Final Report

Department of Energy Grant
Number DE-FG02-98ER82543, Entitled

“The Development of ShortWatch, a Novel
Overtemperature or Mechanical Damage Sensing
Technology for Wires or Cables”

BPW, Inc.
September 7, 2001

Ken Watkins, Jack Morris, C. P. Wong,
and Shijian Luo

DOE Patent Clearance Granted

Mark P. Dvorscak

Mark P. Dvorscak

(630) 252-2393

E-mail: mark.dvorscak@ch.doe.gov

Office of Intellectual Property Law

DOE Chicago Operations Office

2.28.02
Date

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Table of Contents

Title	Page
Introduction	3
Statement of Project Requirements and Goals	3
Program Summary	4
First Year Efforts	4
Second Year Efforts	5
Goals and Follow-on Work	11
Summary and Conclusions	13
Appendix A: Proof-of-Concept Test	14
Appendix B: Georgia Tech Conducting Polymer Materials Study	18
Appendix C: BPW Aging Trials of ShortWatch Sensors	52
Appendix D: Time Domain Reflectometer and Noise Issues	60
Appendix E: Certified Test Report on ShortWatch Cable	64
Appendix F: References	66

Introduction

This report documents the Department of Energy sponsored Small Business Innovation Research (SBIR) Grant number DE-FG02-98ER82543, which is entitled, "The Development of ShortWatch, a Novel Overtemperature or Mechanical Damage Sensing Technology for Wires or Cables."

Statement of Project Requirements and Goals

In response to the Department of Energy SBIR solicitation item Number 32. "Advanced Technologies for Commercial Nuclear Power Plants and Space Power Plants" and in specific subtitle C. "Advanced Characterization Techniques and Modeling Methods to Predict Aging Behavior of Electrical Cable Jacket and Insulation Materials," BPW Incorporated is proud to present its final report for the development of "ShortWatch," a patented overtemperature or mechanical damage sensing technology for electrical wires or cables.

The "ShortWatch" technology addresses the problems identified in the above-mentioned Department of Energy solicitation, which states, "Nuclear plant electric cables are subject to various types of environmental aging, predominantly thermal and irradiation aging. Cables in critical applications are required to function during and after an accident. The functional performance of a safety circuit may be lost if jacket integrity or insulation dielectric strength is inadequate. Grant applicants were sought for technologies that provide advanced techniques suitable for "*in situ*" testing of a cable to (1) characterize cable jacket and insulation material condition, (2) predict the remaining life of a cable based on science-based aging models, and (3) assess the ability of a cable to perform its safety function(s) during design basis events. Nondestructive techniques capable of characterizing the condition/performance of an entire cable run are of primary interest; techniques that require small samples from the ends of cables or very localized samples are also of interest. For condition monitoring techniques that require samples, methods for obtaining samples without compromising cable qualifications are required."

ShortWatch developments described in this final report provide an "in situ" technology, which addresses items (1) and (3) above by providing a real time, mechanical damage and over temperature sensing capability for wire and cable used in the nuclear industry.

Program Summary

This project was completed on time and within its budget. Project goals were demonstrated in successful tests conducted on prototype ShortWatch cable with integrated mechanical damage and over temperature sensors at the Rockbestos Surprenant Cable Corp. facilities on May 16, 2001.

First Year Efforts

Program results for the first year include:

1. Selection of ShortWatch overtemperature sensor "recipe." Sensor tape extrusion trials at Rockbestos confirmed mechanical and electrical specifications determined in Phase 1 of the SBIR. Of several polymers studied and tested, the blend of HDPE and LDPE utilized in a commercial environmentally qualified wire was chosen as the base polymer to introduce as few new variables as possible. The sensor recipe also included a low-structure carbon black and anti-oxidants. Appendix B documents conductive composite studies conducted by the School of Materials Science and Engineering at the Georgia Institute of Technology as part of this project.
2. Wire design completion. A multi-conductor wire design was chosen incorporating a "hybrid" design of ShortWatch which features center filament of ShortWatch conductive polymer sensor (figure 1) that provides overtemperature-sensing capability. A helical wrap of ShortWatch metallic ribbon sensor provides mechanical damage sensing capability. This design was chosen due to the broad applications multi-conductor cables with ShortWatch capability will provide in a plant environment. A second design incorporating a co-extruded ShortWatch sensor in the insulation of a wire or cable had to be deleted from Phase 2 SBIR due to a first year funding reduction. The co-extruded design will be pursued further upon additional funding.
3. ShortWatch sensor filament extrusion. A sensor filament approximately 0.5 mm in diameter, which meets the dimensional requirements of the selected "hybrid" ShortWatch cable design, was extruded at Rockbestos and subjected to mechanical and electrical testing at Georgia Tech and BPW, Inc.

Figure 1: ShortWatch Sensor Filament

4. Cross-linking effects. Positive results on sensor temperature-resistance response at switching were observed by electron beam irradiation of the ShortWatch sensor. Cross-linking eliminated the negative temperature coefficient (NTC) response of the matrix observed at temperatures above the switching (transition) temperature (see Appendix B).
5. Fault location investigations. In-house testing indicated that a Time-Domain Reflectometer (TDR) is able to determine the location of mechanical damage to ShortWatch-capable wire. The location of the damaged area can be determined even *before* the damage is significant enough to result in an electrical fault in the wire. Other methodologies were investigated, including standing wave ratio (SWR) technology.
6. Other investigations. Preliminary investigations included controller design studies to determine general electronic circuitry which would be used to monitor ShortWatch over temperature and mechanical damage sensors, age investigations into accelerated age testing which would demonstrate the ability of the ShortWatch sensors to function over an extended time period and noise immunity investigations to determine electrical noise generated in ShortWatch sensors from energized conductors protected by the sensors.

Second Year Efforts

Program results during the second year of the project included:

1. Fault detection.

Fault detection may be broken down into overtemperature fault detection and mechanical damage detection.

Overtemperature fault detection by ShortWatch is distributed in nature by an extruded strip or filament of conductive polymer, which "switches" at the desired overtemperature. The critical ShortWatch design parameters are switch temperature, switch magnitude and design resistivity. The switch temperature is determined by the base polymers utilized and, in this case, the base polymer of a commercial environmentally qualified wire is used to provide a maximum switch temperature of approximately 130°C, or about 40°C greater than the design temperature of the wire.

The switch "magnitude" is the ratio of sensor resistance at a maximum switch temperature divided by the design (90°C) resistance. Although a switch magnitude of 100 is considered acceptable as far as providing reasonable resolution of overtemperature conditions, the design aim is a switch magnitude of approximately 1000. This magnitude will provide an overtemperature resolution of approximately an inch in 100 feet of ShortWatch cable.

A "trade-off" exists between switch magnitude and design resistivity (resistivity of the overtemperature sensor at 90°C). Studies performed at Georgia Tech (see Appendix B and Figure 2) showed a generally higher switch magnitude at high sensor resistivity. Although switch magnitudes of over 1000 were obtained in ShortWatch samples, lower (approximately 100) initial design switch magnitude was selected in order to reduce sensor resistivity in order to reduce the size (diameter) of the sensor filament.

Figure 2: ShortWatch Filament Sensor Resistance-Temperature Response

A helically wrapped metallic ribbon or wire provides the mechanical damage sensing of the ShortWatch multi-conductor cable. The ribbon is wrapped around the insulated conductors of the multi-conductor cable and inside the outer jacket of the cable. Cutting or abrading the outer jacket will open the ribbon before the conductor insulation is penetrated. ShortWatch instrumentation senses the loss of sensor ribbon continuity, initiating an alarm or control action.

2. Fault location.

We have experimented with a Time Domain Reflectometer (TDR), shown in Figure 3, which determines the location of mechanical damage in ShortWatch capable electrical wiring (see Appendix D). The technology, which is in current use, requires two electrical conductors. We have found that the ShortWatch sensor can be used as one of the

conductors in the TDR experiments. The helically wound metallic outer sensor is an ideal candidate for this application.

Figure 3: The Biddle CFE 510E Time Domain Reflectometer (TDR)

Time Domain Reflectometers have been used for many years and remain the fastest, most accurate way to pinpoint cabling problems. Due to advances in current technology, the operation and interpretation of a TDR have been greatly simplified. Because of its ability to identify cable problems, the TDR is now rapidly regaining popularity throughout communications industries. If a cable is metal and has at least two conductors, it can be tested by a TDR.

Standing wave ratio (SWR) technology was also investigated and demonstrated during the project (see Appendix Test). Work by others (Eclipse International) indicates SWR may have superior "soft" fault detection capability as compared to TDR technologies. Future work is planned to investigate overtemperature fault location by use of this technology.

3. Sensor aging tests.

Thermally accelerated aging tests were carried out by BPW and Georgia Tech to demonstrate mechanical and electrical performance of ShortWatch sensors over the design lifetime of wire and cable utilizing the technology (see Appendix C and Figure 4). The sensor filament demonstrated mechanical integrity over the design life period of the accelerated age test. Switch magnitude decreased significantly over the test period,

although this is believed due to loss of crystallinity of the base polymer (a phenomenon not expected during natural aging).

BPW is currently researching how to utilize accelerated aging results of ShortWatch sensors in predicting remaining useful life. Although not originally anticipated in Phase 2, demonstration of such a capability would significantly advance the goals set forth in the Department of Energy's SBIR solicitation in predicting the remaining life of cable.

Figure 4: Accelerated Age Testing of ShortWatch Sensor Filaments

4. Production of ShortWatch capable wire.

Figure 5 presents a cross-sectional drawing of the ShortWatch multi-conductor cable design selected for prototype production and testing. The multi-conductor jacketed cable utilized three insulated conductors and a ShortWatch conductive polymer overtemperature sensor filament in the center. A ShortWatch metallic sensor ribbon, wrapped helically around the insulated conductors, provides mechanical damage sensing.

ShortWatch Hybrid Cable
 DOWNSIDE, Phase 2
 BFW, Inc.
 11/2/00

Figure 5: Shortwatch Hybrid Cable

Figure 6 presents a photograph of a length of the prototype ShortWatch cable manufactured at Rockbestos Surprenant Cable Corporation of Clinton, Mass. The cable is a 600 volt 3 conductor, 12 AWG stranded cable utilizing cross-linked polyethylene (XLPE) conductor insulation and Hypalon jacket. The cable was manufactured to Rockbestos "Fire Wall 3 specifications. "Fire Wall 3" is an environmentally qualified (EQ) cable commonly used in the nuclear industry. Environmental qualification of the ShortWatch prototype cable was not scoped, nor performed on the prototype cable.

Figure 6: A Length of the Prototype ShortWatch Cable

Figure 7 shows a close-up photograph of the prototype ShortWatch cable showing a stripped end of the cable with the mechanical damage sensing ribbon and the ShortWatch overtemperature-sensing filament visible in the photograph. The mechanical damage sensing ribbon is nickel-plated copper, 0.002" thick, wrapped at approximately 4 turns/inch. The overtemperature-sensing filament is a composite of the conductor insulation (electron beam cross-linked PE) and a low-structure carbon black filler and antioxidants. The filament diameter was 0.020 inches.

Figure 7: A Close-up Photograph of the ShortWatch Cable

5. In-service test of ShortWatch.

Integrated testing was performed on the cable shown in figures 5, 6 and 7. This testing included manufacturer's acceptance testing, cable overtemperature tests, cable mechanical damage testing, fault location testing by TDR and SWR technologies, and multiplexed fault detection demonstration. This testing is described in Appendix A.

Goals and Follow-On Work

This project provided a multi-conductor cable for the nuclear industry, which, for the first time, provides real-time overtemperature sensing and warning of cable mechanical damage *before* an electrical failure occurs. This project fully meets the goals of the Phase 2 SBIR as previously stated. BPW, Inc. has identified several areas for possible follow-on work, which we expect will be of considerable interest in the Department of Energy's broader goal of identifying new technologies relevant to safe and reliable operation of the nation's nuclear power plants:

1. In-service test of ShortWatch cable.

BPW proposes installation of ShortWatch cable in an operating plant system test bed to:

- a. Demonstrate performance of ShortWatch cable in an operational environment;
- b. Reduce perceived "risk" to potential users of this technology; and

- c. Serve as a test-bed for future technology improvements in fault and life-predictive wire and cable.

2. Design and manufacture ShortWatch wire and cable utilizing co-extruded sensors. Co-extrusion has the potential of reducing the cost and manufacturing complexity of ShortWatch-capable wire and cable by eliminating the step of separately extruding and cabling the sensor filament. A filament of the conductive matrix would be co-extruded in the wire or cable jacket during manufacture. This process also has the potential of utilizing a single filament for both overtemperature and mechanical damage sensing, eliminating the need for a metallic ribbon in the cable.

3. Development of Shortwatch-capable cable protection elements for use with existing wire and cable.

Development of ShortWatch-capable sheaths, conduits, and wrapping tape components would allow installation over existing wire and cables to provide mechanical damage and overtemperature sensing capability to installed wire and cable systems. Development of a demonstration protective device utilizing high-temperature materials used in aircraft is being done by BPW under an SBIR funded by the DOD.

4. Overtemperature fault location.

Fault location of ShortWatch mechanical damage sensors has been demonstrated utilizing TDR and SWR technologies. Location of overtemperature faults is more difficult due to the "soft fault" nature and high material impedance of the sensor material. Future work, especially in SWR technology may lead to the ability to locate the resistivity change in ShortWatch sensors due to localized overtemperature conditions. Such a capability would be especially valuable in locating internal or external heating sources before insulation failure, and to locate areas of cable, which may be susceptible to, accelerated aging conditions.

5. Prediction of useful life.

BPW has determined that electrical characteristics of the ShortWatch sensor demonstrate electrical properties, which appear to predict remaining useful life of the sensor. Since polymers used in wire insulation are the primary components of the ShortWatch sensor, this work may extrapolate to prediction of wire insulation degradation over time.

Further work in this area will be required to determine the feasibility of the method and possible correlation with wire insulation life.

If found feasible, this method would be a *significant* advance over current methods of predicting remaining life by destructive mechanical or chemical testing.

Summary and Conclusions

ShortWatch technology, integrated into nuclear-grade cable in this phase 2 SBIR has demonstrated "in situ", non-destructive cable monitoring which addresses the improved cable condition monitoring goals of the program. Sensors distributed in the cable provide real-time warning of mechanical damage to the cable and insulation *before* the conductors become exposed, and warn of over temperature anywhere along the length of the cable.

The project accomplishments include optimization of conductive composite sensor materials for desired temperature sensing capabilities through a rigorous R&D effort with the School of Materials Science and Engineering at Georgia Tech, validation of ShortWatch hybrid cable design by manufacture of a prototype nuclear-grade cable for low-voltage power and instrumentation, and successful test demonstrations of the predictive fault-sensing capabilities of the prototype cable. The testing included real-time, "in situ" demonstration of both mechanical damage sensing and over temperature sensing capabilities of the cable, multiplexed monitoring of several cables, mechanical damage location by use of TDR and SWR technologies, and noise immunity of sensor instrumentation. Accelerated age testing has demonstrated mechanical integrity of the cable sensors over the design lifetime.

Although it was not part of this SBIR, conductive composite behavior discovered during accelerated age testing of the sensors, if validated by further research, could provide an "in-situ" method of predicting remaining life of insulation materials.

The successful implementation of this technology in nuclear power plant applications promises improved safety features as compared to current cable technologies. The predictive fault capability of ShortWatch will result in operating cost savings due to the ability to make repairs/replacements of cable during scheduled downtime instead of unplanned shutdowns.

As part of the Phase 2 effort of this SBIR, BPW Incorporated has developed and tested over one thousand feet of ShortWatch-capable prototype electrical cable capable for use as low-voltage power and instrumentation cable in the nuclear industry. Tests performed on the prototype cable included standard quality control tests, mechanical damage and overtemperature detection, mechanical damage fault location, noise testing and multiplexed fault monitoring of multiple cables. The project was completed on time and within budget.

Appendix A: Proof-of-Concept Test

The final testing of the overtemperature and mechanical damage sensing capability was performed at the Rockbestos Surprenant Facility in Clinton, Massachusetts on May 16, 2001. The purpose of these tests was to demonstrate the overtemperature and mechanical damage sensing capability of our Shortwatch technology in realistic conditions and with a prototype nuclear-capable low-voltage power and instrumentation cable. Attendees included DOE headquarters representatives including the headquarters Technical Manager, BPW Principal Investigator and Senior Engineer for the project, Rockbestos Engineering and R&D representatives, representatives of the School of Materials Science and Engineering from the Georgia Institute of Technology, and representatives from Eclipse International of Corona, California.

The meetings included a project overview by BPW, Inc., and a presentation on the conductive composite work done by Georgia Tech. Tests and demonstrations included overtemperature and mechanical damage fault detection in the prototype ShortWatch cable, mechanical damage fault location in the prototype cable, and multiplexed fault detection of multiple cables.

The furnace and test cable for the overtemperature test are shown in figure A1. The oven temperature was 150C.

Figure A1: Furnace and Test Cable

The overtemperature test demonstrated that an overtemperature condition could be detected in approximately one foot of cable in less than 5 minutes. Alarm time was less than 2 minutes. The results were very acceptable.

The mechanical damage sensing capability of the test cable was demonstrated in the test rig shown below as figure A2. This figure shows the cable installed in the test rig with the Shortwatch controller (in blue and White) and the test rig controller (in gray) in the foreground.

Figure A2: Mechanical Damage Test Rig

This mechanical damage test rig had a mechanical counter, which counted the number of turns of the drum, which is shown in figure A2. The drum had two rectangular dowels attached to it, which acted as abrasers or cutters for the cable. This can be seen in figure A3. The ShortWatch sensor detected mechanical damage of the cable at about 50 turns of the wheel. A current leakage to ground from the main conductors of the test cable was detected at about 500 turns of the wheel. Therefore the Shortwatch mechanical damage sensor gave warning of the damage well in advance of actual current leakage (shorting condition) from the test cable.

Figure A3: Close-Up of Wheel and Cable

The end result of the mechanical damage test is shown in figure A4. The figure presents the test cable, which has the insulation abraded away until one of the primary conductors is exposed.

Figure A4: Test Cable with Mechanical Damage

Tests were also completed on the Eclipse Model 501 Analyzer/multiplexer (Figure A5) to demonstrate that existing equipment could be used to support the ShortWatch-capable

electrical cable. These tests demonstrated the use of the multiplexer to check several Short Watch-capable electrical cables in real time.

The Model 501 is the original Eclipse Analyzer and has become the basis for all Eclipse Analyzers. This device is simple to program and operate with its powerful "Real-time" test software and user-friendly interface. It has the versatility to grow with changing applications by allowing the user to expand the system in small or large increments.

Expandable data lines in the back of the system allow for additional points to be added as the requirements grow. The analyzer can be "Stacked" in standard 19" rack systems with up to 128,000 points of switching. This device and several similar devices are marketed by the Eclipse International Corporation (Phone 909-371-8008) of Corona, California.

Mechanical damage fault location was demonstrated by both time domain reflectometry (TDR) and standing wave ratio (SWR) technologies. A commercially available TDR (Biddle CFE 510, Figure 3) was used to locate a mechanically damaged portion of the prototype cable. A SWR developed by Eclipse International also showed capability of detecting the mechanical fault by digital readout.

Figure A5: Eclipse multiplexer with computer and test wire

Appendix B: Georgia Tech Conducting Polymer Materials Study

Development of PTC Conductive Polymer Composite for ShortWatch Sensor

Shijian Luo and C. P. Wong
School of Materials Science & Engineering
Georgia Institute of Technology
Atlanta, GA 30332

Introduction

Conductive polymer composites containing conductive fillers such as metal powder, carbon black and other highly conductive particles in a non-conductive polymer matrix, have been widely used in the electrostatic dissipation (ESD), electromagnetic interference shielding (EMIS). There is a special group among the electric conductive polymer composites. They are conductive polymer composites with large positive temperature coefficient (PTC), which in some cases are called positive temperature coefficient resistance (PTCR). The resistivity of this kind of composite increases several orders of magnitude in certain narrow temperature range. The transition temperature (T_t) was defined by intersection of tangent to point of inflection of resistivity vs. temperature curve with horizontal from resistivity at 25 °C (ρ_{25}). This kind of smart material can change from conductive material to insulating material or vice versa upon heating or cooling, respectively. The smartness of this kind material not only lies on this large PTC amplitude (defined as the ratio of maximum resistivity at the peak or the resistivity right after the sharp increase to the resistivity at 25 °C), but also its reversibility, its ability in adjustment of the transition temperature, low temperature resistivity and high temperature resistivity. The PTC conductive polymer composite has been successfully developed in this project for ShortWatch sensor. The work in this project was summarized in different phases.

1. Analysis of Commercial Conductive Polymer Composite.

Some commercial products based on the conductive polymer that may show PTC behavior were investigated, and these samples were obtained and analyzed. Some of them are Contrim L.D. and Contrim V.F. from Crystal-X Corporation. Actually, these products are used for antistatic purpose. Their composition, thermal behavior, as well as the resistivity versus temperature were analyzed.

1.1. TGA analysis

The thermogravimetric analysis (TGA) experiments were performed under N_2 with heating rate of 5 °C/min. The TGA profiles are shown in Figure B1. It can be seen that in addition to polyethylene (PE), there is another component (polymer or other organic compound, which accounts for the weight loss in the range of 300-350°C) in the

samples. The residue is supposed to be the conductive filler-carbon black. The compositions of the two samples are found as follows (they are reported in weight percentage).

Contrim L.D.:

LDPE: 53%, Carbon Black: 38%, Unknown component (possibly EVA): 8.8%

Contrim V.F.:

HDPE: 66%, Carbon Black: 29%, Unknown component (possibly EVA): 4.6%

Figure B1. TGA profile of two conductive polymer composites.

1.2. DSC Analysis

Differential scanning calorimeter (DSC) experiments were performed under N_2 with heating rate of 10 °C/min. The DSC analysis results are shown in Figures B2. Both of the two samples showed two melting points (85 °C, and 130 °C), which corresponded to the two polymer components. It can be seen that the PE component in Contrim V.F. has much higher crystallinity than that in Contrim L.D. (The weights of the two samples are almost same).

Figure B2. DSC profile of two conductive polymer composites

1.3. TMA analysis

The thermo mechanical analysis (TMA) experiments were performed under N_2 with heating rate of $1^\circ\text{C}/\text{min}$. The dimension change in the thickness direction was recorded. The dimension increased steadily with temperature. As the temperature approached the melting point, the dimension increased sharply due to the melting of the crystalline polymer. However, for sample Contrim L.D. (Figure B3), the sharp increase occurred at the melting point of the unknown component. After that, the dimension decreased. It did not show increase in the dimension at the melting range of PE. This is because that the crystal is mainly contributed by the unknown component. As is shown in the DSC profile, the melting peak at 85°C is much bigger than that of 130°C .

Figure B3. TMA profile of commercial conductive polymer composite.

For the sample of Contrim V.F. (Figure B3), the dimension increased steadily before the 110 °C and increased sharply when it approached the melting point of HDPE, and it reached the maximum at 130 °C. It did not show any sharp increase in the range of 80-90 °C, as the crystalline portion due to the unknown component is much less than that of HDPE. (It was shown on DSC profile). It should be noted that there are two shoulder peaks (in lower temperature side) before the major peak. They should not be attributed to noise. Actually, they are possibly due to the melting and recrystallization process occurring before the major melting. As the heating rate was very slow in this experiment, the melting and recrystallization were expected to occur before the major melting process.

1.4. Resistivity vs. Temperature

The samples were cut into small pieces and the resistance was measured with conductive adhesive as two electrodes (The resistance of the conductive adhesive is much lower than that of the samples).

Figure B4. The resistivity versus temperature of commercial conductive polymer composite

Figure B4 shows the resistivity vs. temperature in the thickness direction of sample Contrim L.D. The sample was placed in an oven and the temperature of the oven was raised 5 °C at one step and dwelt for 5 minutes, and then the resistance was recorded. The resistivity increased steadily with the increased temperature and increased sharply as it approached to the melting point (85 °C) of the crystal of the unknown components (maybe plasticizer or additive). At 95 °C, the resistance reading was beyond the range of the meter (100 mega-ohm). The resistivity vs. temperature cure is well matched by the TMA profile of the sample. It means that the PTC behavior of the sample is due to thermal expansion of the polymer matrix.

Figure B4 also shows the resistivity versus temperature for sample Contrim V.F. in the thickness direction. There are five ranges in the curve. In the temperature range below 58 °C, the resistivity increased slowly with the temperature. In the temperature range of 58-98 °C, the resistivity increased sharply with the temperature. In the temperature range of 100-120 °C, the resistivity increased slowly with the temperature. In the temperature range of 120-134 °C, the resistivity increased very sharply with the temperature. Beyond 134 °C, the resistivity decreased with the temperature. The sharp increase of resistance in the temperature range of 58-98 °C was due to the melting of the unknown component. The very sharp increase in resistance in the range of 120-134 °C was due to the melting of the crystal of HDPE. The negative temperature coefficient (NTC) effect above 134 °C was due to the reorientation, reaggregation or reassembling of the conductive units.

Figure B5 shows the resistivity vs. temperature for sample Contrim L.D. in the direction parallel to the sheet. The sample was placed in the oven that was heated at the step of 2 °C and dwelt for 2 minutes; the resistance of the sample was read every two minutes. The same trend was observed. However, the increase in the resistivity was less in the lower temperature range, and the resistivity in the direction parallel to the sheet was different from that in the thickness direction. The resistivity was beyond the range of the meter (100 mega-ohm) at 93°C.

Figure B5. Resistivity vs. temperature for sample Contrim L.D. in the direction parallel to the sheet.

From the experiment mentioned above, the compositions of Contrim L.D. and Contrim V.F were disclosed by TGA experiments. The PTC behavior of the Contrim

L.D. and Contrim V.F. is well explained by the thermal expansion of the polymer matrix. The sharp increase in the resistivity of the PTC conductive polymer is due to the melting the polymer crystal.

2. Characterization of Commercial PTC Conductive Polymer

The PTC conductive polymer can also be used in the resettable fuses. It was learned that two companies (Raychem, Bourns) have commercial resettable fuse product based on the PTC conductive polymer. Some resettable fuses were obtained. The resistance vs. temperature behavior of Bourns MF-R800 resettable fuse was investigated. The PTC conductive polymer used in this product was subjected to the thermal analysis, and possible composition was suggested. The intrinsic conductive polymer (doped polyaniline) was analyzed too.

2.1. PTC behavior of Commercial PTC materials

The resettable fuse (MF-R800) was supplied by Bourns. The resistance was measured with four-wire method. The fuse was placed in an oven, of which the temperature was raised at the pace of 5°C and kept for 5 minutes. Around the PTC transition temperature, the temperature was raised at 2°C at each step and kept for 2 min. The resistance was measured at each temperature point. The resistance was also recorded on the cooling cycle. For the cooling cycle, the heating power of the oven was turned off, and the oven was allowed to cool naturally. The resistance at each temperature point was recorded.

Figure B6 shows the resistivity of the conductive polymer used for MF-800 resettable fuse. Obviously, this material shows a PTC transition around 126 °C at heating mode. The resistivity above the transition temperature is five orders of magnitude higher than the value below the transition temperature. And this PTC transition is clearly correlated with the melting of the polyethylene crystal around 130°C, which is shown in DSC profile in Figure B7.

In Figure B6, the resistivity changes, with the temperature in cooling mode, was also shown. The PTC transition is about 8 °C lower than the PTC transition temperature in the heating mode. This is due to the crystallization temperature is always lower than the melting temperature.

The matrix polymer polyethylene is crosslinked. From the profile of resistivity vs. temperature, it was found that there is no negative temperature coefficient (NTC) behavior after the PTC transition; this is evidence that the PE is crosslinked. The resistivity continues to increase after the PTC transition. In the uncrosslinked system, the NTC behavior will occur after the PTC transition, as shown in the case of Contrim V.F.

Figure B6. Resistivity of MF-R800 resettable fuse vs. temperature.

2.2. Thermal analysis of commercial PTC conductive composite

The conductive polymer used for the resettable fuse was taken out after the coating of the resettable was peeled off. The conductive polymer was subjected to thermal analysis. All the thermal analyses were performed according the same procedures used for the analyses for Contrim L.D. and Contrim V.F. The TGA profile of doped conductive polyaniline was also recorded under N_2 with heating rate of $5^\circ\text{C}/\text{min}$.

Figure B7. DSC profile of PTC conductive polymer used for MF-R800 resettable fuse.

In order to find out the composition of the conductive polymer used in the resettable fuse, the TGA experiment was performed on the conductive polymer. The TGA profile was shown in Figure B8. The sample began to lose weight rapidly around 240°C. After 255°C, the weight is slow. And from 550°C, the weight loss was accelerated and nothing is left above 624°C. This TGA profile strongly suggested that the conductive filler in this system is not metal or metal oxide; it is not carbon black either. It was proposed that the conductive filler is intrinsic conductive polymer and the weight loss at 240-255°C is due to the dopant in the conductive polymer.

Figure B8. TGA profile of PTC conductive polymer used for MF-R800 resettable fuse.

In order to prove that intrinsic conductive polymer loses weight completely above 600°C, the conductive polymer Versicon Conductive Polymer form Monsanto Lot # 170/175/178 was subjected to TGA experiment. It was told that this conductive polymer is sulphonic acid doped polyaniline. The material began to lose weight at 220°C, which is due to the sulphonic acid dopant. The weight loss of major component began at 328°C, which account for 84%. The dopant accounts for 12%, and water accounts for 4%. The weight loss is complete at 600°C with negligible residue.

3. Compounding and Characterization of PTC Materials with Carbon black as Conductive Filler

3.1. Experimental

The HDPE (04452N) was supplied by the Dow Chemical Company. It has a melting point of 129-134°C, a density of 952 kg/m³ and a melting index of 4.0 gram/10

min. Five different carbon blacks were used in this study and their characteristics are listed in Table B1. Conductex SC, Conductex 975 and N660 carbon blacks were supplied by Columbia Chemicals. Vulcan XC-72 and BP2000 carbon blacks were supplied by Cabot Corporation. The structure of carbon black is generally characterized by tint strength, CTAB (cetyltrimethylammonia bromide) absorption, DBP (dibutyl phthalate) absorption, and iodine absorption. Carbon black with small particle size shows high tint strength. High-structure carbon blacks contain more void spaces. As a result, a larger volume of DBP is needed to fill the voids between the aggregates. The adsorption of iodine and CTAB serves as the basis for determining the surface area of carbon black.

Table B1. Characteristics of Carbon Blacks

	CTAB Absorption (m ² /gram)	Tint strength (% ITRB)	DBP absorption (cc/100gram)	Iodine absorption (mg/gram)	Iodine absorption (mg/gm)	Average particle diameter (nm)
ASTM Method	D3765	D3265	D2414	D1510	D1510	
Conductex SC	130	123	115	220	220	-
Conductex 975	140	87	169	250	250	-
N660	35	57	90	36	36	70
Vulcan XC72	143	87	174	253	253	30
BP 2000	635	163	330	1412	1412	12

HDPE (or any other polymer) and carbon black were mixed in the mixer unit of a Haake Rhecorder at 200°C, 60 rpm for 20 min, and the equilibrium torque was recorded. The composite was taken out of the mixer after the mixing was complete, and then compression-molded at 200°C into a sheet with a thickness of 0.5 - 1.0 mm. A small square specimen with dimension of 2.0 cm in each side was cut from the sheet. The exact thickness of the small specimen was measured and recorded. An electrically conductive adhesive (silver flakes filled epoxy) was applied onto the upper and lower surface of the specimen, which was connected to the two probes of a multimeter. The electrical resistivity was measured in the thickness direction of the composite sheet. The samples were put in an oven, and heated at 5°C every five minutes in the temperature range below 110 °C, and 3 °C every three minutes when the temperature was above 110 °C. The resistance of the specimen was read for each temperature point at end of each step. The resistivity was then calculated. All the resistivities reported in this work are DC resistivities, and the carbon black concentrations are expressed in weight percentage.

3.2. Effect of carbon black on the processing

During compounding of the composites, the weighed amount of HDPE was first melted in the twin-screw mixer unit at 200 °C, and then the weighed amount of carbon black was added into the mixer. The mixture was mixed for 20 minutes at 200 °C with rotation speed of the screw of 60 rpm. The torque required to keep the screws rotating at certain speed and temperature was recorded by the machine. The torque reading decreased with the experiment time during first 5 to 6 minutes of mixing and finally reached an equilibrium value. Figure B9 shows the equilibrium torque reading of the

mixer for different experiments. The equilibrium torque reflects the viscosity of the polymer melt system. The higher torque reading means that the polymer melt system in the mixer has higher viscosity. Without the addition of carbon, the pure HDPE melt was mixed in the mixer, and the torque required to drive the screws at 60 rpm was about 6.0 Nm. As the carbon black was added into the system, the torque needed to drive the screws increased. This shows that the carbon increased the viscosity of the polymer melt system, which is true for all carbon blacks. However, the extent to which the carbon black affected the viscosity of the melt differed from type to type. This difference is not so obvious at low loadings, but become more obvious as loading increases. Addition of BP-2000 carbon black increased the torque most dramatically, while the addition of N660 carbon black increased the torque reading the least compared to the other carbon blacks. This difference is directly related to the characteristics of carbon blacks.

Figure B9. Torque reading during compounding of the composite at 200 °C, 60 rpm.

As is shown in Table B1, BP 2000 carbon black has the highest CTAB adsorption, tint strength, DBP absorption and iodine absorption among all these carbon blacks. This means BP 2000 carbon black has the smallest particle size (its average particle diameter is 12 nm), highly aggregated structure and highest surface area. These properties contribute to the most obvious torque increase.

N660 carbon black shows lowest CTAB adsorption, tinting strength, DBP absorption and iodine absorption among the five carbon blacks. It has the largest particle size (70 nm), lowest structure and lowest surface area. The addition of N660 carbon black increased the viscosity to the least extent, thus N660 carbon black was the easiest one to disperse.

Vulcan XC72 and Conductex 975 are from different manufactures, but they have similar properties as shown in Table B1. Thus they showed similar behavior as showed in Figure B9. Conductex SC has properties between those of the Conductex 975 and N660,

so the torque readings of polymer melt loaded with Conductex SC were between those of polymer melt loaded with Conductex 975 and N660 at same loadings.

3.3. Effect of carbon black on the base resistivity

Figure B10 shows the resistivity of the conductive composite at different loadings of carbon blacks at 25 °C. It is not surprising that the resistivity decreases with the increase of carbon black loading; and the trend is true for all carbon blacks. Polymer composite with different carbon black at same loading showed different resistivity, and this is also related to the structure of carbon blacks. BP-2000 carbon black has the smallest particle size, highly aggregated structure and high surface area, and these properties lead to low resistivity at same amount of loading of carbon blacks, as it is easier for the BP-2000 carbon black to form conductive path in polymer matrix. While N660 carbon black has large particle size, the less aggregated structure and surface area, the resistivity of the composite filled with N660 carbon black is higher than those of the composites loaded with other carbon black at same loading. As discussed above, Conductex 975 and Vulcan XC72 have similar structure, thus they showed similar behavior of resistivity versus carbon black loading at 25 °C. The resistivity of Conductex SC carbon black filled HDPE was between those of HDPE composite filled with N660 black and Vulcan XC72 carbon at same loading.

Figure B10. Resistivity of different carbon black filled HDPE at 25 °C.

3.4. PTC behavior carbon black filled HDPE

The resistivities of those polymer composites filled with different carbon black versus temperature are shown in Figure B11 to Figure B15.

The resistivities of all the composites at different carbon black loading increased with temperature. The resistivity increased steadily with temperature from room temperature, and increased more rapidly after 120°C as the polymer crystal started to melt. The resistivity reached the peak value around 133°C. The resistivity decreased with further increase of temperature, which is called negative temperature coefficient effect. The NTC behavior was very obvious for composite with low carbon black loading, while it was not so obvious for system with high carbon black loading. This observation is same as reported in the literatures. The PTC anomaly is due to the thermal expansion of polymer matrix during the melting, and the NTC behavior is due to reorganization of carbon black in the mobile polymer melt phase. This reorganization is easy to occur for composite with lower carbon black loading due to its lower viscosity, while it is difficult for system with high carbon black loading and high viscosity. It has been reported that the NTC behavior can be removed by crosslinking of the polymer network. It was observed by Tang et al that the PTC intensity as well as the base resistance decreased with the thermal cycles. The same phenomenon was observed in this study. The specimen always showed lower resistance after being cooled down to room temperature compared to the same specimen before the resistance versus temperature experiment was carried out.

Different carbon black filled composites did not show exactly the same PTC behavior. For BP-2000 carbon black filled HDPE (Figure B11), the PTC amplitude is close to $10^{1.5}$ for composite with filler loading of 10%. Further increase of the loading led to the decrease of the PTC amplitude. With loading above 20%, the PTC amplitude was less than 10, which means that the BP 2000 carbon black filled PE had quite good thermal stability in its resistivity.

Figure B11. Resistivity of BP-2000 carbon black filled HDPE versus temperature (The weight percent of carbon black is showed for composite).

Compared to BP 2000 carbon black filled HDPE, Vulcan XC-72 carbon black filled HDPE had greater PTC behavior (Figure B12). At loading of 15% and 25%, the PTC amplitudes were about 10^3 . With further increase of the loading, the PTC amplitude decreased. The PTC amplitude of the composite with 50% carbon black loading is less than 10. The Conductex 975 carbon black filled PE showed similar behavior as those of Culcan XC-72 carbon black filled HDPE (Figure B13). The PTC behavior for Conductex SC carbon black filled PE (Figure B14) is similar to that of Conductex 975 and Culcan XC-72 carbon black filled HDPE.

Figure B12. Resistivity of Vulcan XC-72 carbon black filled HDPE versus temperature (The weight percent of carbon black is showed for composite).

Figure B13. Resistivity of Conductex 975 carbon black filled HDPE versus temperature (The weight percent of carbon black is showed for composite).

Figure B14. Resistivity of Conductex SC carbon black filled HDPE versus temperature (The weight percent of carbon black is showed for composite).

Among all the carbon blacks tested, N660 carbon black has the largest particle size, lowest surface area and low congregated structure. Thus the composite filled with N660 carbon black shows the lowest melt viscosity, and highest electrical resistivity compared to other composites at same loading, as mentioned above. However the PTC amplitude of the composite with N660 carbon black was the highest compared to those of the composites filled with other carbon blacks. The PTC amplitude of the composites with loading of 25%, 30%, 35% and 40% were all above 10^5 (The resistance reading of samples containing 25%, and 30% carbon black were beyond the range of the multimeter of 120 M Ω . So the actual PTC amplitude of those composites was even higher). Even at loading as high as 50%, the PTC amplitude was still as high as 10^4 . As the loading increased to 60%, the PTC amplitude dropped to $10^{1.5}$.

Figure B15. Resistivity of N660 carbon black filled HDPE versus temperature (The weight percent of carbon black is showed for composite).

From the comparison of PTC behavior of different carbon black filled HDPE, it can be found that large particle size, small surface area, and small extent of aggregated structure lead to the polymer composite with great PTC behavior. This is because the unaggregated individual carbon black particles can be separated more easily under thermal expansion of polymer matrix, which leads to increase of the distance between adjacent particles and decrease of the contact area between the adjacent particles. While, the particles in the aggregated structure are difficult to be separated by thermal expansion of polymer matrix. However, the great PTC behavior can not be simply attributed to the thermal expansion of the polymer matrix, which leads to the conductive filler volume loading fall below the percolation volume fraction as suggested in the literature [2]. As is shown in the PTC behavior of N660 carbon black filled HDPE, the resistivity of the composite with 50% carbon black loading reached 10^6 ohm.cm, which is much higher than the resistivity of the composite with 25%, 30%, 35%, and 40% weight loading at room temperature. However, the volume fraction of conductive filler in the composite with 50% weight carbon black loading at the peak resistivity temperature is still higher than that of the composite with loading of 40% weight at room temperature. So the large PTC behavior of N660 carbon black filled polyethylene is due to some microscopic mechanism under the macroscopic phenomenon of large thermal expansion during the melting of the polymer crystal. Although carbon black particles are dispersed homogeneously in the polymer melt during mixing, carbon particles are pushed out of the crystalline region as impurity in recrystallization process during cooling. Thus, at temperature below melting point of polymer crystal, carbon particles are dispersed in the amorphous region only. As the crystallite melts, those carbon black particles re-disperse into the polymer melt, thus the inter-particles distance increases so significantly that

electron tunneling between conductive particles is hampered, and resistivity increases greatly.

Among the composites filled with different carbon blacks, the N660 carbon black filled PE showed the greatest PTC behavior. Large particle size, small surface area, and small amount of the aggregated structure lead to great amplitude of PTC behavior. The great PTC behavior is due to some microscopic mechanism under the macroscopic thermal expansion of the polymer matrix during the melting of polymer crystal.

3.5. PTC behavior of Polymer Composite Filled with Two carbon blacks.

In order to find out the synergetic effect between two totally different kinds of carbon black, the composite filled with bimodal carbon black was prepared. Figure B16 and Figure B17 show the PTC behavior of polyethylene composite filled with bimodal carbon black of N660 and BP2000.

It can be seen from Figure B16 that with the addition of BP2000 carbon black into the composite of N660 filled HDPE, the resistivity of the composite decreased greatly. The resistivity of composite with 40% N660 carbon black and 10% BP2000 carbon black is 150 times lower than that of with 50% N660 carbon black alone. With further substitution of N660 carbon black with BP2000 carbon black, the resistivity decreased slightly. The PTC amplitude of the composite with bimodal carbon black is much less than the composite filled with N660 carbon black alone at the same amount of loading. With 10% N660 carbon black replaced by BP2000 carbon black, the PTC amplitude decreased from more than 10^4 to less than 100 for composite filled with 50% carbon black.

Figure B16. Resistivity of HDPE composite filled with bimodal carbon blacks versus temperature.

Figure B17 shows the PTC behavior of LDPE composite filled with 40% carbon black. It is clear that with 40% N660 carbon black only, the composite showed high PTC amplitude. While with 5% N660 carbon black replaced by BP2000, the base resistivity did not change much. However, the PTC amplitude decreased greatly. Originally, the PTC amplitude was more than 10^4 , with the substitution of 5% N660 carbon black by BP2000 carbon black, the PTC amplitude decreased to less than 100. With 10% N660 carbon black being replaced by BP2000 carbon black, the base resistivity decreased greatly, and the PTC amplitude was even lower, less than 10. Figures B16 and B17 suggest that the addition of BP2000 carbon black in place of N660 carbon black is not beneficial to increase PTC amplitude, and at the mean time it reduces the base resistivity.

Figure B17. PTC behavior of LDPE composite filled with 40% carbon blacks.

3.6. Effect of Polymer Matrix on PTC Behavior.

Figure B18 shows the PTC behaviors of polymer composites containing 40% N660 carbon black in different polymer matrices. It can be seen that among different polymer matrices, polyethylene (PE) can provide the composite with a large PTC amplitude. Between HDPE and LDPE, the HDPE can provide polymer composite with even higher PTC amplitude. EVA resin is usually introduced to polymer composite to maintain the desired mechanical property at high filler loading. The introduction of EVA to PTC composite led to an increase in room temperature resistivity and a decrease in PTC amplitude. Use of polypropylene instead of PE as polymer matrix led to polymer composite with higher base resistivity and lower PTC amplitude. The PTC transition of polymer composite with PP as polymer matrix also took place at higher temperature, as the melting point of PP (166°C) is higher than that of polyethylene.

Figure B18. Resistivity of composite containing 40% N660 carbon black and different resin versus temperature.

3.7. Effect of Carbon Black on the Crystallinity of Polymer Matrix.

The DSC analysis was used to investigate the effect of carbon black on the crystallinity. Figure B19 shows the recrystallization peak of HDPE, 30% N660 carbon-black-filled HDPE and 50% N660 carbon-black-filled HDPE. It can be seen that there was a slight difference in peak temperature. With the addition of carbon black, the recrystallization peak temperature increased by about 2.5 °C. The carbon did not affect the melting temperature of polymer crystal (Figure B20). From the areas of the recrystallization and melting peaks, the relative crystallinities of the polymer resin weight percentage can be calculated, and they are listed in Table B2. The relative crystallinity of HDPE was taken as 100, the relative crystallinity of HDPE filled with 30% N660 carbon black is around 103, and that of HDPE filled with 50% carbon black is around 97. There is only slight difference in those samples in term of crystallinity. The added carbon black did not significantly affect the melting and recrystallization temperatures, nor did it affect the crystallinity significantly.

Figure B19. Comparison of recrystallization between HDPE and HDPE filled with N660 carbon black.

Figure B20. Comparison of melting peaks of HDPE and HDPE filled with N660 carbon black.

Table B2. Relative crystallinity of HDPE

Material	Recrystallization	Melting
HDPE	100	100
HDPE+30%N660	102.7	104.5
HDPE+50%N660	96.2	98.4

3.8. Summary

Carbon black with large particle size, small surface area, and small amount of the aggregate structure leads to the polymer composite with high base resistivity and great amplitude PTC behavior. Carbon black with small particle size, large amount of aggregate structure leads to polymer composite with low base resistivity and low PTC amplitude. The composite filled with bimodal carbon blacks with both large and small carbon particle does not show both low base resistivity and high PTC amplitude. Carbon black can lead to a slight increase of the recrystallization peak temperature; however, it does not significantly affect the melting temperature nor the crystallinity. Furthermore, PTC behavior also depends on the polymer matrix.

4. Compounding and characterization of ShortWatch tape

4.1. Resistivity measurement in thickness direction for tape materials

It was desirable to use the base resin of cable insulator material for the ShortWatch conductive composite. The materials were compounded in Rockbestos with two basic resin and conductive carbon black N660. Among all the samples, the following phenomenon was observed. The resistance reading was not as stable as commercial available resettable fuse made of PTC conductive polymer composite.

For DFD-6040 resin (standard resin for cable insulation) and NA-317 resin (a much less branched, with a much sharper melting transition) filled with N660 carbon (40%, 45%, 50%, 55%) uncrosslinked and crosslinked sample, their resistance was measured together with their behavior versus temperature. The PTC amplitude (defined as the maximum resistivity after PTC transition to resistivity at room temperature) was found to be above 10^5 . Lower carbon black loading gave higher base resistivity and higher PTC amplitude.

Figure B21. Resistivity in thickness direction of DFD-6040 resin filled with N660 carbon black versus temperature.

Figure B22. Resistivity in thickness direction of NA317 resin filled with N660 carbon black in thickness direction

Crosslinking normally can reduce the NTC behavior after the PTC transition. This effect was confirmed in the system under investigation. However, crosslinking does not significantly affect the base resistivity of the conductive polymer composite. The phenomenon that the resistance reading at individual temperature point (lower range) was not stable suggested that the carbon black may not be mixed very uniformly.

There is one very important phenomenon to mention. After one temperature cycle (heating up to temperature above PTC transition temperature and then cooling down to room temperature), the resistance of same piece of specimen increased (two samples of NA317+50%N660-crosslinked (increased 50 times) and DFD+50%N660-crosslinked (increased 7 times) were tested in this experiment). This strongly suggested that the aging test is necessary for the electricity behavior of material.

4.2. Electrical property measurement in length direction

The resistance was measured in length direction at different temperature of PTC material compounded in Rockbestos. The results were shown and compared in the following figures. There is no significant difference in the resistivity between the two resins. However, the measured resistivity in length direction seemed to be two orders of magnitude lower than that in thickness direction.

Figure B23. Resistivity of NA-317 resin filled with N660 carbon black in length direction

Figure B24. Resistivity of DFD-6040 resin filled N660 carbon black in length direction.

4.3. Mechanical property test for ShortWatch tape

Mechanical property test of the material compounded in Rockbestos was also performed. Dog-bone specimens were cut from the tape sample. The mechanical properties were measured with fair accuracy. The results were summarized in Table B3. It can be seen that two resins showed absolutely different elongation at break. DFD-6040 showed much better mechanical property in terms of elongation. Also, crosslinking improved the elongation too. Low extent of crosslinking can increase the elongation, while too much elongation will lead to decrease of elongation. It can be fairly said that the extent of crosslinking in our project is quite appropriate. With increase of carbon loading, the elongation at break decreased. The lowest one was 9.4% for NA317 resin filled with 50% N660 carbon without crosslinking, while it increased to 22% after it was crosslinked. This is much better than the target value of 5%. It can be seen that crosslinked system showed higher elongation as well as higher strength than uncrosslinked system. As the carbon loading increases, elongation decreases, but average strength increases. There is no significant difference in strength between those two resins, but elongation of DFD 6040 is higher than that of NA 317 resin.

Table B3. Mechanical property of N660 carbon black filled polyethylene

	Average elongation (%)	Average Strength (Mpa)
resin DFD-6040		
40%, uncrosslinked	30.86	14.8
40%, crosslinked	111.8	16.75
45%, uncrosslinked	23.3	15.2
45%, crosslinked	70.0	17.8
50%, uncrosslinked	16.6	18.4
50%, crosslinked	33.0	19
resin NA-317		
40%, uncrosslinked	16.4	14
40%, crosslinked	35.0	15
45%, uncrosslinked	13.1	15.75
45%, crosslinked	20.3	16.75
50%, uncrosslinked	9.4	15.75
50%, crosslinked	22.5	19

4.4. Effect of antioxidant on PTC behavior

Some PTC materials were compounded in Rockbestos with antioxidant (3% Irganox 1010) added into the formulation. And the resistivity of the PTC material was measured both in the thickness direction and in length direction. The results are shown Figure B25 and Figure B26. The resistivity in length direction is less than the resistivity in the thickness direction.

Figure B25. Resistivity in thickness direction vs. temperature of N660 carbon black filled composite (3% Irganox 1010 added).

Figure B26. Resistivity in length direction of composite filled N660 carbon black versus temperature (3% Irganox 1010 added).

The antioxidant added did not affect the resistivity of composites and their PTC behavior. However, the NA317+50% carbon black system became brittle after the addition of the antioxidant. It should also be noticed that there is not much difference in the base resistivity between NA317+50%C and NA317+45%C.

It should also be noticed that with same amount of carbon black loading, composite with DFD6040 as matrix showed significant higher resistivity than the composite with NA317 as matrix. Also the PTC amplitude of composite with DFD6040 as matrix is significantly higher than that of composite with NA317 as matrix.

5. Comparison of PTC behavior of ShortWatch tape and filament

Two different geometries of materials were manufactured from ShortWatch PTC materials: filament and tape. ShortWatch filament showed lower switching magnitude than the Shortwatch tape prepared earlier. It was suspected that this is maybe due to lower crystallinity of polymer phase in filament due to the fast cooling. Two approaches might solve this problem. One is cooling the filament slowly, and the other one is annealing the filament at elevated temperature. Both of these two approaches should be able to increase the crystallinity.

Thermogravimetric analysis (TGA) experiment was performed to check if the carbon black (CB) loading was at 50%. The TGA curve of the filament (Figure B27) showed the weight loss of the filament versus temperature. Polymeric material starts decomposing at high temperature under nitrogen, while carbon black does not decompose at high temperature. The residue at temperature above 500 °C is carbon black. From the curve, we can say that the carbon black loading is about 50%. The carbon black loading

for tape sample of DFD6040+50%CB was also checked, and the result is shown in Figure B28. The carbon black loading is also 50%. So there is no significant difference in carbon black loading between the two samples. The difference in switching magnitude may be caused by polymer resin or processing.

Figure B27. TGA profile of ShortWatch filament (heating rate: 5°C/min, under N₂)

Figure B28. TGA profile of ShortWatch tape (DFD6040+50%CB) (heating rate: 5°C/min, under N₂)

Measurement of resistivity versus temperature was performed in Georgia Tech too. The results are shown in Figure B29. The lower switching magnitude is also observed. The filament was annealed at 110°C for 10 hours and slowly cooled down in an oven. The resistivity versus temperature was measured again after annealing, and is also shown in Figure B29. No improvement in switching magnitude was observed. This indicates that the low switching magnitude cannot be solved by annealing the filament

A narrow strip (0.54 mm in thickness, 1.20 mm in width, and 40.81 mm in length) was cut from the tape sample prepared earlier (DFD6040+50% Carbon black, crosslinked). The resistivity of this strip versus temperature was also measured, and the results are shown in Figure B29 too. The strip showed a little bit higher cold resistance than the filament, and the switching magnitude was much higher than the filament. It should be noticed that the resistance of this strip at 115 °C was beyond the range of the multimeter of 120 MΩ, but 120 MΩ was taken as the reading at 115 °C. The actual switching magnitude is higher than it is showed here. This shows that the geometry is not a factor affecting the switching magnitude, as the strip is close to the geometry of the filament. The difference is due to the processing, which may introduce different distribution of carbon black in the composite.

Figure B29. Resistivity of ShortWatch filament and narrow strip cut from tape versus temperature. (The resistance reading for strip at 115 °C was actually out of the range of multimeter 120 MΩ, but 120 MΩ was taken as it's reading)

Differential scanning calorimeter (DSC) was also used to analyze the melting, and recrystallization of filament as well as the tape by heating the sample to 150 °C then cooling it to 25°C. Figure 30 shows the DSC profile during heating cycle. The melting peak of filament was around 106.5 °C. After the filament was annealed at 110 °C for 10 hours and then oven cooled, the melting peak temperature (105.7 °C) is not changed significantly. However, above the major melting peak, there is a small melting peak with peak temperature at 113°C. This showed that there was some change during the heat treatment. Some crystal became more perfection, thus showed another melting peak at a higher temperature.

The melting peak of the tape sample was at a higher temperature 109.4 °C. After the tape sample was heated to 115 °C for resistance measurement, it was kept at 100 °C for 1 hour, and 90 °C for another one hour, and then oven cooled. The DSC profile showed no significant difference from that of the sample without heat treatment.

Figure B30. DSC profile of filament and tape (heating rate: 5 °C/min)

The DSC cooling profiles for those four samples are shown in Figure B31. The crystallization started at higher temperature for the tape specimen than for filament specimen. This indicates that there may be some subtle difference in the microstructure of the tape and filament specimen. There is no significant difference in area of recrystallization peak, which are compared in Table B4. However, significant difference exists in peak area among different samples. Peak area of tape sample is obviously greater than peak area of filament sample, indicating the tape specimen has higher crystallinity than the filament. Annealing of the filament did not significantly increase the crystallinity.

Figure B31. DSC profile of filament and tape (cooling rate: 5 °C/min)

Table B4. Peak area for melting peaks and recrystallization peaks (J/g)

	melting peak	recrystallization peak
filament, not annealed	42.8	38.4
filament, annealed	43.4	38.4
tape, not annealed	47.6	38.5
tape, annealed	47.2	39.2

It was mentioned that the resistance never returned to the original value after the material is cooled down from high temperature. This is related to the structure of the polymer composite. At high temperature, the structure of carbon black is broken, and the broken structure cannot be repaired completely after the material is cooled down. The continuous slow decrease of resistance at room temperature is due to the molecular motion of polymer chain of amorphous region (This kind of motion takes place at temperature above the glass transition temperature of polymeric material). High crosslinking may help restrain the motion of polymer chain of amorphous region. However, high crosslinking will also increase brittleness of material. Several samples with different crosslinking density (with different E-beam dose) may be prepared and tested if further optimization of the processing condition is desired.

It was observed that the filament shrank during PTC test. Shrinking of the filament is normal. During extrusion of filament, orientation of polymer chain is introduced. During heat treatment, these oriented chains disorientate, and thus shrink. This shrinking problem can be solved by annealing the filament at elevated temperature.

Different heating rate will give different behavior of resistivity versus temperature. The PTC behavior is related to the melting of polymer crystal, and melting of polymer is heating rate dependant. Usually, high heating rate leads to high melting point, thus higher PTC transition temperature. There is no significant difference in the

transition temperature for measurement taken at heating rate of 1.0 °C/min and 0.1 °C/min. This probably indicates that there is no significant influence in heating rate in the range tested (0.1°C/min to 10 °C/min). The difference in transition temperature obtained at heating rate of 10 °C/min is possible due to experimental error or non-uniformity among different samples.

It was also observed that there is variation in PTC behavior of the filament manufactured at different batches shown in Figure B32.

Figure B32. Variation of PTC behavior of ShortWatch filament.

6. Aging Test on ShortWatch Materials

PTC filament was subject to aging test at 160°C. The mechanical property and the electrical property were measured after different aging time. It is easy to understand that durometer increased steadily to near hard state. This is due to the crosslinking of polymeric matrix during aging, which also leads to the increase in density. The slow decrease in the cool resistivity of the sample versus storage time at room temperature after aging at high temperature is due to the slow crystallization process at room temperature. Crystallization can take place the temperature range between glass transition temperature and melting temperature.

The increase in resistivity in the initial aging test is probably due to the wetting of polymer resin on the surface to carbon black and/or the even farther separation of carbon black particles. The drop of the resistance in later aging stage is possibly due to the increase of volume fraction of carbon black. The crosslinking of polymer matrix will reduce the crystallinity; possibly increase the density of polymer matrix, as the crosslinking increase the density in the amorphous region. PTC conductive polymer composite with higher crystallinity polymer matrix will give lower base resistance and higher switching magnitude. Higher density of polymer matrix (after aging) will lead to

decrease of the base resistivity as the volume fraction of carbon black increases. Also, long time, high temperature aging in an oxidative environment may lead to the oxidation of polymer matrix and possible oxidation of carbon black surface. All these possible factors will affect the resistivity and switching magnitude. It may not be a simple process. In order to better understand what happens in this aging process, more fundamental study with TEM, AFM, XPS, and DSC can be done. Also, it should be kept in mind that there is no direct correlation between electrical property of sample at long term with the accelerated aging at high temperature and mechanical property. Actually, the total loss of PTC behavior of composite after 900 hours aging at 160°C is very interesting behavior (Figure B33).

Figure B33. PTC behavior of ShortWatch material after aging.

Electrical property after long time high temperature has not been reported for PTC conductive polymer composite in the literature. People have just done aging for a few thermal cycles rather than long time high temperature aging. For the material to be used, how long time the product will be exposed to the high temperature should be understood for the high temperature aging. The material during aging is at totally different state (above the melting point of polymer crystal, with no crystalline phase) from the working state (below the melting point of polymer crystal, with crystalline phase in the composite). We suspect that the crosslinking takes place in the melt phase of original crystal. After 900 hours aging at 160°C, there is no crystal phase left even after the materials cool down, thus there is no PTC amplitude (switching magnitude) observed after 900 hours aging. DSC can be used to find out the change in crystallinity after aging at high temperature.

Differential scanning calorimetry (DSC) analysis was performed on the aged ShortWatch filament samples. The Figure B34 shows the DSC profile of the sample during DSC heating scanning. In the heating scan, the melting of crystal can be detected. From here we can find out the melting peak temperature and relative crystallinity (percent of crystal phase in polymer). Before aging, the melting peak temperature is 106°C, and the melting enthalpy is 42.7 J/g (the peak area). After the filament was aged at 160°C for 286 hours, the melting peak moved a low temperature of 96.7°C, and the melting enthalpy is 32.2 J/g, indicating that the crystallinity decreased to 80% of the crystallinity of filament before aging. While after the filament was aged at 160°C for 883 hours, no obvious melting peak was detected (No crystal left!). This analysis results suggested that aging at 160°C has significant effect on crystallinity and melting temperature: it leads to lower crystallinity and lower melting temperature. The reason for lower switching magnitude after aging and eventual disappearing of switching magnitude is exactly what we proposed: decreasing and eventual disappearing of crystallinity of the polymer after long time high temperature aging. The DSC results confirmed our previous analysis. In addition, the lower melting temperature will lead to lower switching temperature, which can be observed on one of charts "Sensor R-T Response" (Figure B33).

Figure B34. DSC heating profile of ShortWatch filament. (heating rate: 5°C/min)

The crystallinity of commercial PTC materials used for resettable fuse showed a similar loss with the thermal aging. It was also noticed that the switching temperature of aged Raychem materials moved to lower temperature accompanied by a lower switching magnitude. This is what happened in our PTC materials, which is due to lower melting temperature (smaller crystal size) after high temperature aging.

Conclusion

PTC conductive polymer composite for ShortWatch sensor has been successfully developed with carbon black as conductive filler. Carbon blacks with large particle size, small surface area and small amount of aggregate structure lead to composite with high base resistivity and great PTC behavior. The great PTC behavior is due to microscopic mechanism under the macroscopic thermal expansion of the polymer matrix during the melting of polymer crystal. It was found that there is anisotropy of PTC behavior in ShortWatch sensor materials, which is mainly due to the processing. Aging of PTC material for ShortWatch sensor at high temperature (160°C) can eliminate the crystallinity, thus the PTC behavior.

Appendix C: BPW Aging Trials of ShortWatch Sensors

1. Introduction

IEE 323 and IEE 383 establish environmental qualification (EQ) requirements for wire and cable. Although EQ testing was not in the scope of work of this SBIR project, thermal accelerated aging trials were conducted to (1) demonstrate mechanical integrity of the ShortWatch conductive composite sensor over a typical accelerated age test period used for thermal aging of wire and cable in the nuclear industry and (2) demonstrate acceptable electrical performance of the conductive composite sensor after thermal aging.

2. Test Approach

24 test samples were prepared from ShortWatch sensor filament received from Rockbestos Surprenant Cable Corp. on May 30, 2000. Sensor filament specifications:

Nominal extruded diameter:	.020"
Base polymer:	LDPE/HDPE blend (Rockbestos "Fire Wall 3")
Conductive filler:	N660 carbon black (50% by weight)
Anti-Oxidant:	3% Irganox 1010
Measured Resistivity:	0.94 Ω -cm @ 23C

The filament was electron-beam cross-linked after extrusion.

Figure C1: Sample extrusion line (Rockbestos)

Figure C2: Sample filament coil

Sample filaments (Figure C2) were cut to 8.0 cm and inserted into 2.0 mm diameter glass tubes open at both ends for support of the filaments during aging.

Figure C3: Sample filament in glass support tube

Sample glass support tubes (Figure C3) were inserted into insulative glass fiber sleeves (Figure C4) to reduce quenching effects of air-cooling and to improve cooling uniformity

when removed from the aging oven. The following photograph (Figure C4) shows the assembled sample and container.

Figure C4: Assembled filament sample and container

All filament samples were aged at 160C in an aging oven (Fisher Scientific Isotemp® 800 series, forced air) for times ranging from 1 hour to 883 hours. Pre-age measurements included sample length and diameter (for volume measurements), DC resistance in the length (extruded) direction, and initial hardness (durometer). Oven age time, aged resistance, length, diameter, and hardness were recorded for each sample.

Figure C5: Prepared samples

Figure C6: Prepared samples in aging oven

Figure C7: Durometer for measuring sample hardness

Electrical resistance (Figure C8) was measured at one hour and 24 hours after removal from the oven to compensate for resistance changes with time due to re-crystallization effects.

Figure C8: DC resistance measurements

Figure C9 shows the resistivity and sample durometer vs. oven age time for sample times from 1 hour (arbitrarily assigned as unaged) to 880 hours. The 296-hour aging time corresponds to an extrapolated 40% reduction of elongation-at-break (EAB) for the base polymer after 40 years of aging at 90C. The tests were extended to 880 hours to determine the eventual failure mechanisms of the sensor filaments.

The selection of 160C for accelerated aging was partly necessitated by time available in the project. Lower temperatures (ideally below the transition temperature of 121C) would have been preferable, but would have required excessive aging times.

As can be seen from the graph, the durometer (hardness) increases from an initial value of 80.5 to 83 at the defined end of life (296 hours). Hardness at 880 hours was 88, corresponding to sufficient brittleness to cause breakage from normal handling.

The initial increase in resistivity of the sensor filaments is not completely understood, but may be due to several factors including (1) "rewetting" of the carbon particles during long time periods at melt temperatures, (2) re-distribution of the carbon particles under melt conditions and (3) loss of crystallinity due to cross-linking of the polymer above the transition temperature. (see Appendix B from Georgia Tech). This cross-linking "locks" the polymer and prevents re-crystallization upon cooling below the transition temperature. The eventual reduction of resistivity at the extreme end of life is believed due to the high level of cross-linking resulting in reduction of volume fraction of the base polymer as compared to the inert (carbon black) conductive filler. We believe that the initial increased level of resistivity is primarily a function of the elevated aging temperature (above the melt temperature) and would be at a significantly reduced level under natural aging conditions. In this sense, the testing was conservative in nature.

Figure C10 shows sensor resistance vs. temperature (switching) for age times of 1 hour (unaged), 96 hours, 296 hours (nominal end of life) and 880 hours (failure) at the age temperature of 160C. The switching magnitude, defined as the ratio of sensor resistance at 130C to 90C (design temperature) is reduced from slightly over 2 decades at the unaged condition to about one-half decade at nominal end of life. Switching magnitude is reduced to nearly zero at failure (880 hours). The reduction of switching magnitude is believed to be related to loss of crystallinity of the sensor material during aging above the transition temperature. The loss of crystallinity was confirmed by DCS measurements

carried out at Georgia Tech (see appendix B). Loss of switching magnitude would result in the reduced resolution of overtemperature sensing by the filament.

Figure C9: Resistivity vs. temperature (switching magnitude)

Naturally aged samples measured during the project did not demonstrate any initial increase in resistivity (and subsequent loss of switching magnitude) of the accelerated age samples. Figure C11 shows resistance vs. time for naturally aged samples over a nine month period of the project. These results further suggest the conservative nature of the accelerated aged sample results.

Figure C10: Resistance vs. natural age

3. Conclusions

Age testing carried out by BPW, Inc. demonstrates mechanical integrity of the conductive polymer sensor filament for the design life of the cable. The eventual failure mechanism is brittleness of the sensor. Accelerated aging also resulted in a significant loss of switching magnitude. This loss of switching magnitude is attributed to loss of crystallinity of the base polymer (electron beam cross-linked polyethylene) as a result of aging above the crystalline transition temperature. Overtemperature sensing capability at reduced resolution is maintained over life of the sensor.

4. Future work

The extreme sensitivity afforded by changes in resistivity of conductive composites as a result of small changes in volume fraction of the base polymer appears to provide a powerful tool for investigating aging effects of the polymer. Although unrelated to the development of a distributed overtemperature and mechanical damage sensing wire and cable completed under this SBIR, aging studies of composites as their use as a condition monitoring approach will be pursued in subsequent work and research proposals by BPW, Inc.

Appendix D: Time Domain Reflectometer and Noise Issues

Time Domain Reflectometer (TDR)

One of the goals of this project has been fault location, that is, the determination of the exact location of an electrical fault after the existence of a fault had been discovered. We conducted many early experiments with a Tektronix 1503 time domain reflectometer (TDR) (see Figure D1) to ascertain the TDR's usefulness in fault location. This TDR served us well in the early proof-of-concept testing.

Figure D1: The Tektronix 1503 Time Domain Reflectometer

Any TDR requires two, more or less parallel, conductors to operate. If a fault occurs in one of the two conductors, the TDR can determine, quite accurately, the distance from the TDR to the fault. Basically the TDR sends a short duration electrical pulse down the conductor and measures the time required for the electrical reflection from the detected electrical fault to arrive back at the instrument to determine the fault location. The distance to the fault is calculated from the measured time delay and the velocity of propagation of the electrical impulse in the considered wire. The velocity of propagation (VOP) of the electrical impulse is a specific characteristic of the electrical wiring under consideration and must be either measured or predetermined. The easiest method to determine the VOP is to measure the actual distance to a known electrical fault in the electrical wiring under consideration and to calibrate the TDR reading to the appropriate distance. The VOP can then be read directly from the TDR. The 1503 TDR is an older unit designed for longer ranges and of limited portability (but which can be purchased used at very reasonable cost), so after we determined that a TDR could be of use we started a search for a more practical unit. After considering several different TDRs we selected the Biddle CFL 510E (figure D2). This unit is very portable and also reasonably priced (about \$1500).

Figure D2: The Biddle CFL 510E Time Domain Reflectometer

The Biddle CFL510E has:

- Six ranges for testing power, cellular, CATV, and telephone cables
- Large high resolution backlit LCD
- 25, 50, 75, and 100 ohm output impedance
- Gain, balance, and contrast controls front-panel accessible
- Auto ranges around the cursor for best view of fault

This instrument is an advanced instrument capable of identifying a wide range of cable faults using Time Domain Reflectometry. It offers exceptional features and a range capability normally associated with larger, more expensive instruments. The measurement range spans from 30 feet to 9,000 feet, with an advertised minimum resolution of four inches.

The Model CFL510E can be used on any cable consisting of at least two insulated metallic elements, one of which may be the sheath or shield of the cable. The CFL510E

has internal matching networks to allow testing of 25-, 50-, 75-, and 100-W cables. (These correspond to power, cellular, CATV, and telephone cable).

In figure D2, the maximum range under consideration is 90 feet (lower left) and the measured range is 22.1 feet (lower center). The device is set for 100-ohm cable with a velocity of 0.6 times the speed of electrical propagation in a vacuum (the speed of light). The first group of reflections (reading the signal from left to right) is from the connections between the TDR and the cable under consideration. The second large reflection is from a fault 22.1 feet from the TDR. The TDR is calibrated for arbitrary cable, as described above, by using a similar cable with a known fault at a specific distance. The controls are adjusted to set the correct (known) distance and these control settings are used for determining faults in similar cable with faults at unknown distances. It should be noted that for a helical conductor (like the ShortWatch metallic sensor) the distance measured by the TDR to a fault in the ShortWatch sensor is the distance along the helix.

The experiments with both TDR's demonstrated that a fault in the metallic outer sensor of ShortWatch can be located very accurately (within the accuracy of the TDR), if the geometry of the metallic sensor is known and if one of the other conductors in the electrical wire or cable under consideration is used to complete the requirement for two conductors stated earlier. The conducting polymer sensor cannot be used as the second conductor because of the enormous difference in impedance between the metallic sensor and the conducting polymer.

Noise Testing

During the development of ShortWatch there was a concern that the metallic Shortwatch sensor would act as an "antenna" and pick up external electronic noise from 60 Hertz AC equipment and the higher frequency electronic "hum" from florescent lights and electric motors. We simulated the metallic ShortWatch sensor and located this simulation close to 60-hertz electrical wires and to florescent light and found that a very simple low-bypass filter could eliminate any noise concerns. Initially we used a R-C low bypass filter but later found that an even simpler 0.1-microfarad capacitor to ground was all that was required. The equation governing the low bypass filter is:

$$V_{out} = V_{in} \left(X_c \frac{1}{\sqrt{R^2 + X_c^2}} \right)$$

Where:

V_{out} = output voltage as a function of frequency (in volts)

V_{in} = input voltage (AC noise or hum) as a function of frequency (in volts)

$X_c = 1/(2 \pi \times \text{Frequency in Hertz} \times C)$

C = capacitance of the grounding capacitor (in Farads)

R = the inline resistance (in Ohms).

This equation can be used to determine the ratio of R/C to get particular voltage attenuation at a specific frequency. We chose R and C so the V_{out} was five percent of

Vin at 60 Hertz. A Microsoft Excel spreadsheet model of the above equation was used to determine the appropriate resistors and capacitors. Later tests indicated that the resistance R could be eliminated for our purposes and we simplified the circuit to just a 0.1 microfarad grounded capacitor.

Appendix E: Certified Test Report on Shortwatch Cable

1 of 2

CERTIFIED TEST REPORT

Customer	IES UTILITIES INC	Order No.	49129
Purchase Order No.	153209	Shop Order No.	19697
Specification no.	RSC-2-821	Product Code	CS20200
Description	3/C 12 AWG (7/STH) XLPE/HD 402M CONTROL CABLE	Quantity	2270 ft.
Item No.	01	Total # Reels	1
JACKET TRAC #	0000356 OC 105A	P/N	P193366

	ELECTRICAL DATA			DIMENSIONAL DATA			
	DIELECTRIC DRY AC	INSULATION RESISTANCE MΩ.KM/CS-M	CONDUCTOR RESISTANCE Ω/KM/CS-M	OVERALL Ø MMETER	INSULATION		JACKET
					MIN WALL	MIN AVE WALL	MIN WALL
Required	6.00 kv/ 5.00 min	6666	1.7500	6.479 in	0.0270 in	0.0300 in	0.0350 in
Lowest	PASS	250000	1.5091	0.445	0.0270	0.0300	0.0350
Highest		375912	1.6118	0.450	0.0300	0.0320	0.0390

The test data noted above reflects the range of all data points from the total population of the inspection for noted above.

INSULATED WIRE		PHYSICAL PROPERTIES		OUTER JACKET	
TEST	REQUIRED	ACTUAL	TEST	REQUIRED	ACTUAL
Tensile strength Unaged (PSI) Min.	1000	2027	Tensile strength Unaged (PSI) Min.	1000	2252
Elongation Unaged (%) Min.	250	321	Elongation Unaged (%) Min.	300	350
Air Oven Aging (168 hrs. @ 150 C.)			Tensile Stress (700 % Modulus) Psi Min.	750	1130
Tensile Strength (%) of Unaged Min.	85	127	Sec. Break Max.	20	1.5
Elongation (%) of Unaged Min.	85	111	Air Oven Aging (168 hrs. @ 100 C.)		
Heat Distortion 1 hr. @ 121 C (1470) Max.	70	1.6	Tensile % of Unaged Min.	85	115
Hot Creep Testing			Elongation % of Unaged Min.	85	79
Flotation (15min. @ 150 C.) 20.0 PSI Max.	100	20.0	Oil Immersion (168 hrs. @ 121 C.)		
Sec. (5 min @ 150 C) No Load Max.	5	0	Tensile % of Unaged Min.	75	103
Vertical Flame Test (UL-44, W-11)	60	0	Elongation % of Unaged Min.	75	70
Vertical Flame-Out (sec.) Max.	25	0			
Burning at Indicator (2) Max.	None	None			
Cotton Ignition					

It is hereby certified that the material described above complies with all applicable requirements of procurement documents in the quantity shipped. Test data are on file in the In-Process Quality Control Department.

Debra E. Blum
Authorized Signature Date: 10/1/00

ROCKBESTOS
SURPRENANT
CABLE CORPORATION
 150 8011 REGISTERED

211 Bradley Park Road
 East Granby, CT 06026 USA
 Tel. 860-653-8300
 Fax. 860-653-8420

CERTIFICATE OF CONFORMANCE
FIREWALL III CLASS IE

Customer	VER UTILITIES INC	Sales Order No.	40129
Purchase Order No.	DUNE ARROW ENERGY CENTER 752297	Ship Order No.	194027
Specification No.	RSS-3-021	Product Code	ES20030
Description	S/C 12 AWG (7/STN) RUPE/HTP 800V CONTROL CABLE	Quantity	2270 ft.
Item No.	01	Total # Reels	1
JACKET TRAC #	00K0334G DC 1650	P/N	P115366

The R-SCC Reel Numbers noted below comprise the total population of the inspection lot noted above.

00K0334G

IT IS HEREBY CERTIFIED THAT THE MATERIAL COMPLIES WITH ALL APPLICABLE REQUIREMENTS OF THE PURCHASE DOCUMENT IN THE QUANTITY SHIPPED.

IT IS ALSO CERTIFIED THAT THE MATERIAL MEETS OR EXCEEDS THE REQUIREMENTS AS OUTLINED IN RSS-3-021-REVISION 14, U/L-44, ICEA S-66-524, S-19-81, IEEE-323-1974, AND IEEE-383-1974. ALSO, ICEA VERTICAL FLAME TEST (S-66-524, 6.12.5), (S-19-81, 6.19.6), IEEE-383-1974 SECTION 2.5.6 FLAME TEST, AND CLASS 1E QUALIFICATION REPORT -

OR 5805, REV. 2 DATED 7/2/87 - IRRADIATION CURE

MATERIALS NOTED ABOVE ARE MANUFACTURED IN ACCORDANCE WITH THE ROCKBESTOS-SURPRENANT QUALITY MANUAL LEVEL 4, DATED 01/15/99, WHICH COMPLIES WITH ANSI N45.2 AND 10 CFR 50 APPENDIX B. ANY NONCONFORMANCES IDENTIFIED WILL BE REPORTED IN ACCORDANCE WITH THE TERMS OF 10 CFR 21.

[Signature]
 QUALITY ANALYST

[Signature]
 DATE

Appendix F: References

1. Linda Smith, Kimberly Long, "1993 Residential Fire Loss Estimates," U.S. Consumer Product Safety Commission, Washington, DC 20207.
2. Kimberly Long, EHHA, Memorandum entitled "1992 National Estimates of Electrocutions Associated With Consumer Products," dated July 27, 1995, U.S. Consumer Product Safety Commission, Washington, DC 20207.
3. Charles V. Schwab, Indiana State University Extension Pub# Fact Sheet Pm1265a, January 1992.
4. Milton S. Greenhalgh, U.S. Patent No. 4,707,686, "Over temperature Sensing System for Power Cables," issued November 17, 1987.
5. Edwin R. Mills, U.S. Patent No. 4,607,154, "Electrical Heating Apparatus Protected Against an Overheating Condition and A Temperature Sensitive Electrical Sensor for Use Therewith," issued August 19, 1986.
6. Karl F. Schoch, Howard E. Saunders, "Conductive Polymers," IEEE Spectrum, June, 1992
7. Kenneth S. Watkins, Jr., Ralph E. Pope, PCT application WO95/24757 entitled Electrical Safety Device, published 14 September, 1995, World Intellectual Property Organization.
8. Donald G. Fink, H. Wayne Beaty, Editors, "Standard Handbook For Electrical Engineers," Twelfth Edition, McGraw-Hill, 1987.
9. Donald Fink, Donald Christiansen, Editors, "Electronic Engineers' Handbook, Third Edition," 1989.
10. Ahmad Hammoud, Mark W. Stavnes, Editors, "First NASA Workshop on Wiring for Space Applications," NASA CP-10145, NASA, Washington, D. C. (Held July 23-24, 1991).
11. (Authors Not Available), "Second NASA Workshop on Wiring for Space Applications," NASA CP-3244, NASA, Washington, D.C. (Held Oct. 6-7, 1993.)
12. Ahmad Hammoud, Mark W. Stavnes, Editors, "Third NASA Workshop on Wiring for Space Applications," NASA CP-10177, NASA, Washington, D. C. (Held July 18-19, 1995).
13. Ralph E. Pope and Kenneth S. Watkins, U. S. Patent No. 5,541,803, "Electrical Safety Device," issued July 30, 1996.
14. A. Brent Strong, "Plastics: Materials and Processing," Prentice-Hall Inc., 1996.
15. V. E. Gul', "Structure and Properties of Conducting Polymer Composites," VSP, The Netherlands, 1996.