FAILURE ANALYSIS OF RUBBER PROTECTIVE GLOVES

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Abstract

Line mechanics working with energized distribution lines up to 34.5 kV are double glove protected by a Class 4, rubber insulated glove-sleeve worn under a leather glove. Localized surface crazing was noted in both older and relatively new rubber gloves. Discharge during in-house tank testing confirmed this damage impacts glove integrity. Analytical investigation shows the damage results from mechanical fatigue. Results suggest the following other causes for concern; corona damage, depletion of antiozonant and the transfer trace metal contaminants known to accelerate rubber degradation.

Introduction

Damage with the appearance of fine crazing was noted in the Class 4 rubber protective gloves worn by line mechanics working with energized distribution lines up to 34.5 kV. During use, the rubber gloves are protected from mechanical damage by an all leather top glove.

The crazing appears isolated to the following locations:

- in the palm area adjacent to the well between the fourth and fifth fingers and

- in the palm area adjacent to the well between the thumb and first finger.

There are documented instances of this damage appearing in new gloves after only several hours of use. Very preliminary observations from the qualification of a second leather glove supplier suggested the new rubber-leather glove combination is not as susceptible to this damage.

Initial work focused upon analytical characterization of the leather and rubber gloves so as to better understand their composition. Subsequent work focused upon analysis of the damage with the goal of identifying the sources so that the appropriate preventative actions could be instituted. Parallel work focused upon understanding the discrepancy between the two leather top gloves.

Samples

Several sets of new and well used gloves were supplied. The collection included leather gloves from both suppliers. Sections of high voltage conductor were also provided.

Results

Analysis of Leather gloves

A variety of analytical testing was performed to characterize the leather protective glove from the current supplier. Thermal Gravimetric Analysis (TGA) shows a 8-12% low temperature mass loss which results from loss of water. Single step decomposition is visible above 300°C. Results show ~5% inorganic residue after switching from nitrogen to oxygen purge at 800°C. Energy Dispersive X-ray Spectroscopy (EDX) shows this residue is primarily chromium (~85%) with small amounts (~5%) of silicon and phosphorous (Figure 1). The presence of chromium suggests the leather underwent chromium tanning. Tanning reportedly creates “cross-links” between proteins thus strengthening the final product.

One initial hypothesis suggested that the observed damage may result from incompatibility between rubber and additives, conditioners and oils in the leather gloves. Thermal desorption Gas Chromatography Mass Spectroscopy (TD-GC/MS) was used to characterize low molecular weight volatiles in the leather (Figure 2). The following compounds were prevalent: 2-phenyl tridecane, hexadecanoic acid, hydrocarbon mixture, water and morpholine. Hexadecanoic acid is present in some animal fats and thus may be intrinsic to the hide. The hydrocarbon mixture may reflect the presence of leather conditioners. Morpholine is reportedly a component in leather polish and an antimicrobial agent for leather. None of the compounds identified raised a red flag.

In light of initial observations suggesting that rubber gloves worn with the leather top gloves from the second supplier maybe less susceptible to damage, leather gloves from supplier B were also evaluated. TGA results were similar. EDX of ~6% inorganic residue isolated by TGA shows it is predominantly chromium

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(~35%) and oxygen (~47%) with lesser amounts of sodium, aluminum and silicon (~5%).

Analysis of Rubber glove

The submitted Class 4 rubber protective glove consists of a thick yellow rubber inner layer and a thinner black rubber top coat. Fourier Transform Infrared Spectroscopy (FTIR) suggested both layers are filled polyisoprene. Differential Scanning Calorimetry showed a distinct glass transition temperature at approximately -60°C as expected and no hint of any crystallinity. Both layers show a small, low temperature (<150°C) mass loss (~0.5%) by TGA which may reflect the loss of processing aids. This is followed by a single step decomposition >300°C. The onset of thermal decomposition was consistently slightly higher in the yellow layer thus suggesting it is slightly more thermally stable than the black top layer. This trend was also supported by Oxidation Induction Temperature (OITemp) experiments. Both layers show ~ 14% inorganic residue which EDX suggests is predominantly zinc (~50%), silicon (~20%), sodium (15%) and aluminum (~8%) in the black layer and zinc (~50%), silicon (~10%), sodium (10%) and titanium (20%) in the yellow layer.

Low molecular weight volatiles were characterized by TD-GC/MS and are summarized in Table 1. The more predominant species are denoted by "XX". The two compounds of particular interest are Antioxidant #1 and the unknown cyclic (MW 226).

Antioxidant #1 is a hindered phenol type antioxidant added to protect the rubber from oxidation degradation. The attack of rubber by atmospheric oxygen is a free-radical reaction accelerated by heat and by long term use above room temperature. It typically proceeds rapidly and results in chain scission, crosslinking and the generation of oxygen containing functional groups (i.e. carbonyl, aldehydes, etc.). The resulting changes in surface polarity will impact electrical resistance and susceptibility to biological attack. The resulting change in molecular weight has a significant impact on mechanical properties. Hindered phenols, like Antioxidant #1, sacrifice themselves by reacting with the free radical. The resulting reaction product is stabilized by aromatic resonance and thus rendered harmless. Once thus reacted, the antioxidant molecule becomes inactive thus this additive is consumed with time.

The MS spectra for the unknown (possible cyclic, MW 226) suggests the presence of aromatic group and -N-N=O groups. These groups are seen in some chemical antiozonants. Like oxidation, ozone attack in the presence of oxygen results in cleavage of the C=C bond and the generation of oxygen containing functional groups. Chemical antiozonants, such as alkyl aryl amines and para-phenylenediamines, react more readily than C=C and diffuse from the bulk to the surface as needed. Once reacted, they remain at the surface resulting in the buildup of a dark-colored protective film which acts as a gas barrier. This film continues to thicken and self-heal with further migration until the antiozonant is depleted.

Scanning Electron Microscopy images shows the undamaged surface consists of fused particles (Figure 3). The particle size, uniformity and degree of fusion are a reflection of the glove manufacturing process.

Analysis of Damage

Although the original intent of this study was to evaluate the "crazing" damage noted in the rubber protective gloves, visual examination suggested four types of damage of possible concern:

1. "crazing", in the palm between the fourth and fifth fingers and between the thumb and first finger,
2. dull areas, most prominent at the finger tips and along the finger backs,
3. surface streaks running down the cuffs and
4. perforating hole, generally associated with the "crazing".

Most of the used gloves showed one or two of the above described damages. It was rare to find all four within one glove. Each of these will be discussed individually.

"Crazing"

Optical and SEM images of this damage can be found in Figures 4 & 5. The SEM images show inter-particle fracture. Cross-sectioning shows these fractures occasionally penetrate to significant depths (~150um). None penetrated into the yellow rubber layer below.

This damaged has been referred to as "crazing" because it visually resembles crazing in other polymers such as polymethyl methacrylate and polycarbonate. Crazing typically results from chemical incompatibility and is not common in rubber products. Cracking is reported and typically results from either mechanical fatigue or chemical attack.

Mechanical fatigue of rubber results in cracks which nucleate and grows from pre-existing flaws such as filler agglomerates, impurities, nonuniformity (i.e. additives, crosslinking) or imperfections in mold surfaces. To determine if mechanical fatigue was a possible root cause here, a section of rubber (~4"x~2") was removed from a new glove cuff. This section was wrapped around the section of high voltage cable provided such that the black rubber surface was in direct contact with the cable. The section was grasped firmly then twisted back and forth several times in an attempt to mimic in-use handling. Visual inspection showed this resulted in a series of relatively parallel micro-creases similar in organization to the observed “crazing”. SEM confirmed these are accompanied by small inter-particle tears. This would seems to suggest that mechanical fatigue is a likely source for the observed “crazing”.

When wearing the current leather protective glove over the rubber glove, it was noted that bulky seams in the former create distinct high points at the very locations of the observed crazing. These seam “bumps” would be forced into the rubber glove whenever the line mechanic grapples with the high voltage conductor. Subsequent lateral movement during gripping would result in creasing and micro tears in the observed configuration. The seam configuration in the secondary supplier is completely different and does not exhibit bulk in these areas. This explains the apparent elimination of this damage by switching leather glove suppliers.

Rubber cracking also results from environmental or chemical attack (UV, oils, ozone, and oxidation), possibly due to the formation of an inelastic “skin”. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) is a highly surface sensitive mode of FTIR and well suited to monitor the functional group changes expected to result from oxidation and ozone attack. Although spectral differences were noted neither the used nor “crazed” surfaces show the growth of oxygen containing functional groups.

Although it proved impossible to confirm that the black rubber had been weakened by oxidation or corona attack, these analytical results do suggest that the potential for this type of attack is higher in the used and “crazed” areas. This conclusion can be made for the following reasons:

1). EDX spectra collected from six different areas within the “crazed” surface show the presence of chromium. This element is not expected to be in the rubber and it was not found on any of the other rubber surfaces examined. Its presence reflects migration from the leather to the rubber in areas of intimate contact such as those noted in “crazed” areas. It is important to note that oxidation and ozone attack is reportedly accelerated by the presence of certain trace metal contaminants such as chromium. Subsequent TGA and OITemp confirm that the “crazed” surface is slightly more susceptible to thermal degradation and oxidation.

2) TD-GC/MS of black and yellow rubber from new, used and crazed regions show a prominent drop in the concentration of the unknown cyclic compound suspected to be an antiozonant (Figure 6). This suggests that the glove is exposed to significant ozone in use and that the antiozonant is being consumed, as is expected, to form a protective layer. The concentration is extremely low in the “crazed” surface thus suggesting future protection against ozone attack may soon be compromised.

Similar trending of the antioxidant shows its level increases in the damaged region (Figure 7). The antioxidant is also expected to migrate from the bulk to the surface to provide the necessary protection. The increased surface area in the “crazed” region may be responsible for the observed trend. This result suggests oxidation damage maybe of lesser concern.

It was of interest to note that similar analysis on the leather glove shows the presence of Antioxidant #1 in leather taken adjacent to the “crazed” region. This again suggests very close contact between the leather and rubber in the damage prone area.

Dullness

Several of the gloves exhibited pronounced dullness at the finger tips and along the backs of the fingers (Figure 8). In many cases, this dullness was surrounded by dark, shiny areas. SEM images (Figure 9) show this corresponds with texturally rough areas surrounded by relatively large, smooth surfaced “islands”. It was proposed that this may result from erosion/vaporization in the dull regions accompanied by either re-deposition of low molecular weight material or melting and coalescence of granules in surrounding areas. Corona damage was suspected.

To confirm, a section from a rubber glove was placed on a grounded piece of aluminum and exposed to the direct discharge of a tesla coil (Figure 10). After approximately 5 minutes, a small dull region surrounded by a dark, shiny region was seen. The induced damage was visually identical to that seen on the used gloves.

Surface streaks

Several of the gloves exhibited pronounced surface streaks running down the cuff (Figure 11). Their appearance and configuration is suggestive of draining fluid, perhaps after wet cleaning. SEM images of these same areas (Figure 12) show localized loss of surface granules in a linear pattern. Subsequent discussion revealed that this streaking is often visible on brand new gloves and thus must result from variation within the manufacturing process.

Perforating Hole

Occasionally cylindrical holes were found associated with the crazing damage (Figure 5). SEM images (Figure 13) show the pinhole (~450um diameter) is surrounded by splay. This damage results from discharge during the in-house tank testing used to validate glove integrity. Its association with regions of crazing confirms the latter's negative impact on glove integrity with regards to electrical insulation.

Conclusions

The submitted Class 4 rubber protective gloves showed four distinct types of damage: "crazing", dullness, streaking and perforating hole. Subsequent analytical investigation suggests the "crazing" may result from mechanical fatigue induced by bulky seams in the leather top gloves. This failure may be exacerbated by transfer of chrome from leather and depletion of protective additives. The former is expected to accelerate oxidative degradation. Dullness noted at the fingertips and finger crests appears to reflect corona damage. The streaking noted down the glove cuffs are a surface defect induced by the manufacturing process. The perforating hole associated with the "crazing" is a result of discharge during glove integrity testing.

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Key Words

rubber failure analysis chrome leather corona fatigue

	Yellow layer	Black layer
Antioxidant #1	**XX ***	**XX**
Hexadecanoic acid	X	X
Octadecanoic acid	X	X
mixture hydrocarbons	X	
Unknown (possible cyclic, MW 226)	**XX**	**XX**
Unknown (possible cyclic, ~20.8min)	X	X

* More predominant compounds are denoted by "**XX**"

Table 1: Low molecular weight compounds in rubber, identified by TD-GC/MS

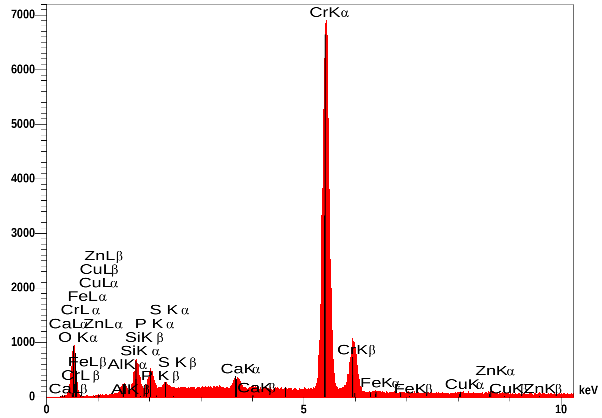

Figure 1: EDX of inorganic residue after above TGA.

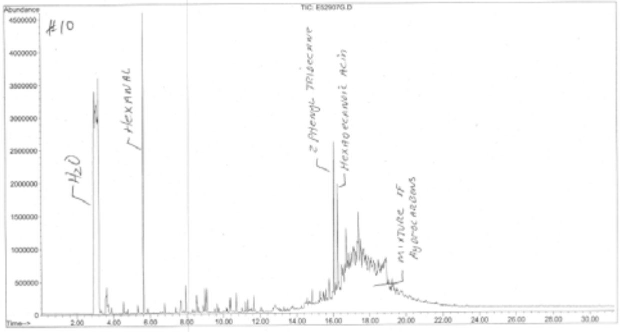

Figure 2: TD-GC/MS of new leather glove from the current supplier (200’C, 2 min delay).

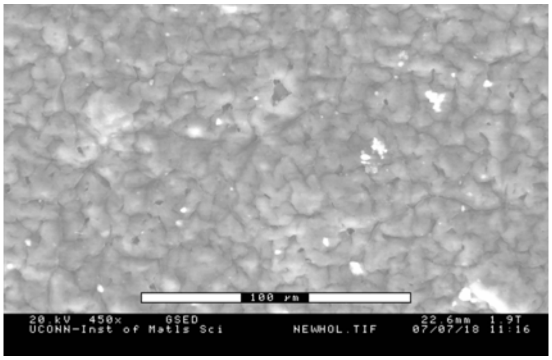

Figure 3: SEM image of black rubber outer surface, undamaged region.

Figure 4: Optical microscopy image of “crazing” damage and perforation hole in black rubber outer surface.

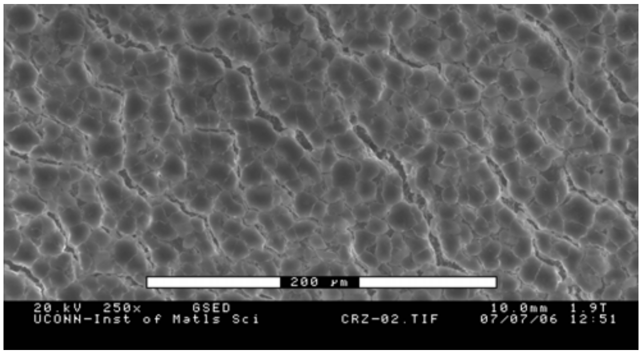

Figure 5: Higher magnification image of crazed surface. (SEM)

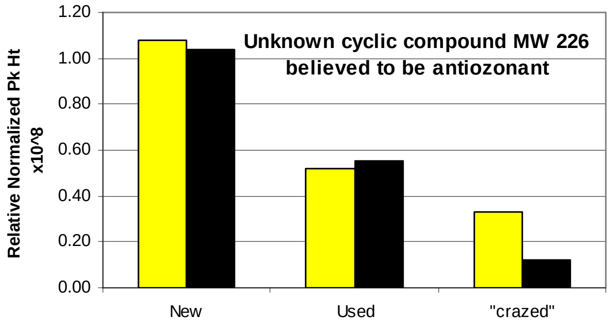

Figure 6: Change in level of suspected antiozonant with use (TD-GC/MS).

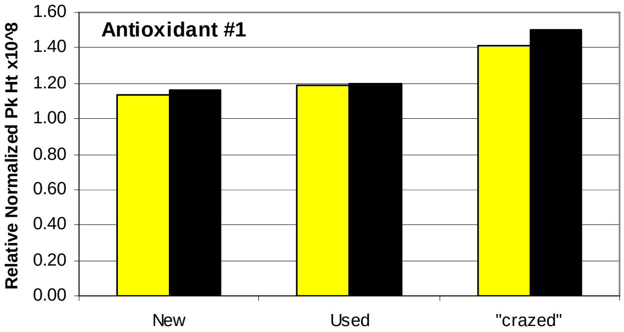

Figure 7: Change in level of antioxidant with use. (TD-GC/MS)

Figure 8: Image showing dullness at the fingertips of a used rubber glove.

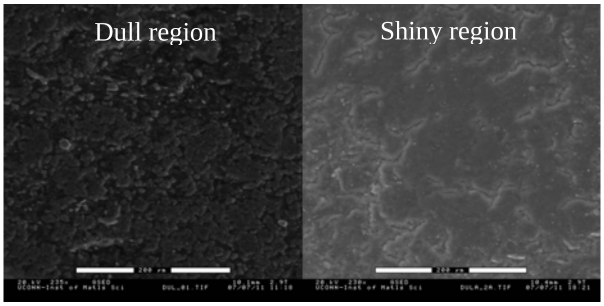

Figure 9: Higher magnification (SEM) images of dull and surrounding shiny regions shown in above image.

Figure 10: Inducing corona damage in the lab via tesla coil.

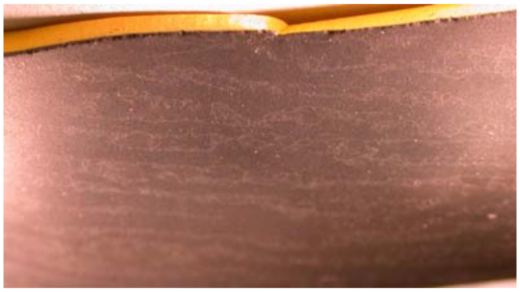

Figure 11: Image showing streaking down cuff.

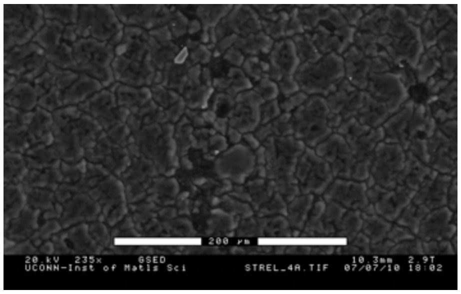

Figure 12: Higher magnification (SEM) images of streaking shown in above image.

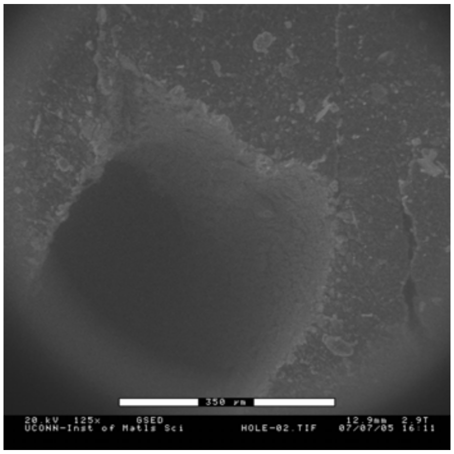

Figure 13: Higher magnification (SEM) images of pinhole similar to the one shown in Figure 4.