EXPERT KNOWLEDGE
FAILURE ANALYSIS
OF ELASTOMER COMPONENTS

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Ozone Cracks on Elastomeric Seals and Components:
A Common, But Preventable Cause of Failure

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1. Classification and Frequency of Failure

Out of the four main failure mechanisms, ozone cracks are classified in the second group mentioned below:

1. Media
► **2. Temperature / Aging**
3. Mechanical / Physical Damages
4. Manufacturing Errors

According to the analysis of more than 2000 failures processed by our laboratory, ozone cracks are among the 5 most common causes of failure of elastomeric seals.

2. Professional Background Knowledge about Damage Symptoms

Ozone is reactive oxygen (O_3) which, in proximity to earth, is produced mainly during the reaction of nitrogen oxides with oxygen under the influence of UV-radiation.[1] The ozone concentration in proximity to earth is 2-50 pphm depending on environmental impact (temperature, humidity, wind, pollution, season, etc.).[2]
It has already been known for 150 years[3] that natural rubbers can be severely damaged by ozone found in ambient air. At the beginning of the 20th century, relations were explored in detail by HARRIES.[4] Later, it was detected that some synthetic rubbers are also affected by this phenomenon. Despite these insights, even today, the failure is often found in practice.
An important precondition for ozone cracks is that the seals are stressed or deformed. Deep cracks can already develop at minor stretching (e.g. 5%). When stretching increases, more cracks evolve. Due to the great depth of cracks this is usually unacceptable for the application.
All unsaturated rubbers, i.e. diene rubbers that have double bonds in the main chain, are prone to the development of ozone cracks. The double bonds can be attacked by ozone. Diene rubbers can be identified by the 'R' in their short term (e.g. NB**R**, SB**R**, N**R**, B**R**,…). An exception is a fully hydrogenated HNB**R** that has a relatively good resistance against ozone cracks. M-, Q- and O-rubbers (like e.g. FP**M**, VM**Q**, EC**O**) are regarded as having good to very good ozone resistance.

3. Damage Symptoms

3.1 Description of Damage Symptoms and Problematical Areas

Ozone cracks always develop vertical to the direction of stress. Cracks are deep and can lead to the tearing of the seal. The damage is irreversible and can only be rectified by the replacement of the seal.

[1] TRIMBACH, Jürgen: Schutz von dienhaltigen Elastomeren gegen Ozonrisse in: GAK – Gummi Fasern Kunststoffe, Dr. Gupta-Verlag, Ratingen, Heft1 / 2015, 68.Jg., S. 30
[2] Ibid., S. 30
[3] „Ozonisirter [sic!] Sauerstoff greift die Gutta[percha] stark an." ('Ozonized Oxygen severely attacks the gutta-percha.') in: KOPP, H und WILL, H. (Hrsg.): Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften für 1859, J. Ricker'sche Buchhandlung, Giessen, 1860, S. 519
[4] HARRIES, Carl Dietrich: Ueber den Abbau des Parakautschuks vermittelst Ozon in: Berichte der deutschen chemischen Gesellschaft, Commissionsverlag von R. Friedländer & Sohn, Berlin, 37. Jg., Juni **1904**, S. 2708-2711

Figure 1: Pre-installed NBR O-Ring, severely cracked after several weeks of storage

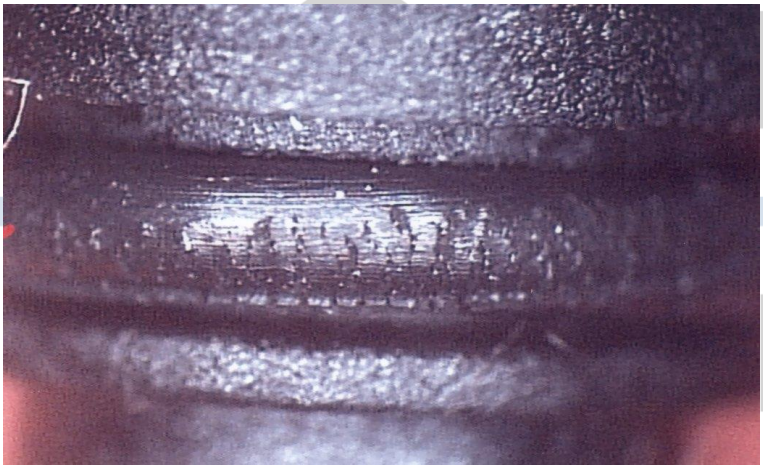

Figure 2: The development of ozone cracks resembles the formation of fatigue cracking, example NBR O-Ring

Figure 3: Cracks on a static pre-stretched bellow made of a BR/IR-elastomer

3.2 Effects of Damage

Leakages up to sealing failure (tearing of seal) and consequently failure of the overall system can occur due to ozone cracks.

3.3 Differentiation from Similar Damage Symptoms

The damage symptoms of ozone cracks resemble closely the damage symptoms of fatigue cracking by cyclical dynamic stress. If the history, or the kind of stress, is known, a clear differentiation is possible. The difference to chemical degradation is shown in the greater depth of cracks and in stress-dependent cracks, which appear usually in parallel alignment. Frequently, ozone cracks are found on pre-installed assemblies if they are exposed directly to ambient air during intermediate storage. Cracks can even develop after a few days.

Figure 4: Fatigue cracking on FKM-membrane

Figure 5: Cracks after chemical degradation (30x magnification)

4. Preventive Measures

- Change of rubber formula (e.g. use of antiozonant or antiozonant wax)
- Coating of seal, which reduces ozone attack, even grease or oil can lead to a significant improvement of ozone protection
- Blending of eroded rubber with ozone resistant rubbers or PVC
- Use of higher-value and ozone resistant M-, Q- or O-rubbers (however, often resulting in higher costs)
- Design measures (e.g. reduction of ambient air admission to damaged seal or minimization of gas admission by circulation with fluids)
- Logistical measures: Never store seals prone to ozone cracking in stressed condition.

5. Practical Tips (Testing Possibilities / Standard Recommendations)

If unsaturated elastomers in deformed condition are exposed to ambient air in the application for a longer period of time, an ozone resistance test (ISO 1431) is recommended (see **Figure 6**). If possible, this test should be performed directly on the finished part to check the effectiveness of the applied ozone protection in the compound. At the Richter O-Ring Test Laboratory two ozone test cabinets are available (see **Figure 7**). The ozone test at the O-Ring Test Laboratory was accredited in 2016. Both Ozone cabinets are continually monitored by an independent ozone measuring station.

Figure 6: Example of elastomer specimen after ozone test (condition after 48h / 40°C / 20% stretching / 50 pphm ozone concentration / 55% relative humidity): Sample is still in stretched condition and has long, moderately wide cracks (stage 2 assessed based on DIN 53509) (10x magnification)

Figure 7: Performance of ozone test: Employee of Richter O-Ring Test Laboratory in front of an open ozone cabinet

6. Miscellaneous

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