Investigating premature degradation of NR dry suit seals

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Natural rubber-based dry suits commonly are used for cold water diving expeditions. Face, neck and wrist seals are bonded to the dry suit and are trimmed to assure proper fit for the end user. Some of these dry suit seals have been failing unexpectedly, well before their expected useful lifetime. As shown in **Fig. 1**, the sealing areas appear to have a "melted" appearance consisting of shiny patches of black, sticky, degraded rubber. The premature degradation of the seals has been occurring for years and appears to escalate during the summer months. Degraded seals were discovered primarily in seawater dives, but the same type of degradation also was identified in a suit used exclusively in fresh water.

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The purpose of this investigation is to determine the root cause of the premature degradation of the face, neck and wrist seals used for diving expeditions. A combination of the following analytical techniques will be employed: Attenuated Total Reflectance–Fourier Transform Infrared (ATR–FTIR) Spectroscopy, Thermal gravimetric analysis (TGA), Pyrolysis-Gas Chromatograph/Mass Spectrometry (PY-GC-MS), Inductively Coupled Plasma–Mass Spectroscopy (ICP–MS) and Scanning Electron Microscope–Energy Dispersive Spectroscopy (SEM-EDS).

Experimental
Materials

Table 1 summarizes the face, neck and wrist dry suit seals that were received for the investigation. Sample A is a virgin neck seal sample that was kindly provided by the seal manufacturer. For each dry suit, either used face, neck or wrist seals (B to F) were provided, and all samples displayed some physical sign of advanced degradation. The actual age of the dry suit seals unfortunately was unknown, but it is known that they were well within their expected service lifetime. After their use in a diving expedition, dry suits are normally hung up vertically to dry in a dark locker environment.

Experimental techniques

Infrared spectra were collected on a Fourier Transform Infrared Spectrometer (Thermo Scientific) with the attached Smart iTR accessory and inserted germanium window for use in the attenuated total reflectance mode, which allows for analysis of the first few microns of the sample surface. Spectra were measured using a series of 32 scans and a resolution of 4 cm⁻¹ and a DTGS KBr detector was employed. Spectra were recorded from 4,000 to 500 cm⁻¹.

A TGA250 thermogravimetric analyzer (TA Instruments) was

Executive summary

A series of dry suit face, neck and wrist seals displaying extensive evidence of degradation in terms of soft, black material and cracking have been analyzed. The soft and sticky material located primarily around the trimmed edges in the degraded seals was identified as oxidized natural rubber. The chlorinated rubber surface showed signs of cracking and chlorine level decreased as a function of the degree of degradation. The later stages of oxidation of natural rubber include hardening and rubber cracking.

The oxidation of the rubber likely is caused by the presence of transition metal elements such as iron (up to 550 ppm) and copper (up to 100 ppm), which were identified in high concentrations in the degraded samples. Metal contamination is taking place primarily from the outside of the suit. The direct detection of iron oxide particles on the sample surface suggests that the contamination is likely coming from the soil being stirred up with the water during diving expeditions.

employed to monitor the weight loss of a specimen while heating it from room temperature to 600°C in an inert atmosphere (nitrogen), at a rate of 20°C/minute, followed by heating in an oxidative atmosphere (air) to 800°C. The three temperature ranges employed for the measurement of weight loss were 100-300°C (low temperature volatiles), 300-500°C (polymer) and 610-630°C (oxidation).

Pyrolysis–Gas Chromatograph/Mass Spectrometry (PY-GC-MS) was carried out using a Trace Gas Chromatograph coupled with a DSQII Mass Spectrometer (Thermo Electron Corp.) for separation and detection, respectively, of the pyrolyzed samples.

The Inductively Coupled Plasma–Mass Spectroscopy (ICP-MS) analysis was carried out by a DRC-e inductively coupled plasma-mass spectrometer (Perkin-Elmer Elan). Quantitative analysis of the chemical elements present in a sample is possible down to 1 ppm (parts per million). Following ASTM D4004-06 Method D, 0.1 gram samples were accurately weighed into separate porcelain crucibles and reduced to ash at 550ºC for a minimum of an hour. The samples were cooled and accurately reweighed in order to determine the percentage loss upon ashing. In order to dissolve the remaining residue, 20 ml of 1:1 HCL was added to each crucible followed by heating at low temperature on a hot plate. The samples were cooled, transferred into separate 100 ml volumetric flasks and diluted to volume with

Fig. 1: Pictures of highly degraded wrist (left) and neck (right) seals used in Kodiak dry suits.
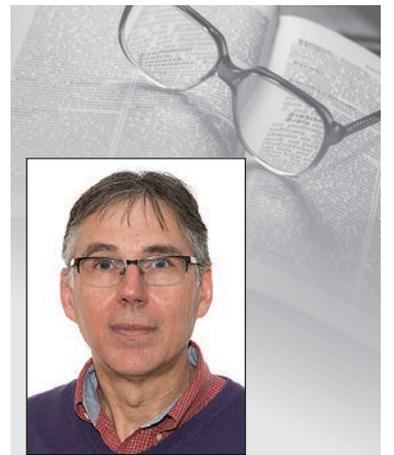
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deionized water and then analyzed by ICP-MS.

A tabletop Scanning Electron Microscope (SEM) (Hitachi TM3000) was used to take highly resolved images of the sample surface. The integrated Energy Dispersive Spectroscopy (EDS) unit allows for identification of elements within the first few microns of the sample surface. A rapid quantification is possible for elemental concentrations greater than approximately 0.2 weight percent. For measured values less than 0.2 weight percent, the concentration was reported as 0 weight percent.

A SZX16 stereo-optical microscope (Olympus) fitted with a digital camera (DP71) was used to obtain optical micrographs of the sample surface topology.

Results and discussion
Optical microscopy of seal degradation

Representative seals displaying the extent and features of the premature degradation (samples B, C and E) from **Table 1** were examined under low magnification on the optical microscope. Degradation was noticed directly on the sealing edge of the face seal of sample B as shown in **Fig. 2**. The degraded area consists of a shiny, soft and sticky rubber. Other areas away from the sealing area appear to be undamaged and elastic in nature upon stretching, showing little visual signs of degradation.

Fig. 3 displays the type of degradation observed in the neck seal of sample C. The normally trimmed sealing edge appears to have disappeared (melted) with some areas containing the black viscous material on the edge and an area away from the edge where this same viscous liquid may have flown. The wrist seal of sample E (see **Fig. 4**) illustrates a very high level of degradation comprising a combination of some black, shiny and soft material along the edge and an extensive array of cracking away from the edge area. The cracking area is composed of hard and embrittled rubber at the seal edge inward. All degraded samples in **Table 1** possessed the black, sticky material in the edge area of the seals. Some samples, such as the wrist seal (sample E) in **Fig. 4**, showed advanced degradation in addition to severe cracking and rubber hardening.

Investigation by ATR-FTIR
The ATR–FTIR spectrum of virgin neck sample A was compared directly to that of the shiny, black, viscous material of the heavily degraded seal of sample C as shown in **Fig. 5**. Sample A was analyzed on a freshly cut surface representing a cross-sectional edge. The characteristic =C-H out-of-plane deformation of poly(isoprene) at 843 cm^{-1} is readily observed in sample A, but hardly noticeable in sample C. In the oxidized sample, substantial growth of peaks in the 3,100-3,600 (-OH), 1,700-1,760 (C=O) and 1,300-1,000 cm^{-1} (C-O) regions is seen. These IR active vibrations are due to the presence of carbonyl type groups and are characteristic of the oxidative degradation of natural rubber. The soft degraded areas of all the samples showed similar IR spectra. Thus, the soft, black rubber was identified as degraded and oxidized natural rubber. No additional identification of the oxidized components by ATR–FTIR was possible.

Thermal analysis by TGA
Wrist sample E of **Fig. 4** along with the control neck sample A were analyzed in detail by TGA. Sample E was divided up into two families for testing: areas representing heavily degraded zones comprising soft rubber and cracking; and undamaged (good) areas away from the degraded zones that were still exhibiting elastic behavior with no visual signs of cracking. All TGA test results are summarized in **Table 2**.

The virgin sample A contains no plasticizers (no low temperature volatiles) and is highly polymer rich, reinforced with a small amount of carbon black (oxidative degradation) and containing small amounts of inorganic residues. Inorganic residues may be due to the addition of a mineral-based filler or the presence of a metal oxide such as zinc oxide, which is commonly used in combination with sulfur during the vulcanization of natural rubber compounds.

Examining the undamaged areas away from the degradation in sample E reveals significant differences by TGA. Compared to the control sample, the amount of low-temperature volatiles has increased by about 4 percent with the amount of polymer decreasing about the same level. Given the findings from ATR–FTIR, it is likely that the low-temperature volatile region comprises low molecular weight oxidized poly(isoprene), since base polymer concentration has been lost. It also appears that additional inorganic-based foreign matter is present (up to 0.4 weight percent compared to the control).

In summary, these areas of the dry suit seals display an onset of degradation but the material properties still are elastic and acceptable. The heavily degraded areas of sample E display low temperature volatile and base polymer degradation weight losses of 11 percent and 84 percent, respectively. These results clearly suggest that the base polymer is degrading into lower molecular weight molecules upon oxidation. The decrease in elastomer concentration contributes to the overall loss of rubber elasticity, increasing the viscous component of the viscoelastic material. Additional oxidizable chemical substances (about 1 to 1.5 weight percent) appear to present in the degraded areas. Apart from carbon black, the identification of these extra molecules cannot be inferred by TGA analysis. Furthermore, additional inorganic residues (up to 0.8 percent) are found in the degraded samples. These results suggest that the degraded areas contain a small amount of highly heat stable foreign matter (2 to 2.5 weight percent) in both organic and inorganic forms.

PY-GC-MS analysis
Pyrolyzed poly(isoprene) gives rise to a characteristic array of 4 primary retention peaks as displayed in **Table 3**. In addition, a molecular fragment at a retention time of 2.55 minutes was detected in the heavily degraded areas of sample E. The best match from the chemical database was methyl vinyl ketone. It is likely that this oxygen containing alkene is related to the mobile oxidation products being produced during the oxidation of poly(isoprene).

SEM-EDS sample analysis
SEM-EDS was the method of choice in order to analyze all dry suit seal samples. An SEM photograph of the sealing edge along with the large surface of the unused neck seal sample A is shown in **Fig. 6**. The large outside surface of sample A appears gray and composed of a network of fine, black cracks are confined to the surface layer. The straight sealing edge area possesses a black smooth surface due to the trimming process.

An elemental analysis was performed on both outside and inside large surfaces and the sealing edge of sample A in order to investigate any difference in chemical surface composition. These results are summarized in **Table 4**. Total carbon levels are much higher on the edge versus the large surface. Chlorine was detected in high levels on the large surfaces along with lesser amounts of sodium and silicone. On the black edge surface, neither chlorine, silicone nor sodium were detected. Both oxygen and sulfur levels were higher on the surface versus the edge. Rinsing the sample with de-ionized water (three times) did not significantly change the weight percent values. Furthermore, the outer and inner surfaces present similar values in surface chemical composition.

The high carbon level is due to the natural rubber base polymer and to a lesser extent, the carbon black reinforcing agent (as seen by TGA results earlier). As the chlorine is organic in nature since it is not removed by the de-ionized water, the rubber was chlorinated in order to improve its surface characteristics. This likely explains the contrast between the gray and black zones seen in **Fig. 6** (i.e. surface versus edge).

Surface chlorination is an effective method to reduce the coefficient of friction of natural rubber.[1-3] The modified surface characteristics increase the level of hydrophilicity due to the generation of chlorinated and oxidized structures.[2] The reduced coefficient of friction is advantageous for the donning process of rubber articles such as gloves.[3] Surface cracking, however, can

Table 1: Summary and description of dry suit seals samples received for the investigation. (*virgin sample).

Sample	Seal Type		
	Face	**Neck**	**Wrist**
A*		X	
B	X	X	
C		X	
D			X
E			X
F			X

Fig. 2: Sample B (face seal) showing degradation at the seal edge in a) and b).
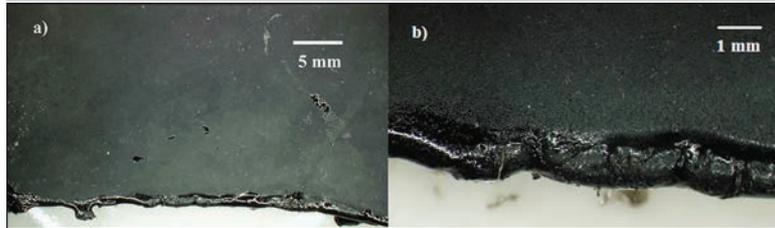

Fig. 3: The edge of the neck seal of sample C.

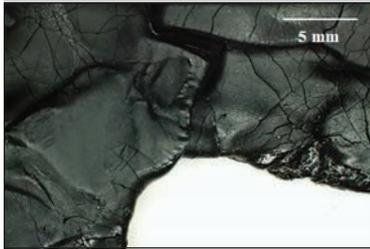**Fig. 4: Sample E showing the outer edge of the wrist seal.**

Fig. 5: Overlay of ATR-FT-IR spectra of the virgin sample A (bottom) and of the soft degraded area of sample C.
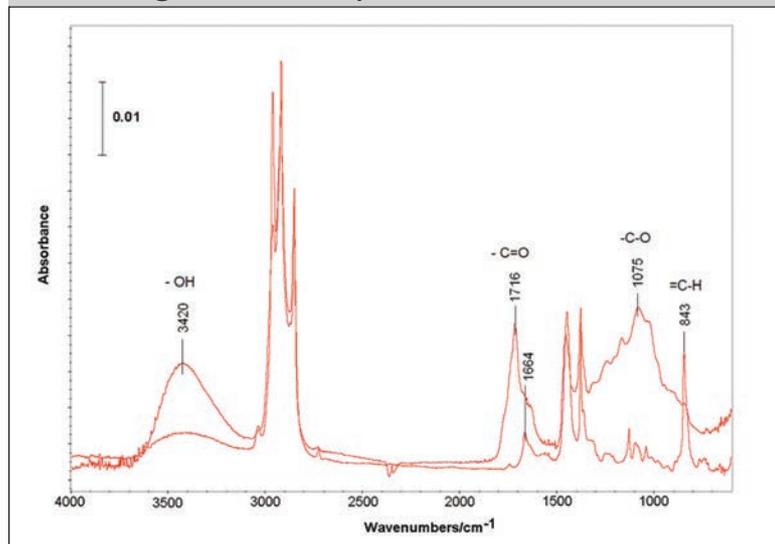

Table 2: TGA weight loss (%) results for samples A and E.

Sample	Low Temperature Volatiles	Base Polymer Degradation	Oxidative Degradation	Inorganic Residue
A	0	97.5	1.5	1.0
E (undamaged areas)	4.1	93.2	1.2	1.4
E (degraded zone)	11.0	84.4	2.8	1.8

Table 3: Summary of the primary peaks observed in samples A (control) and E (degraded area) and their identification by PY-GC-MS analysis. *Additional small peak present only in sample F.

Retention time (min)	M_w (g/mol)	Molecule Identification
2.55*	70	Methyl vinyl ketone
5.7	92	toluene
8.5	106	xylene
10.47	136	1-methyl-5-(1-methylethenyl)-(R)-cyclohexene
11.9	136	1-methyl-4-(1-methylethenyl)-(R)-cyclohexene

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develop for high levels of chlorination or extended reaction times, causing both surface roughening and, thus, reducing the thermal stability of the material.[2,3] The network surface cracking seen on the virgin sample in **Fig. 6** appears to be a by-product of the chlorination process. Crack propagation can occur from these defects upon stretching the dry suit. As tearing or ripping was not the major failure event, the surface cracking was not considered as a factor in the premature degradation of the dry suits.

A sulfur vulcanization system was used for crosslinking the natural rubber due to the high presence of sulfur. The higher sulfur concentrations on the large surface versus the edge is indicative of possible sulfur blooming. The presence of some silicone on the large surface area indicates the use of a silicone-based mold release agent to help in the demolding process. The presence of calcium could be related to the use of calcium oxide, calcium carbonate or a processing aid like calcium stearate.

The EDS analysis of the undamaged areas of the neck seal of sample B is shown in **Table 5**. The area examined showed no adverse degradation effects such as soft rubber or crack formation. The sample was also rinsed three times with de-ionized water. Before rinsing, the outside surface possesses significantly more chlorine, oxygen and sodium than the inside surface. Rinsing the sample brings about a loss of both sodium and chloride, likely due to the exposure to sea water. In addition, oxygen levels decrease after rinsing the outside surface, possibly due in part to the removal of oxygen containing inorganic based minerals containing zinc, calcium and magnesium. The inside surface possesses less chlorination on the surface (about 4 percent weight). Sulfur blooming is taking place toward both the outside and inside of the neck seal. No significant difference is observed in the elemental compositional of the matrix, which is given by the edge results in comparison with those in **Table 4**. Chemical compositional changes are taking place primarily in the surface layer of the degraded and used seals.

The EDS analysis on the face seal area of sample B shows some significant differences, depending on sample location (see **Table 6**). Square-like samples were taken around the face sealing area where extensive degradation (soft, black rubber) was noted. The low chlorine levels on the outside surface confirm that either chlorination did not take place or that the chlorinated barrier surface has been essentially removed due to wear or to aging effects on the seal.

Upon rinsing the sample, the chlorine and sodium levels drop together, indicating the presence of sodium chloride. Iron surprisingly was detected at levels just above 0.2 weight percent. The inside or reverse surface showed heavy areas of degradation indicated as black areas on the SEM images and consisted mainly of just carbon, oxygen and some sulfur. Moving away from the degradation toward where mineral salts were present confirmed the presence of sodium and calcium chloride, but a higher amount of chlorine indicating that the surface is chlorinated. Rinsing this surface removed the mineral salts but left the remaining chlorine levels high and comparable to the values seen in the neck region. Levels of iron on the inside surface were insignificant, signifying that iron contamination is coming from the outside of seal.

The degraded edge is comprised primarily of carbon, oxygen and some sulfur. Examining a cut edge about 2 mm away from the degraded edge caused the oxygen weight percent to drop almost 10 percent while the carbon level increased by about the same amount (see **Table 6**). This difference in oxygen content demonstrates the high level of oxidation of the rubber at the edge of the seal. This concurs with the fact that higher levels of oxidized rubber (volatiles) were reported earlier in the heavily degraded areas analyzed by TGA.

The topology of the outer surface of the used face mask seal (sample B) is heterogeneous as depicted in **Fig. 7**. EDS was used to attempt to identify the particles identified from 1 to 5 which are present on the sample surface. Some of the particles on the surface include clays (particles 1 and 4), silica (particle 3) as well as recrystallized sulfur from the rubber formulation (particle 2). Particle 5 was identified by EDS as containing predominantly iron and oxygen signifying that it is an iron-oxide-based mineral. Notwithstanding the sulfur, these mineral-based particles are contaminants not included in the rubber formulation. Given this finding, it was decided to continue the examination of the other degraded seals with particular interest to metal concentrations on the outside surface of the samples.

The outer surface of the wrist seal of sample E (see **Table 7**) contains a significant amount of iron (0.4 weight percent) and much less chlorine compared to a typical chlorinated seal sample. The inside surface shows evidence of 4 times more chlorine, and hence the chlorination process, since upon rinsing with de-ionized water, the chlorine count increased due partly to the removal of sodium chloride. The picture shown in **Fig. 8** attests to the remains of the chlorinated surface (white areas) in combination with an irregular surface morphology. There is a loss of the protective chlorinated surface due to wear and/or aging.

In summary, EDS analysis shows the loss of the protective chlorinated layer in the undamaged areas on both the inside and outside surfaces. Samples experiencing extensive loss of chlorine generally correlate to ones with the highest oxygen and lowest carbon levels. Iron contamination was evident, and in most of the cases when iron is detected, both chlorine and carbon levels are lower than normal, while oxygen levels are high. It also appears that when iron is present, there are also increased levels of both aluminum and silicone.

ICP-MS investigation

Given the high levels of metal contamination seen by EDS in many of the degraded samples, a representative sample (sample E wrist) was selected for an in-depth ICP-MS analysis. EDS confirmed quantitative concentrations of silicone, iron and aluminum on the surface in this particular sample (**Table 7**). The TGA results in the heavily degraded regions of sample E confirmed that inorganic residue concentrations increased by up to 1 weight percent. In order to check for transition metal ion contamination which may be the cause of the premature degradation comprising oxidized natural rubber, the concentrations of iron, copper and manganese were analyzed. The same test specimens that were analyzed by TGA (A control, E good and damaged areas) were used for ICP–MS. The percentage loss in weight upon ashing as well as the concentrations of iron, copper and manganese in µg/g (or ppm) are provided in tabular form in **Table 8**.

Upon ashing the samples, it was found that the degraded areas contained up to 1 percent by weight more inorganic residue in the heavily degraded areas (sample E degraded) versus other areas away from the degradation (sample E good). This observation agrees with the TGA results on the same samples. The control sample A had the lowest ash level as expected. These results confirm that inorganic residue levels are highest in the heavily degraded areas, followed by the undamaged areas of the same sample and, finally, lowest in the control sample. Low levels of iron, copper and manganese were measured in the control sample A, likely representing typical levels for a rubber based formulation. Iron levels display the highest increase in the heavily degraded areas, five times over the undamaged areas of sample E and 25 times higher than the control. Copper concentrations increased fourfold in all areas (good or heavily degraded) of sample E to an average of about 100 ppm. Manganese values are very low in the degraded samples. In parallel with the SEM–EDS results, these findings confirm the high concentrations of iron that are present in the used dry suits seals. These results also reveal that copper is present at significant concentrations (over 100 ppm). Iron concentrations are much higher in the heavily degraded areas where the sealing takes place suggesting that it is being transported to the sealing area.

Metal contamination

The preceding results and discussion point to the fact that metal contamination appears to be the key repeating element occurring in combination with the premature degradation. It is known that trace amounts of transition metals such as iron, cobalt, copper and manganese are enough to accelerate the oxidative degradation of natural rubber based products.[4-6] The oxidation rate has been shown to follow the sequence of Co^{2+} > Mn^{2+} > $Cu+$ > Fe^{3+}. The effectiveness of the ion as a catalyst was found to depend on the number of electrons transferred by the metal ion during redox reactions.[5] Transition metals catalyze the rubber oxidative reactions by accelerating the breakdown of peroxides which in

Fig. 6: SEM image displaying the large surface and edge portion of the unused sample A.
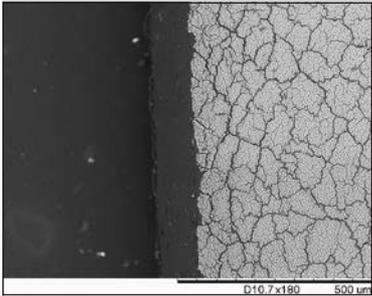

Table 4: Elemental analysis (wt%) by SEM-EDS of the large surfaces and edge of control sample A. Reported values are the average of three measurements.

| Element	Outside	Inside	Edge
C	74.3	72.7	95.3
Cl	16.5	18.5	0
O	6.7	6.4	3.7
S	1.1	1.0	0.4
Zn	0.4	0.3	0
Na	0.4	0.3	0
Ca	0.2	0.2	0
Si	0.3	0.3	0

Table 5: Elemental analysis (wt%) of the neck seal area of sample B. Elemental weights after rinsing are given in the rounded brackets. The edge represents a freshly cut surface.

Element	Outside	Inside	Edge
C	65.1 (70.2)	75.2 (78.2)	95.1
Cl	19.2 (17.2)	15.0 (13.0)	0.2
O	11.7 (9.6)	6.7 (6.6)	3.5
S	1.6 (1.6)	1.3 (1.1)	0.6
Zn	0.3 (0)	0 (0)	0
Na	1.8 (0.4)	1.0 (0.3)	0
Ca	0.3 (0)	0.5 (0.4)	0
Si	0.2 (0.3)	0 (0)	0
Mg	0.2 (0)	0 (0)	0

Table 6: Elemental analysis of the face seal area of sample B. Elemental weights after rinsing are given in the rounded brackets.

Element (wt%)	Outside Good area	Inside Degraded	Inside Good area	Degraded Edge	Fresh Cut Edge
C	81.0 (82.3)	88.3	71.0 (74.2)	84.1	94.3
Cl	**2.4 (0.8)**	0.2	**11.5 (13.0)**	0	0
O	11.2 (13.1)	10.4	10.9 (10.2)	**14.9**	**4.7**
S	1.0 (0.9)	0.3	1.3 (1.2)	0.2	0.3
Zn	0 (0)	0	0 (0)	0	0
Na	1.9 (0.6)	0.2	3.1 (0.3)	0	0
Ca	0.7 (0.7)	0	1.2 (0.2)	0	0
Si	0.5 (0.6)	0	0 (0)	0	0
Mg	0.5 (0.3)	0	0 (0)	0	0
Fe	**0.2 (0.2)**	0	0 (0)	0	0
Al	0.3 (0.3)	0	0 (0)	0	0

Fig. 7: Close-up of outer surface of the face mask seal (sample B) after rinsing in de-ionized water. Elemental composition of each of the particles: 1–potassium, aluminum, silicon, titanium. 2–sulfur, 3–silicon. 4–calcium, aluminum, silicon, oxygen. 5–iron, oxygen.

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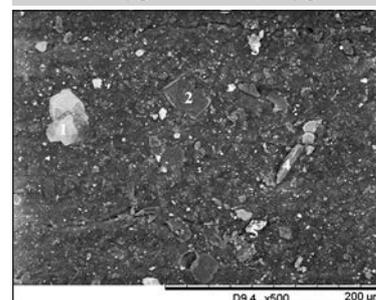
turn propagate the oxidation reaction. For example, compounds comprising natural rubber mixed with copper salts having concentrations of 0.02 to 0.06 weight percent (200 to 600 ppm) lose up to 50 percent of their tensile strength after heat aging for 12 days at 70°C.[6] The rate of oxygen absorption has been shown to increase dramatically after 6 hours for a natural rubber sample containing approximately 1.7 percent by weight of iron.[7] Fe^{3+} ions were shown to have more catalytic action than Fe^{2+} ions on oxidative degradation of crepe rubber, and total iron concentrations were recommended not to exceed 30 ppm in the rubber for optimal storage stability.[8] The final result of transition contamination is chain degradation with loss of molecular weight and the production of small, oxidized, labile molecules of poly(isoprene).

Given the extremely low concentration of dissolved iron, copper and manganese in sea water (see **Table 9**), and that discrete mineral particles were observed by SEM on the outside surface of the samples, it is likely that the metal contamination is coming from the soil environment. **Table 10** lists the average values for selected surficial element concentrations in soils tested across the U.S. It is not unreasonable to expect similar values for the geology of Canada and for the soil found in ocean or sea beds. Silicon, which is found in sand (silicon dioxide), and many components of clays like aluminum, calcium and potassium dominate the list. Of particular interest is the high concentration of iron and the presence of both manganese and copper. Suit contamination from soil containing a form of iron is a good probability for divers walking on ocean or sea beds.

Poly(isoprene) oxidation

The generally accepted oxidation mechanism for poly(isoprene) has been summarized in **Fig. 9**.[11] The oxidation of poly(isoprene) commences with the reaction of oxygen at the tertiary center of the isoprene group giving rise to a stable cycloperoxide. Radical transfer takes place onto the neighboring tertiary carbon center. Repetitive reaction with oxygen leads to a clustering of oxidized polymer in a localized area along the chain backbone. Application of heat causes these clustered cycloperoxides to decompose, provoking chain cleavage and loss of molecular weight. Transition metals accelerate cycloperoxide decomposition. Small molecules such as levulinaldehyde are released during the process and the material softens. Other small oxidized molecules are possible containing end groups such as carboxylic acid and alcohol. The presence of the methyl vinyl ketone that was observed by PY-GC-MS for the oxidized natural rubber in the degraded dry suit seals can be explained by the breakdown of levulinaldehyde by pyrolysis into two fragments, namely formaldehyde and methyl vinyl ketone.

Natural rubber under longer conditions of time and heat/oxygen exposure will exhibit hardening due to subsequent secondary oxidation reactions, which tie up the polymer chains due to crosslinking. This mechanism would explain the presence of cracking seen in the heavily oxidized samples.[12]

Premature seal degradation explanation

In summary, metal contamination is taking place on the dry suit seals from the outside surface. In terms of concentration, iron—and to a lesser extent, copper—appear to be the metals of concern since they are widely known to accelerate oxidation reactions in natural rubber. Some of these metals in the dissolved ionic state are able to penetrate into the subsurface beneath the chlorinated surface of the seal. Catalyzed oxidative reactions also are possible on the chlorinated surface and possibly within the fine surface cracking network. This may, in part, explain for some of the deterioration of the chlorinated surface seen in the SEM micrographs for the degraded samples. Once oxidation is initiated, it is known to increase exponentially. Small and labile oxidized degradation by-products such as levulinaldehyde appear to preferentially migrate like a plasticizer within the polymer matrix due to the effects of gravity for a hung dry suit. At the same time, metal ions such as iron appear to be dragged along with the oxidized natural rubber molecules to the seal edge which is non-polar in nature (non chlorinated) where they can easily exude from the seal. The increased concentration of metal ions near the seal edge will only worsen the effects of degradation, causing continued localized deterioration of the sealing area. This proposed mechanism can explain the appearance of the viscous rubber material around the trimmed edges of the seals.

Assuming that a regular maintenance and rinsing schedule of the dry suits is followed in order to decontaminate the outer surface of the dry suits, certain antioxidants are highly effective in reacting with metal ions to form inert complexes through chelating. Dry suit seals made with additional antioxidants effective against iron and/or copper contamination may help to prolong the life of the dry suit seals and slow down the oxidation effect in the natural rubber. Finally, creams, skin lotions, insect repellents and sunscreens containing transition metal elements such as iron, copper or manganese should not be used when wearing the dry suit as they will accelerate the premature aging of the seals.

Conclusions

A series of dry suit seals (face, neck and wrist) displaying extensive evidence of degradation (soft, black material and cracking) have been analyzed. The soft and sticky material located primarily around the trimmed edges in the degraded seals was identified as oxidized natural rubber. The protective chlorinated rubber surface is partially or completely destroyed in samples showing degradation. The later stages of oxidation of natural rubber include hardening and rubber cracking. The oxidation of the rubber is being caused by the presence of transition metal elements such as iron, which were identified in high concentrations (550 ppm) in highly degraded samples. The presence of copper also was identified in concentrations of 100 ppm. Transition metal elements are well known to speed up the oxidation degradation reaction of natural rubber. Metal contamination is taking place primarily from the outside of suit (not from the inside). The detection of iron oxide particles on the sample surface suggests that the contamination could be coming from the soil stirred up with the water during a diving expedition. Other sources of contamination also might be possible. It appears that the oxidized natural rubber products, which include levulinaldehyde, a well-known oxidation product of natural rubber, easily can migrate toward the non-polar trimmed areas where it blooms and gathers at the edge bringing along with them, the transition metal ions such as iron. Degradation can therefore be enhanced in this region causing the appearance of more black viscous rubber. Solubility and diffusion effects dictate this phenomenon.

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Table 7: Elemental analysis (wt%) near the degraded area of wrist seal sample E.

Element	Outside	Inside
C	71.0	74.2 (74.8)
Cl	1.3	4.0 (5.5)
O	20.9	17.0 (15.7)
S	0.7	0.8 (0.9)
Zn	0.2	0 (0)
Na	0.8	0.4 (0)
Ca	0.4	0.2 (0)
Si	3.5	3.0 (2.4)
Mg	0.3	0 (0)
Fe	0.4	0 (0)
Al	0.4	0 (0)
K	0.2	0 (0)

Fig. 8: SEM photograph of the inside surface of wrist seal sample E.

Table 8: Micrograms/gram or parts per million (ppm) of Fe, Cu and Mn on samples A and E as determined by ICP-MS. Reported values are the average of 3 measurements.

Sample	Ash (wt.%)	Fe (µg/g)	Cu (µg/g)	Mn (µg/g)
A	0.7	20	30	<1
E (good)	1.1	110	120	2
E (degraded)	2.2	550	100	8

Table 9: Ionic concentrations of some of the major inorganic elements found in sea water at 3.5% salinity.[9]

Element	Concentration (ppm or µg/g)
Sodium	10,800
Chlorine	19,400
Magnesium	1,290
Sulfur	904
Potassium	392
Calcium	411
Manganese	0.0004
Iron	0.0034
Copper	0.0009

Table 10: Selected element concentrations in soils in conterminous U.S.[10]

Element	Concentration (ppm)
Silicon	310,000
Aluminum	72,000
Iron	26,000
Calcium	24,000
Potassium	15,000
Sodium	12,000
Magnesium	9,000
Titanium	2,900
Sulphur	1,600
Manganese	550
Copper	25

Fig. 9: Summary of oxidation mechanism to explain the degradation of poly(isoprene) leading to chain cleavage and softening and finally the liberation of small volatile molecules such as levulinaldehyde (adapted from ref. 11). Under pyrolysis conditions, the levulinaldehyde continues to b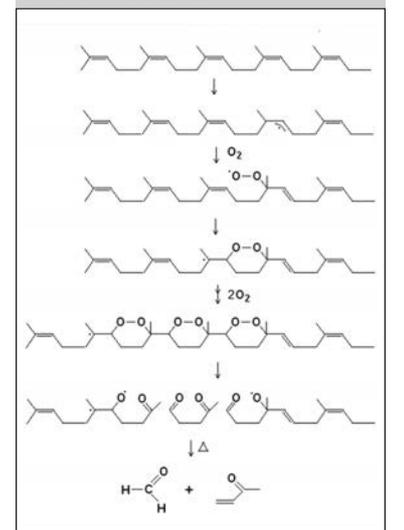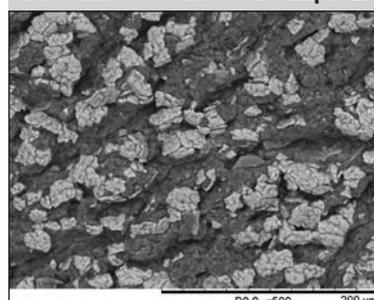reak down into smaller molecules.