*
5095	125V dc	*20.6*	*S*	D	30-DEC-89/ 03-JAN-86	3.9	GE	ELECT	DIV 1 EDG FAILED TO START	MISAPPLICATION/CURRENT LOAD LOW	*CL*
5111-1	22V dc	8.6	*S*	E	23-JUL-91/ 15-JAN-85	6.6	GE	ESF	CON'T ISO OF RWCU SAMPLE VLV - ST	RELAY STUCK	*DC, NE, V, OV (24Vdc)*
5111-1	22V dc	8.6	*S*	E	19-JUL-91/ 15-JAN-85	6.6	GE	ESF	CIS, SBGT START, CRHVAC ACT	HIGH CONTACT RESIST, BUT TEST OK	*DC, NE, CL, OV (24 Vdc)*
5146	28V dc	*10.3*	*S*	E	12-APR-91/ 15-JAN-88	3.2	CE	ELECT	B ECWS PP FAILED TO RUN - ST	CONTACTS FAILED TO CLOSE *PALO VERDE - OVERSIZE COIL*	*DC, NE, MD, OV (24 Vdc)*
5147	32V dc	*10.3*	*S*	E	06-JUL-90/ 19-SEP-86	3.7	CE	RSP	A MSIS RPS TRIP DIDN'T RESET - ST	ALL CONTACTS FOUND OPEN	*DC,NE, V*
5151	*125V dc*	10.3	*S*	E	09-MAY-92/ 01-JAN-91	1.4	GE	CAN	CONT ATM VALVE POSITION INOP	RELAY STUCK	*V, NE*
6091	118V ac	*12*	*M*	E	25-JUL-90/ 01-MAR-88	2.3	W	ESFAS	EDG - ST	2 CONTACTS FAILED TO CLOSE	*M, DC, NE*
7032	28V dc	18.7	*M*	E	25-SEP-92/ 30-SEP-91	1.0	CE	ESFAS	ESFAS CHANNEL INOP - ST	SHAFT BINDING: MANUFACTURE DEFECTS	*M, DC, MD, NE*
7032	28V dc	18.7	*M*	E	11-NOV-89/ 26-MAR-80	9.6	CE	CS	CSAS BYPASS DIDN'T STOP NaOH PP	CONTACTS CLOSED SLOWLY	*M, DC, V, NE*
7032	28V dc	30.8	*M*	E	28-MAR-89/ 27-JAN-86	3.2	CE	ESFAS	VALVE OVERRIDE INDICATION INOP	OVERVOLTAGE OUTGASSING FAILURE	*M, DC, V, NE OV*
7032	28V dc	30.8	*M*	E	25-JAN-89/ 18-JAN-88	1.0	CE	ESFAS	B LPSI PP RECIRC VLV INOP - ST	OVERVOLTAGE OUTGASSING FAILURE	*M, DC, V, NE OV*
7032	28V dc	30.8	*M*	E	10-JAN-89/ 18-JAN-88	1.0	CE	ESFAS	ESFAS OVERRIDE SWITCH INOP - ST	OVERVOLTAGE OUTGASSING FAILURE	*M, DC, V, NE OV*
7032	28V dc	30.8	*M*	E	09-JAN-89/	2.2	CE	ESFAS	SIAS TRAIN SIGNAL FAILED -	OVERVOLTAGE OUTGASSING	*M, DC, V, NE*

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P&B MOR Relay Failure Data

Model No. (MDR-)	Coil Rated Volts	Coil Watts	*Coil Size*	E/D	Failure/ Inservice Date(s)	Fail Time (Yr)	NSSS	System	Results of Failure	Relay Failure Mechanism	*NOTES*
					18-SEP-86				ST	FAILURE	*OV*
7032	28V dc	30.8	*M*	E	02-AUG-88/ 18-SEP-86	1.8	CE	ESFAS	"B" AFAS SIGNAL FAILURE - ST	OVERVOLTAGE OUTGASSING FAILURE	*M, DC, V, NE OV*
7032	28V dc	30.8	*M*	E	03-JUN-87/ 27-JAN-86	1.3	CE	ESFAS	"B" CONT. SPRAY SIGNAL INOP	OVERVOLTAGE OUTGASSING FAILURE	*M, DC, V, NE OV*
7032	28V dc	30.8	*M*	E	25-MAY-87/ 18-SEP-86	0.2	CE	ESFAS	"B" SIAS SIGNAL FAILURE - ST	OVERVOLTAGE OUTGASSING FAILURE	*M, DC, V, NE OV*
7032	28V dc	30.8	*M*	E	26-NOV-85/ 18-SEP-86	0.2	CE	ESFAS	"B" AUX FW SIGNAL FAILURE - ST	OVERVOLTAGE OUTGASSING FAILURE	*M, DC, V, NE OV*
7032	28V dc	18.7	*M*	E	07-MAR-85/ 01-APR-84	0.9	CE	ESFAS	ESF TESTING FOUND BAD RELAY	END OF LIFE	*M, NE, DC*
7032	28V dc	18.7	*M*	E	12-SEP-84/ 01-APR-84	0.4	CE	EFW	RELAY FOUND BAD IN ESF - ST	END OF LIFE	*M, NE, DC*
7032	28V dc	18.7	*M*	E	13-AUG-84/ 08-AUG-83	1.0	CE	ESFAS	PREVENTATIVE MAINTENANCE	NOT OPERATING PROPERLY	*M, NE, DC*
7033	28V dc	18.7	*M*	E	07-NOV-87/ 08-AUG-83	4.2	CE	ESFAS	"A" SIAS TRAIN INOP - ST	WEAROUT DUE TO AGING	*M, NE, DC*
7034	36 Vdc	30.8	*M*	E	08-DEC-91/ 27-MAY-85	6.5	CE	EFW	"B" EFW INOP - ST	ROTOR STUCK-OUTGASSING/CORROSION	*M, DC, NE, V, OV*
7034	28V dc	18.7	*M*	E	27-JUN-89/ 24-SEP-85	3.8	CE	CIS	EFW & S/g BLOWDOWN VLVS INOP - ST	STUCK IN ENERGIZED POSITION	*M, NE, DC, V*
7034	28V dc	18.7	*M*	E	22-JAN-89/ 08-AUG-83	5.4	CE	ESFAS	DIDN'T ACT. ALL "B" SATS EQUIP	RELAY NOT WORKING PROPERLY	*M, NE, DC, V*
7034	36V dc	30.8	*M*	E	19-DEC-88/ 18-SEP-86	2.3	CE	ESFAS	MSIS CHANNEL INOP IN BYPASS - ST	CONTACT CORROSION - OFFGASSING	*M, DC, NE, V, OV*
7034	28V dc	18.7	*M*	E	07-NOV-88/ 08-AUG-83	5.2	CE	ESFAS	LPSI PUMP FAILED IN 2ND TEST	CYCLING/CONTACT RESIST	*M, NE, DC, V*

Table 1: Expanded Appendix C of AEOD Report S93-06

P&B MOR Relay Failure Data

Model No. (MDR-)	Coil Rated Volts	Coil Watts	*Coil Size*	E/D	Failure/ Inservice Date(s)	Fail Time (Yr)	NSSS	System	Results of Failure	Relay Failure Mechanism	*NOTES*
7034	36V dc	30.8	*M*	E	05-AUG-88/ 18-SEP-86	1.9	CE	ESFAS	"B" MSIS INOP - ST	OVERVOLTAGE OUTGASSING FAILURE	*M, DC, NE, V, OV*
7034	36V dc	30.8	*M*	E	09-MAY-88/ 18-JAN-88	0.3	CE	ESFAS	"A" CSAS INOP - ST	OVERVOLTAGE OUTGASSING FAILURE	*M, DC, NE, V, OV*
7034	36V dc	30.8	*M*	E	03-MAY-88/ 18-SEP-86	1.6	CE	ESFAS	"B" RECIRC ACT SIG FAILED - ST	OVERVOLTAGE OUTGASSING FAILURE	*M, DC, NE, V, OV*
7034	28V dc	18.7	*M*	E	07-APR-88/ 26-MAR-80	8.1	CE	NSW	ENERG POND SW VALVE INOP - ST	RELAY STUCK ON DE-ENERGIZATION	*M, NE, DC, V*
7034	36V dc	30.8	*M*	E	31-DEC-87/ 18-SEP-86	1.3	CE	ESFAS	"B" SIAS SIGNAL FAILURE - ST	OVERVOLTAGE OUTGASSING FAILURE	*M, DC, NE, V, OV*
7034	28V dc	18.7	*M*	E	01-APR-87/ 01-APR-84	3.0	CE	ESFAS	INTERMITANT CONT. ISO. SIGNAL	SPURIOUS SIGNAL	*M, NE, DC, **
7034	36V dc	30.8	*M*	E	11-FEB-87/ 18-SEP-86	0.4	CE	ESFAS	CHILLED WATER VALVE INOP	OVERVOLTAGE OUTGASSING FAILURE	*M, DC, NE, V, OV*
7034	28V dc	18.7	*M*	E	09-NOV-86/ 08-AUG-83	3.2	CE	ESFAS	"B" CIAS INOP - ST	HIGH CONTACT RESISTANCE	*M, DC, NE, **
7034	28V dc	18.7	*M*	E	11-FEB-86/ 26-MAR-80	5.9	CE	ESFAS	REACTOR TRIP ON "A" MSIV CLOSURE	HIGH CONTACT OHMS - 5 MDRs REPLACED	*M, NE, DC*
7061	32V dc	20.4	*M*	E	04-OCT-90/ 28-JAN-85	4.7	CE	ESFAS	SPRAY CHEM PP VALVE INOP - ST	DEFECTIVE CONTACTS DIDN'T CLOSE	*M, NE, DC*
7061	32V dc	20.4	*M*	E	16-MAR-89/ 28-JAN-86	3.2	CE	CS	ESFAS SUBGROUP FAILED - ST	CONTACTS DIDN'T CLOSE-OFFGASSING	*M, DC, NE, V*
7061	32V dc	20.4	*M*	E	13-FEB-89/ 28-JAN-86	3.1	CE	RPS	"D" SIAS INOP - ST	CONTACTS DIDN'T CLOSE-OFFGASSING	*M, DC, NE, V*
7061	32V dc	20.4	*M*	E	02-FEB0-89/ 28-JAN-86	3.1	CE	ESFAS	DIDN'T CLOSE RWT ISO VALVE - ST	ROTOR STUCK - OFFGASSING	*M, DC, NE, V*

Table 1: Expanded Appendix C of AEOD Report S93-06

P&B MOR Relay Failure Data

Model No. (MDR-)	Coil Rated Volts	Coil Watts	*Coil Size*	E/D	Failure/ Inservice Date(s)	Fail Time (Yr)	NSSS	System	Results of Failure	Relay Failure Mechanism	*NOTES*
7062	32V dc	*20.4*	*M*	E	05-APR-90/ 28-JAN-85	4.3	CE	ESFAS	"B" ESFAS CHANNEL LOST - ST	2 CONTACTS DIDN'T CHANGE STATE	*M, DC, NE, **

Table 1: Expanded Appendix C of AEOD Report S93-06

P&B MOR Relay Failure Data

Model No. (MDR-)	Coil Rated Volts	Coil Watts	*Coil Size*	E/D	Failure/ Inservice Date(s)	Fail Time (Yr)	NSSS	System	Results of Failure	Relay Failure Mechanism	*NOTES*
7063	32V dc	*20.4*	*M*	E	13-DEC-88/ 19-SEP-86	2.2	CE	ESFAS	ESFAS FAILED, THEN OK - ST	INTERMITTENT OP FROM OFFGASSING	*M, DC, NE, V*
7063	32V dc	*20.4*	*M*	E	01-NOV-88/ 28-JAN-86	1.9	CE	RPS	"B" CIAS CHANNEL LOST - ST	ROTOR STUCK - OFFGASSING	*M, DC, NE, V*

REPRINT OF ARTICLE:

STUDIES ON AKROFLEX CD ANTIOXIDANT LOSS FROM NEOPRENE RUBBER

JOURNAL OF APPLIED POLYMER SCIENCE VOL. 18, PP. 3543-3553 (1974)

Studies on Akroflex CD Antioxidant Loss from Neoprene Rubber. I. The Determination of Antioxidant Content and the Loss Mechanism During Aging

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Synopsis

An analytical procedure for determining the antioxidant (i.e., Akroflex CD) content in neoprene rubber has been developed. The method is based on the infrared absorption analyses of chloroform extractables from the cured rubber at 1600 cm^{-1} and 1300 cm^{-1}. Good agreement is found between these two independent sets of measurements. In an attempt to elucidate the antioxidant loss mechanism found with neoprene, thermal aging studies were carried out over the temperature range of 80°–200°C. Using the infrared analytical procedure, antioxidant loss rates at the different temperatures were established. The activation energy value (5.1 kcal/mole) for the loss rate as well as other aging data suggest that the antioxidant is lost by a diffusion mechanism.

INTRODUCTION

Neoprene elastomers have found widespread usage in recent years, particularly in areas where a high degree of resiliency has to be combined with oil, solvent, heat, and weather-resistant properties, e.g., for lining tanks and chemical equipment. It is common practice in the cure of neoprene formulations to add a small amount of an antioxidant (usually about 1.0%) to prevent oxidative degradation of the polymer and subsequent deterioration of the elastomers' engineering properties. Most of these antioxidants are fugitive in nature, and significant loss can be found under normal service conditions.

In the absence of other available criteria, it has been suggested that the serviceable lifetime of an elastomer such as neoprene can be predicted by determining the rate of consumption of the antioxidant used in any particular formulation. This is based on the premise that, after all the antioxidant has been consumed, the rubber becomes vulnerable to rapid oxidative degradation and its useful service life is reduced significantly.

Consequently, there is a real need for simple analytical techniques for determining the antioxidant contents of rubbers such as neoprene during service and storage conditions so that the effective lifetime of the elastomer can be determined. Sometimes, a further stipulation on these analytical

techniques is that only small plug samples should be removed from "in service" elastomers so that loss of function can be prevented.

This paper describes an analytical method based on absorption infrared spectroscopy which has been developed to monitor the antioxidant content in a standard neoprene rubber formulation referred to as MINS-132.

The antioxidant in question (Akroflex CD from du Pont[1]) has a composition consisting of 65% phenyl-beta-naphthylamine and 35% N,N′-diphenyl-*p*-phenylenediamine and is present in the neoprene formulation at a level of ~1.0% (by weight).

As an aid to elucidate the mechanism responsible for the loss of antioxidant from the neoprene, accelerated aging studies have also been carried out over the temperature range of 80°–200°C both on the neat Akroflex CD antioxidant and on fully compounded neoprene elastomer samples containing the antioxidant. The infrared analytical method was used to determine the antioxidant loss from the cured neoprene compound at each temperature.

EXPERIMENTAL

Solvents

Several solvents were initially screened as a selective extraction medium for the antioxidant. Chloroform was finally selected for this analytical work for the following reasons: (1) It is anhydrous and will not fog the NaCl plates used in infrared work. (2) It has a clear "window" area in the infrared part of the spectrum of most direct interest to this work (i.e., 2500 cm^{-1} to 1250 cm^{-1}). (3) It is an excellent solvent for Akroflex CD. (4) Because it is volatile, the extracts from the neoprene rubber can be easily concentrated by solvent evaporation.

Although chloroform also dissolved some of the other organic components used in the neoprene formulation, these materials did not appear to interfere with the infrared analyses.

Infrared Spectral Analyses

A Perkin-Elmer-6700 spectrophotometer was used for this study. Demountable, NaCl-window, liquid cells with 1-mm spacers were found to be useful for this work. Fisher C-298 chloroform was used for both the extraction media and the reference cell.

Akroflex CD antioxidant (0.11–0.01 g) was dissolved in 25 ml chloroform, and an aliquot was placed in the sample cell with fresh chloroform in the reference cell. The heat-aged antioxidant samples were treated in the same manner. Spectrum 1 in Figure 1 shows a typical infrared spectrum obtained from a 0.114 g/25 ml solution of Akroflex CD in chloroform. The extracts from the neoprene samples were diluted to 25 ml with chloroform and run on the spectrophotometer as described previously. A typical infrared trace thus obtained is shown by spectrum 2 of Figure 1.

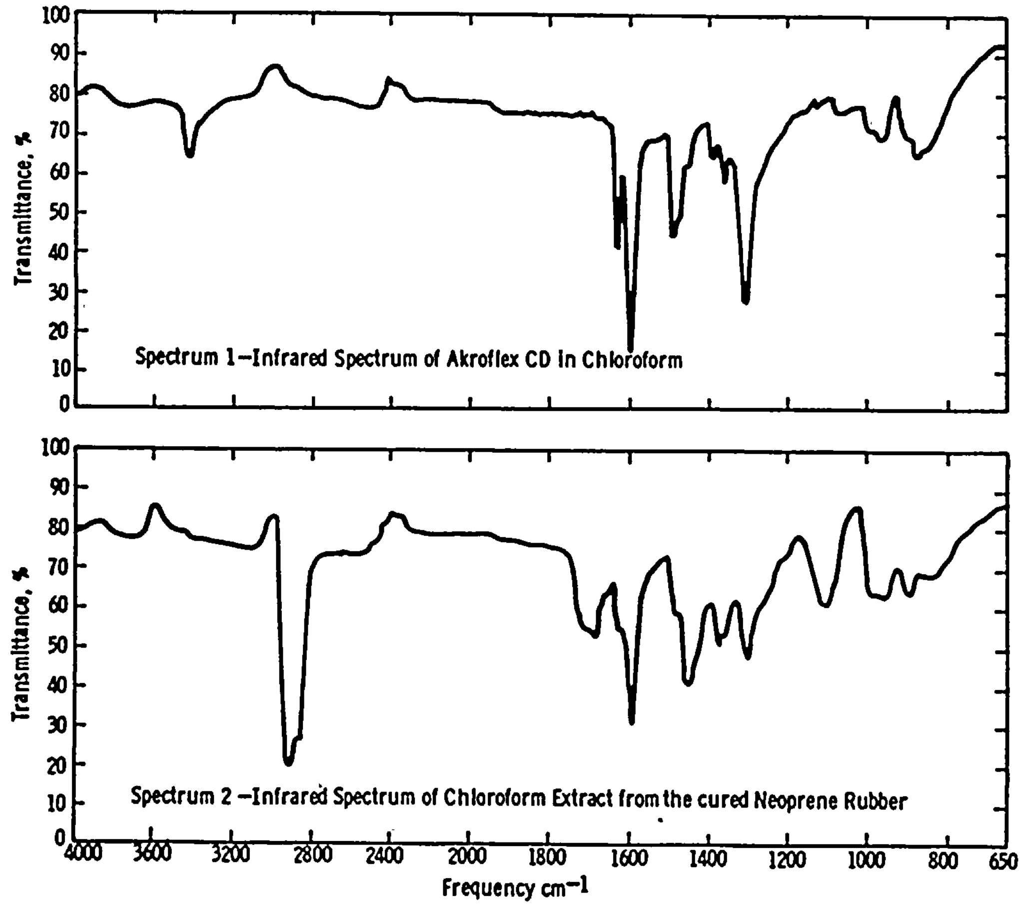

Fig. 1. Chloroform solution infrared spectra.

Accelerated Thermal Aging Tests

Antioxidant. Approximately 2-g samples (weighed to 0.1 mg) of Akroflex CD were placed in a 50-ml Pyrex beaker, covered with a watch glass, and then aged in a forced-air oven at the desired temperature for the prescribed time. The aging temperatures chosen for these studies were 80°C, 110°C, 150°C, 175°C, and 200°C. A total aging time of 192 hr was employed on each sample.

Elastomer. Plugs, $^3/_8$-in. diameter, were cut with a cork borer from the neoprene material and masticated on a two-roll, cold rubber mill. The mill was set to an opening of approximately 0.001 in., and each plug was passed through the rolls ten times. Both cured and uncured samples were prepared in the same manner.

Approximately 5.2 g (weighed to 0.1 mg) of the milled material was placed in 3-in. glazed crucibles, with covers, and aged as described above.

Extraction Method

A Soxhlet extraction apparatus was employed consisting of a 300-ml round flask, a Soxhlet extraction tube, and an Allihn-type condenser, all

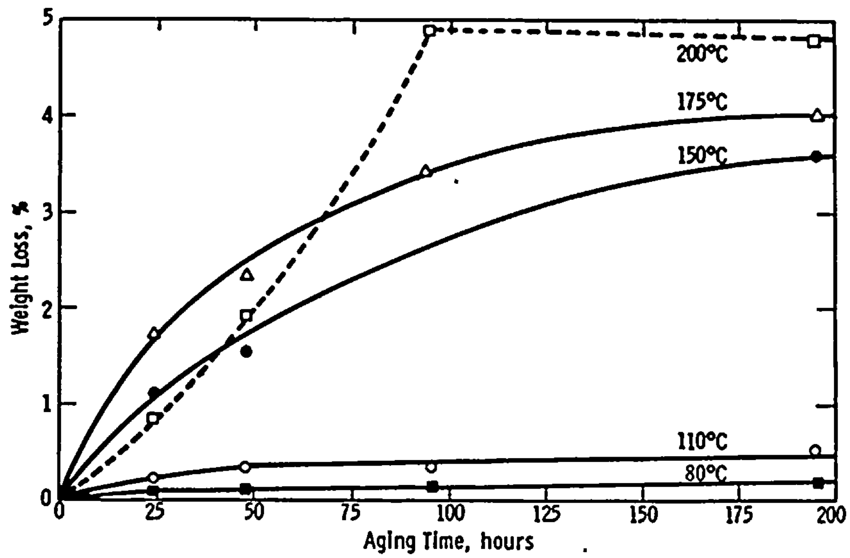

Fig. 2. Thermal aging weight loss data for neat Akroflex CD.

connected by interchangeable ground-glass joints. The extraction thimble (33 mm × 80 mm) used was of the single-thickness cellulose type. Chloroform (125 ml, Fisher C-298) was charged to the flask, and one Boileezer (Fisher B-365) was added to prevent bumping of the solvent upon heating. The weighed sample (~5 g), prepared as described above, was then placed in the extraction thimble and inserted into the extraction tube. The extraction tube with condenser attached was then fitted to the flask. All ground-glass joints were lubricated with a minimum of Dow Corning High-Vacuum Grease (Silicone). Cold water was passed through the condenser continuously throughout the extraction operation. A rate of 15 to 20 passes per hour of fresh solvent through the sample was maintained for 2 hr after the initial charging of the extraction tube. The extract was then removed from the apparatus and the chloroform solution concentrated by gentle heating to a volume of 15–20 ml. After cooling the solution to ambient temperature, the volume was adjusted to give a concentration of 5.2 g sample/25 ml chloroform. The infrared analyses were then carried out on the extracts as described above.

Weight Loss

Weight loss was determined by the differential weighing method. The aged samples were cooled to ambient temperature in a desiccator (containing Drierite to prevent moisture absorption) and then weighed. Weight loss data at 80°C, 110°C, 150°C, 175°C, and 200°C are shown in Figure 2 for neat Akroflex CD and in Figure 3 for the fully cured neoprene formulation.

Infrared Calibration Curve

The relationship between the absorption of a particular wavelength of radiation and the number of molecules absorbing (i.e., molecular concen-

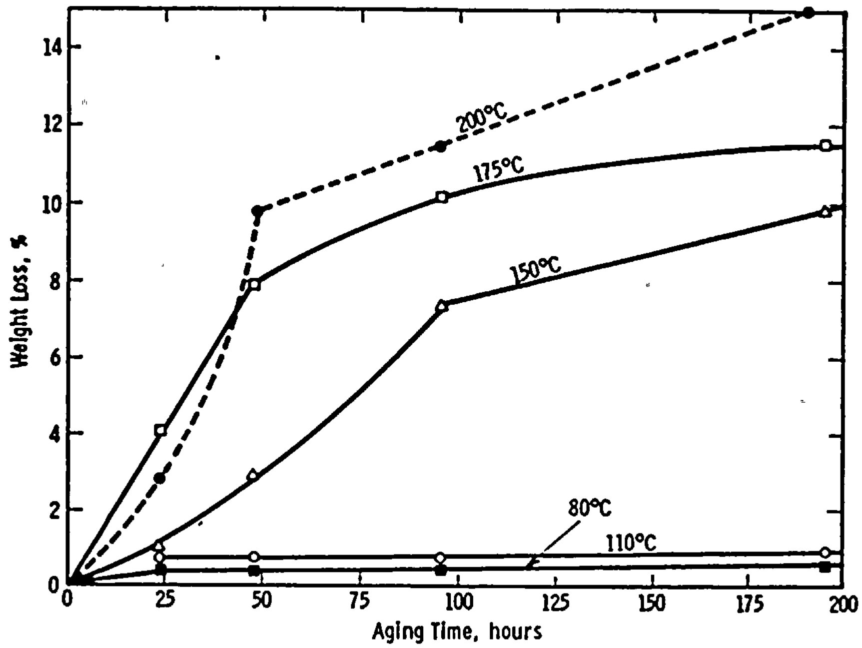

Fig. 3. Thermal aging weight loss data for the cured neoprene rubber.

tration) is referred to as the Beer-Lambert absorption law.[2] This can be written as

$$I = I_0 e^{-abc}$$

or more normally as

$$A = \log_{10} I_0/I = \log_{10} 1/T = abc$$

where A = absorbance or "optical density," b = cell path, cm, c = material concentration, g/l., a = specific absorptivity of the material, I_0 = intensity of infrared radiation incident on the sample, I = intensity of infrared radiation transmitted by the sample, and $T = I/I_0$ = transmittance = fraction of infrared radiation transmitted.

The infrared spectrum of Akroflex CD in chloroform solution (at a concentration of 4.560 g/l.) in a 1.0-mm cell is shown in spectrum 1. It can be seen that the spectrum exhibits strong absorption bands at 1600 cm^{-1} and 1300 cm^{-1} (from the $>C=C<$ and $C_6H_5-N<$ stretching vibrations); both of these were used to construct Beer-Lambert calibration curves for Akroflex CD in chloroform.

In this calibration curve, six different concentrations of Akroflex CD in chloroform were made up (ranging from 4.560 g/l. to 0.285 g/l.) and the infrared spectra were recorded in 1-mm liquid cells. The % transmittance (T_s) was determined for each sample at 1600 cm^{-1} and 1300 cm^{-1}; and, after correcting for the "baseline" absorbance (T_0), a plot of $\log_{10} (1/T_c)$ versus absorbance (A/b) was made, as shown in Figure 4. In this computation,

$$T_c = T_0 + T_s$$

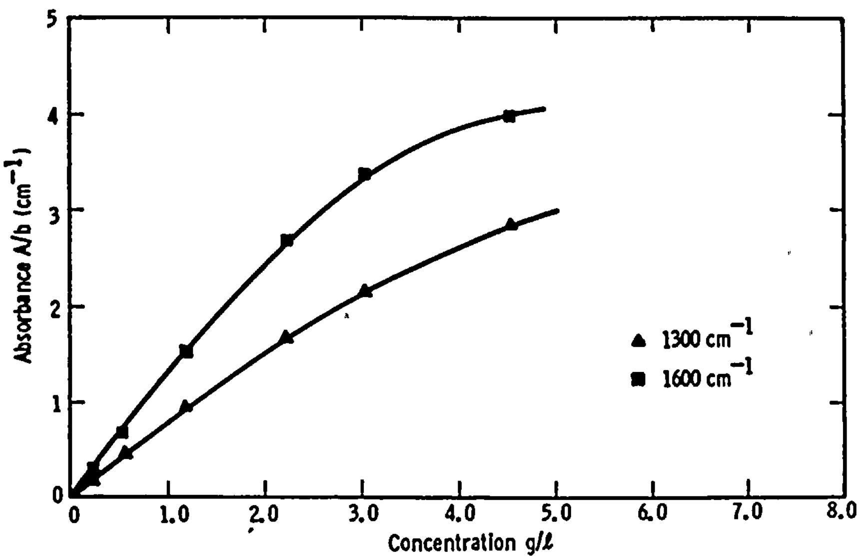

Fig. 4. Akroflex CD calibration curve (infrared absorption) in chloroform using bands at 1300 cm^{-1} and 1600 cm^{-1}.

where T_0 = baseline transmittance, T_s = sample transmittance, and b = cell thickness (0.1 cm).

It can be seen from Figure 4 that neither 1600 cm^{-1} nor the 1300 cm^{-1} absorption bands give linear dependence of absorbance on Akroflex CD concentration, thereby showing that deviations from the Beer-Lambert law are occurring. (However, below a concentration of 2.5 g/l., linearity does seem to be observed by both absorption bands.) The deviations in the absorption law in no way render this analytical procedure invalid since the concentration values can be read directly from the calibration curves. (If the Beer-Lambert law is obeyed, the values can normally be calculated algebraically.)

Thus, this analytical method can be used to measure Akroflex CD contents in the neoprene rubber. The statistical treatment of several determinations on the Perkin-Elmer 700 spectrophotometer showed that the experimental accuracy of these measurements was ±4%. A greater degree of accuracy would be anticipated on a higher resolution infrared spectrophotometer.

Sources of Contamination

Early spectra gave rise to some unexplained peaks for the known samples in solution as compared to similar samples in KBr pellets. It was found that contamination from some or all of the following items led to erroneous spectra: (1) contaminated solvent, (2) dirty NaCl windows, (3) plasticizer from washing bottle, (4) Fisher Cello-Seal lubricant (used for glass joints), (5) moisture from the atmosphere, and (6) leaking sample cells. However, with due care and attention, these sources of contamination can be eliminated.

RESULTS

Weight Loss Data

As might be expected, greater weight losses are shown by the higher temperature samples with the neoprene rubber (Fig. 3) showing considerably more than the neat Akroflex CD (Fig. 2). This suggests that oxidative degradation or volatilization of some of the organic components in MINS-132, in addition to Akroflex CD loss, is occurring. Below 110°C, the data suggest that for both the neat Akroflex CD and the neoprene samples, the oxidative degradation is proceeding at a very low rate (after a more rapid initial rate). Above 110°C, the degradation proceeds at appreciably higher rates.

Infrared Spectral Studies

The studies on the neat Akroflex CD samples showed that after aging at elevated temperatures for periods more than 24 hr, some minor changes in the spectra were detectable. This is shown in Figure 5, where a comparison of the thermally aged material (200°C for 192 hr) is made with the original. (These samples were recorded as pressed KBr pellets.)

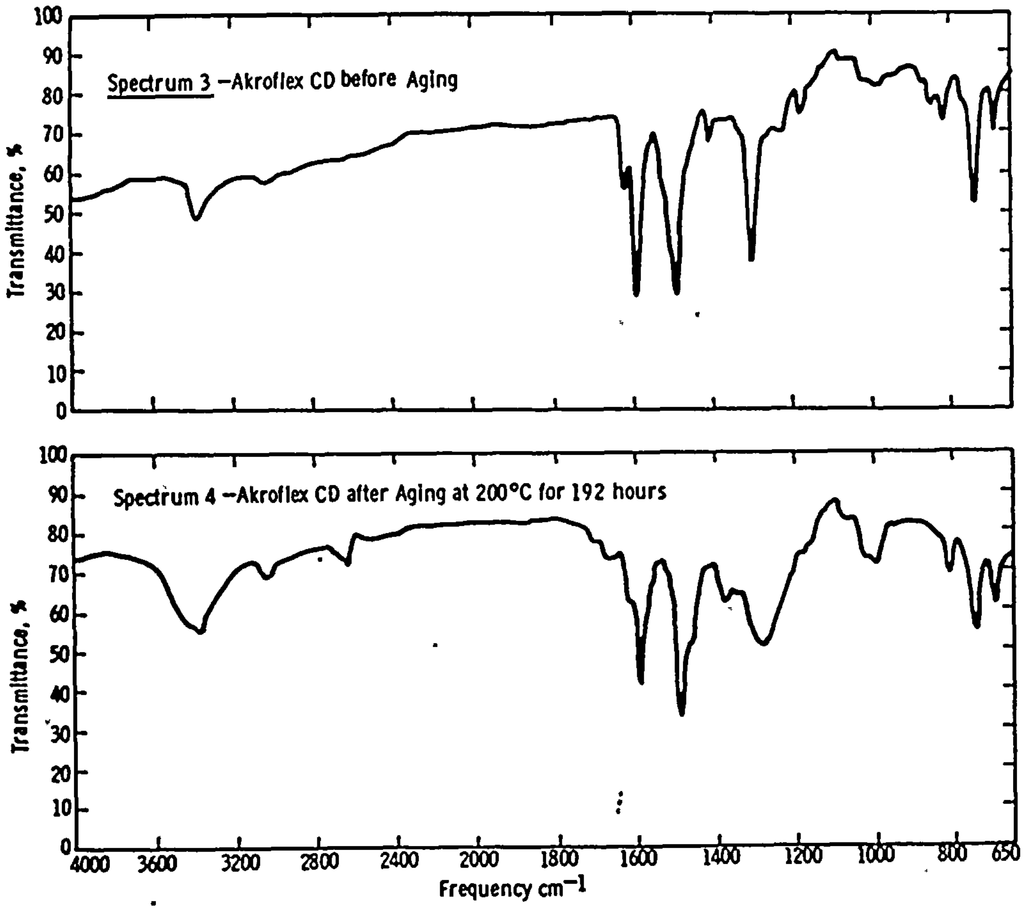

Fig. 5. Infrared spectra of neat Akroflex CD before and after aging.

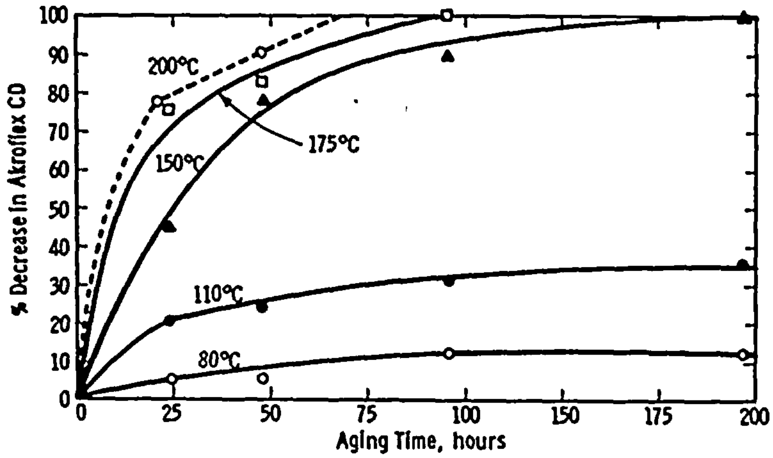

Fig. 6. Loss rate of Akroflex CD from cured neoprene with aging at different temperatures (using 1600 cm^{-1} infrared band).

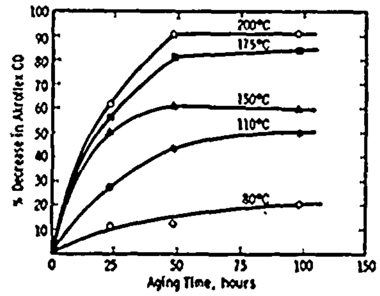

Fig. 7. Loss of rate of Akroflex CD from cured neoprene with aging at different temperatures (using 1300 cm^{-1} infrared band).

It is observed that this aged sample does exhibit noticeable changes in its spectrum. The sharp absorption band at 1300 cm^{-1} (from the $C_6H_5—N\langle$ stretching vibration) shows a reduction in intensity compared to the other bands (e.g., at 1500 cm^{-1}). The absorption band at 1300 cm^{-1} also becomes broader, and a shoulder peak develops at 1380 cm^{-1}.

The spectrum of the aged material also exhibits enhanced absorptions at 3400 cm^{-1} and 1000 cm^{-1} compared to the original sample. These spectral changes would appear to be associated with oxidative modification of the amine groups in the antioxidant.[3] These spectral modifications were also shown by the samples that were aged at the lower temperatures, but the changes were somewhat less marked than those found with the 200°C samples.

The neoprene samples that had been subjected to thermal aging were analyzed for Akroflex CD content using the chloroform extraction procedure described previously. From the calibration curves, the rate of disappearance of the antioxidant at the different temperatures could be estimated. Two separate and independent sets of curves could be constructed, i.e., for the infrared absorption measurements at 1600 cm^{-1} and 1300 cm^{-1}, as shown in Figures 6 and 7, respectively.

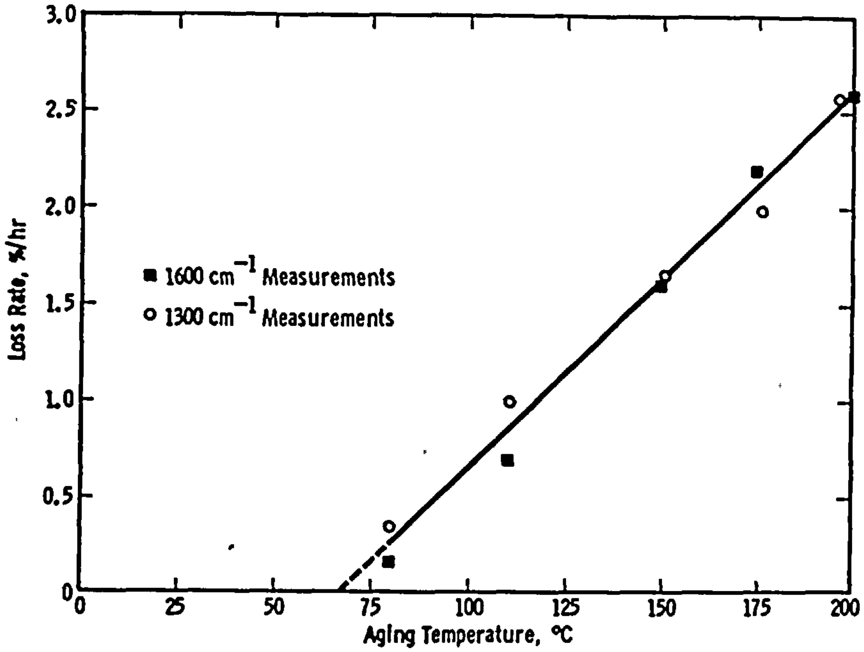

Fig. 8. Dependence of Akroflex CD loss rate (initial) on aging temperature of cured neoprene.

In the case of the 1300 cm^{-1} data, the Akroflex CD rate of disappearance was only followed up to 96 hr as shown in Figure 7. Interference of an oxidized by-product from the neoprene in the infrared measurements at that wavelength gave rise to erratic results. However, the similarities between the rate data obtained at 1600 cm^{-1} and 1300 cm^{-1} are very striking (i.e., a very rapid initial loss rate followed by a slower one).

This is shown more clearly by making a plot of the initial loss rate (i.e., the *average* % rate of decrease in Akroflex CD content over the first 50 hr of aging) against the aging temperature. This is shown in Figure 8, where it can be seen that very good agreement is obtained by the Akroflex CD initial loss rate values for the two methods of measurement.

Extrapolation of these data to "zero % loss rate" suggests that below 68°C, no decrease in the Akroflex CD content will occur during aging (at least not under *static* aging conditions). This then suggests that below ~68°C the decrease of Akroflex CD content due to diffusion will be extremely slow. However, losses that occur below 68°C will most likely be due to the interaction of the antioxidant with oxygen from air diffusing into the rubber. This type of antioxidant consumption is not defined by the present mechanism.

DISCUSSION

Using the data of Figure 8, an Arrhenius plot, i.e., $\log_{10}$ rate versus $1/T$(°K), can be made for the neoprene samples. This is shown in Figure 9. In this plot, the 80°C rate data have been omitted because of the temperature spread.

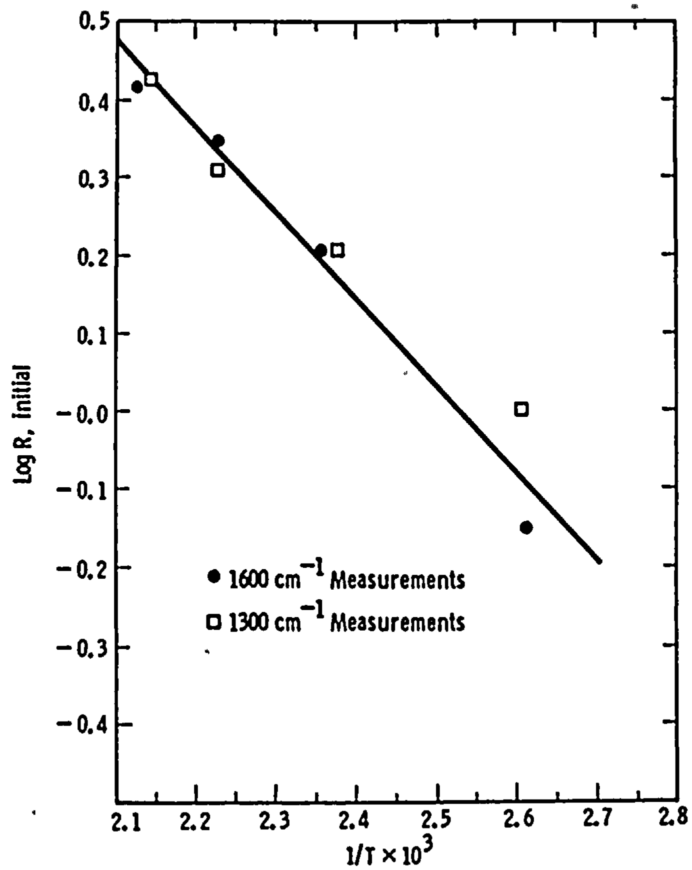

Fig. 9. Arrhenius plot for Akroflex CD loss rate from cured neoprene.

It is noted that a fairly good linear plot is obtained with the eight rate values. From this gradient, the activation energy (ΔE) was calculated to be 5.1 kcal/mole.

This value is somewhat low for a normal free-radical oxidative-type reaction where values four to five times higher are usually obtained. This is predictable on the basis of the oxidative aging studies on the neat Akroflex CD samples where it was found that only minor changes in the structure of the antioxidant will occur even after prolonged heating at 200°C. It has long been suspected that the Akroflex CD is fugitive in neoprene rubber formulations and that loss occurs by migration to the surface during aging. This would be consistent with the low activation energy value obtained in this work. The migration of Akroflex CD through this neoprene rubber can be interpreted as a diffusion phenomenon. Low activation energies are usually found in such reactions. Barrer[4] has determined the activation energies of diffusion for a series of gases (including water vapor) through neoprene rubber and found that the values lie in the range of 6.0–11.1 kcal/mole.

Corman et al.[5,6] have studied the activation energies of diffusion for hydrocarbon oils through a series of rubbers using ^{14}C-labeled compounds. The activation energies found ranged from 3.1 to 9.9 kcal/mole. They

concluded that the similarities of the activation energies for the various hydrocarbon oils provided evidence that the diffusion of large organic molecules in rubber is much more dependent upon the nature of the polymer than on the nature of the diffusing species.

On this basis, it would seem that the antioxidant loss in this particular neoprene formulation is almost completely a thermally induced diffusion effect. The contribution from oxidative degradations to this loss would be very minor.

Although the effects of ozone were not evaluated in this work (the aging tests were run in forced-air ovens), it would be expected that exposure to the more severe ozone environment would result in more rapid oxidation of the residual unsaturation of the neoprene rubber. However, it is unlikely that the loss rate values for the Akroflex CD at the different temperatures would deviate greatly under these conditions from the values found in this work.

It should also be pointed out that the neoprene accelerated aging tests in this work were carried out under essentially *static* conditions (i.e., the rubber samples were not subjected to any stress or strain during aging). It would be anticipated that under more *dynamic* conditions of testing, e.g., continuous flipping, higher diffusion rates would be encountered.

Thus, the diffusion rate values found in this series of experiments are only valid for neoprene rubber under static conditions of aging in the temperature range of 80° to 200°C. Below 80°C, the thermal diffusion of antioxidant becomes less important and other loss mechanisms may predominate.

The effect of dynamic aging on antioxidant loss and the influence of these losses on the physical properties of neoprene will be the subjects of future publications in this area.

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