

EXPERT KNOWLEDGE FAILURE ANALYSIS OF ELASTOMER COMPONENTS

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Autoxidation – Rubber Poisons Can Rapidly Accelerate Elastomer Aging

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1. Classification and Frequency of the Damage Pattern

Of the four main damage mechanisms, autoxidation is assigned to the 2nd main group:

1. Mediums
- ▶ **2. Temperature / Aging**
3. Mechanical / Physical Effects
4. Manufacturing Defects

The 2nd main group can be divided into four subgroups: overheating, wrong material for the application, poor formulation and aging. Aging can be caused by external factors such as ozone, fatigue or heavy metals. The latter, which are heavy metal ions such as manganese or copper, are the main cause of autoxidation.

This defect pattern caused failures on approx. 50 of over 2000 elastomer seals tested in the O-Ring Prüflabor Richter. This individual damage mechanism therefore has an important

practical significance, although it can hardly be found in the technical literature on sealing damage cases.

2. Technical Background Knowledge on the Damage Pattern

2.1 Definition of Oxidation / Autoxidation

Autoxidation¹ is a phenomenon that has long been described in the literature on the chemistry of elastomers. As the name suggests, autoxidation is an autonomous absorption of oxygen. As a rubber material ages, oxygen is absorbed from the ambient air and "partly bound in the vulcanization, partly released again in the form of carbon dioxide, water and other low-molecular oxidation products."²

Even small amounts of oxygen have a detrimental effect on elastomers, which can easily be seen from the strong decrease in tensile strength and elongation at break. The aging temperature influences the reaction speed of the oxygen with the rubber material; the higher this temperature is, the faster the aging reaction takes place.

The mechanism of oxidation, meaning the destruction of the elastomer network, is usually initiated by radicals, which can form as a result of high temperatures, mechanical stress, radiation and other causes. "The formation of peroxy radicals ($R\cdot + O_2 \rightarrow ROO\cdot$ therefore, $ROO\cdot + RH \rightarrow ROOH + R\cdot$), which form hydroperoxides and polymer radicals by abstraction of an H atom, is assumed to be the starting reaction of autoxidation."³ The destruction of the existing elastomer network takes place through a radical chain reaction initiated by decomposed peroxides or other radicals.

In the case of sulfur-crosslinked elastomers, hydroperoxides can also attack the crosslinking bridges. "The fission products (sulfoxides, sulfenic acid) do not participate in the chain reaction and act as antioxidants."⁴

During autoxidation, hardening may occur as a result of tighter post-crosslinking or re-crosslinking (cyclization) as well as softening due to chain splitting. Either one of these effects predominates or they occur relatively equally. This also explains the fact that both effects can occur on one and the same damaged seal. In the long term, these effects lead to depolymerization of the elastomer.

2.2 Rubber Poisons and their Effects

The term autoxidation is closely associated with the so-called rubber poisons. These are heavy metal complexes that act as catalysts for the relatively slow decomposition of hydroperoxide. This allows complete depolymerization in the typical temperature range of an elastomer to take place within a few months.

¹ Other English spellings: autooxidation, autoxydation, former English spelling: autoöxidation

² KEMPERMANN, Th.: Alterungsschutzmittel in: BOSTRÖM, Siegfried (Hg.): Kautschuk-Handbuch, Berliner Union, Stuttgart, Bd. 4, 1961, Kap. 2.8, S.355

³ RÖTHEMEYER, Fritz und SOMMER, Franz: Kautschuktechnologie, Hanser Verlag, München, 2001, S.339

⁴ Ebd., S.340

Since this damage is most pronounced when natural rubber is combined with manganese, it was recognized relatively early and has been the subject of continuous scientific research since the end of the 19th century.⁵

Even the smallest amounts of copper and manganese accelerate the autoxidation very strongly and destroy the material in a short time, especially with elastomers made of NR and IR. In contrast, saturated synthetic rubbers are less susceptible to autoxidation. If the copper or manganese content in the mixture is 0.001% by weight or less⁶, in most cases no damaging effect is to be expected.

Bivalent iron salts are particularly harmful to SBR elastomers. Cobalt and nickel are also regarded as rubber poisons, but only in higher concentrations than copper and manganese compounds do they become hazardous for elastomers.

The decisive factor is the form in which the heavy metals are present. The more soluble they are in the rubber, the more dangerous they are.⁷ Copper stearate [see Tab. 1] and copper oleate as soluble compounds strongly accelerate aging; copper sulphate and copper chloride, copper oxide and copper metal follow in a sequence of decreasing activities.⁸ However, there are also copper compounds which have no damaging effect on rubber, such as copper dimethyldithiocarbamate.

Percentage of Copper Stearate [%]	0	0.05	0.1	0.2
Unaged				
Tensile Strength [N/mm ²]	16.2	17.8	17.1	15.7
Elongation at Break [%]	551	564	554	554
Stress Value at 300% Elongation [N/mm ²]	5.0	5.1	5.1	4.9
Tensile Strength After Aging in the Oxygen Bomb at 70°C and 20.7bar				
After 2 Days	8.9	8.5	8.3	4.0
After 4 Days	8.6	6.3	3.6	0
After 6 Days	7.8	0	0	0
After 8 Days	7.6	0	0	0

Tab. 1: Influence of copper stearate on a NR mixture after aging in the oxygen bomb⁹

⁵ Z.B. LASCELLES- SCOTT, India Rubber Journal, 1888, 4, 169 oder THOMSON, W. und LEWIS, F.: On the action of different Metals, Metallic Salts, Acids, and Oxidising Agents on India-rubber in: Memoirs and proceedings of the Manchester Literary & Philosophical Society, 1891, 4 (4) S.266 (Permalink to this publication: <http://biodiversitylibrary.org/page/35486586>)

⁶ KEMPERMANN, Th.: Alterungsschutzmittel in: BOSTRÖM, Siegfried (Hg.): Kautschuk-Handbuch, Berliner Union, Stuttgart, Bd. 4, 1961, Kap. 2.8, S. 357

⁷ Vgl. SEEBERGER, D.: Alterung und Alterungsschutzmittel (Antioxidantien) (=Kap. 7.4) in: HOFMANN, Werner und GUPTA, Heinz (Hrsg.): Handbuch der Kautschuk-Technologie, Ratingen, 2001, Kap. 7, S. 74 Side note: This literature reference also contains the information listed above on the effect of the respective heavy metals on certain elastomers..

⁸ KEMPERMANN, Th.: Alterungsschutzmittel in: BOSTRÖM, Siegfried (Hg.): Kautschuk-Handbuch, Berliner Union, Stuttgart, Bd. 4, 1961, Kap. 2.8, S. 357 nach VILLAIN, H., Rubber Chemistry and Technology, 23 (1950), S. 352

⁹ Untersuchungen von B.N. Leyland in: BUIST, J.M. in Ageing and Weathering of Rubber, W.Heffer & Sons Ltd., Cambridge, 1956, S.30

2.3 Contamination Possibilities with Rubber Poisons

Rubber poisons can enter the compound either through the natural environment (e.g. manganese-polluted grounds in rubber plantations¹⁰) or through compound components (often undetected). In the early days of rubber production, mineral fillers such as chalk were contaminated with rubber poisons. Likewise, fabrics dyed with natural mineral or copper-containing paints were contaminated, so that a rubber coating was disturbed.¹¹ After all, the finished elastomer product can also come into contact with rubber poisons and be damaged as a result.

2.4 Current Seal Damages due to Autoxidation

With the advent of numerous synthetic rubbers, the technical significance of natural rubber has decreased. In addition, the purity of fillers and synthetic fabrics is increasing, so that the problem of natural rubber-manganese has become less and less important.

Today, autoxidation is a phenomenon that occurs mainly in peroxidically crosslinked EPDM hot water seals. At first it seems surprising that with peroxidically crosslinked EPDM, which is considered stable, autoxidation damage occurs. However, this is due to the fact that sulfur-cured EPDM is not used in hot water applications. In addition, aging is always accelerated by temperature, as is the case with hot water applications. This type of damage only occurs locally, since a certain water quality is required for this, which causes the brass fittings to be dezincified.

Copper and zinc are alloys of brass whose corrosion resistance can be improved by adding further elements (e.g. Al, Sn).

Brass containing more than 20% zinc and exposed to certain environmental conditions (high chloride, mostly soft water) may be subject to dezincification, which is a form of selective corrosion.¹² Dezincification may be limited to a small area of the brass component or may spread on the surface. This type of corrosion can also penetrate the component.¹³ During dezincification, the copper is excreted as a spongy mass, but also the zinc dissolves. "After dissolution of the brass, however, the copper is deposited again in spongy form because of its more noble potential, while the zinc is removed in dissolved form".¹⁴ Or the zinc is deposited as basic salt over the corrosion site.¹⁵

The released copper then harms elastomer seals as a rubber toxin. This process is significantly accelerated by the increased temperatures in the hot water area.

With copper contents of less than 62.5% in brass, the β phase, which contains more zinc, is added to the α phase. During dezincification, the β phase in particular is getting corroded. The

¹⁰ Devi Dwi Siskawardani, Jumpen Onthong, Khwunta Khawmee, Chakkrit Poonpakdee: Manganese status in upland and lowland rubber-growing soils in Songkhla province, southern Thailand in: Agriculture and Natural Resources, July 2016, S. 321-325 Open Access: (Zugriff am 11.09.2018)

¹¹ Vgl. KLUCKOW, Paul: Technische Gummiwaren in: HAUSER, E.A.: Handbuch der gesamten Kautschuktechnologie, Union Deutsche Verlagsgesellschaft, Berlin, 1935, Band I, S.400ff.

¹² Überblick über die Korrosionsformen: <https://www.kupferinstitut.de/de/werkstoffe/system/korrosionsverhalten-kupferwerkstoffe/korrosionsformen.html> (Webseite abgerufen am 14.09.2018)

¹³ Vgl. <https://de.wikipedia.org/wiki/Entzinkung>

¹⁴ Korrosionsbeständigkeit verschiedener Kupferwerkstoffe, Rubrik „Kupfer-Zink (Messing)“, Webseite abgerufen am 14.09.2018: <https://www.kupferinstitut.de/de/werkstoffe/system/korrosionsverhalten-kupferwerkstoffe/korrosionsbestaendigkeit-verschiedener-werkstoffe.html>

¹⁵ Nach <https://de.wikipedia.org/wiki/Entzinkung>

β phase can be reduced by suitable heat treatment of the brass, which makes the material resistant to dezincification. With the so-called D(Z)R brass ("dezincification resistant"), the more stable α phase predominates.¹⁶ "The trick of DR brass is that the α phase is quite effectively inhibited against dezincification by adding small amounts of arsenic. Unfortunately, this is not possible with the β phase, which is required for hot forming. The final heat treatment serves to convert the β -phase back into an α -phase after the forming process."¹⁷

Dezincification can only take place if certain material-water quality pairs occur. In 1961, the British M. Turner¹⁸ published the diagram named after him. It represents the chloride content by carbonate hardness. Originally, this diagram was created in England from empirical data. It is divided into two parts: One with combinations of these parameters that can cause dezincification and another with uncritical combinations of these parameters. Turner's diagram was originally prepared for Ms58 (CuZn40Pb2), an alloy that is much more susceptible to dezincification than today's D(Z)R grades (CW602N).

In heating systems, dezincification problems hardly occur because these systems are nearly free of oxygen.¹⁹

In the case of EPDM elastomers, the mixtures can vary considerably depending on the structure with regard to susceptibility to this damage mechanism.

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¹⁶ Nach DEUTSCHES KUPFERINSTITUT. Messing ja – Entzinkung muss nicht sein!, S.1f.

Two-page Internet publication (accessed 14.09.2018):

https://www.sonderlote.de/WebRoot/Store4/Shops/62173412/MediaGallery/DKI_Infos/Messing/DKI_Messing_Entzinkung_muss_nicht_sein.pdf

¹⁷ Written notification by Dr. Peter Dierschke from 11.10.2018,

<https://gfkorr.de/Forschung/Experten/Dierschke.html>

¹⁸ TURNER, M. E. D.: The Influence of Water Composition on the Dezincification of Fittings in: Proceedings of the Society for Water Treatment and Examination, 1961, S. 162-179

¹⁹ Nach DEUTSCHES KUPFERINSTITUT. Messing ja – Entzinkung muss nicht sein!, S.1

Two-page Internet publication (accessed 14.09.2018):

https://www.sonderlote.de/WebRoot/Store4/Shops/62173412/MediaGallery/DKI_Infos/Messing/DKI_Messing_Entzinkung_muss_nicht_sein.pdf

Turner Diagram CW617 and DZR brass

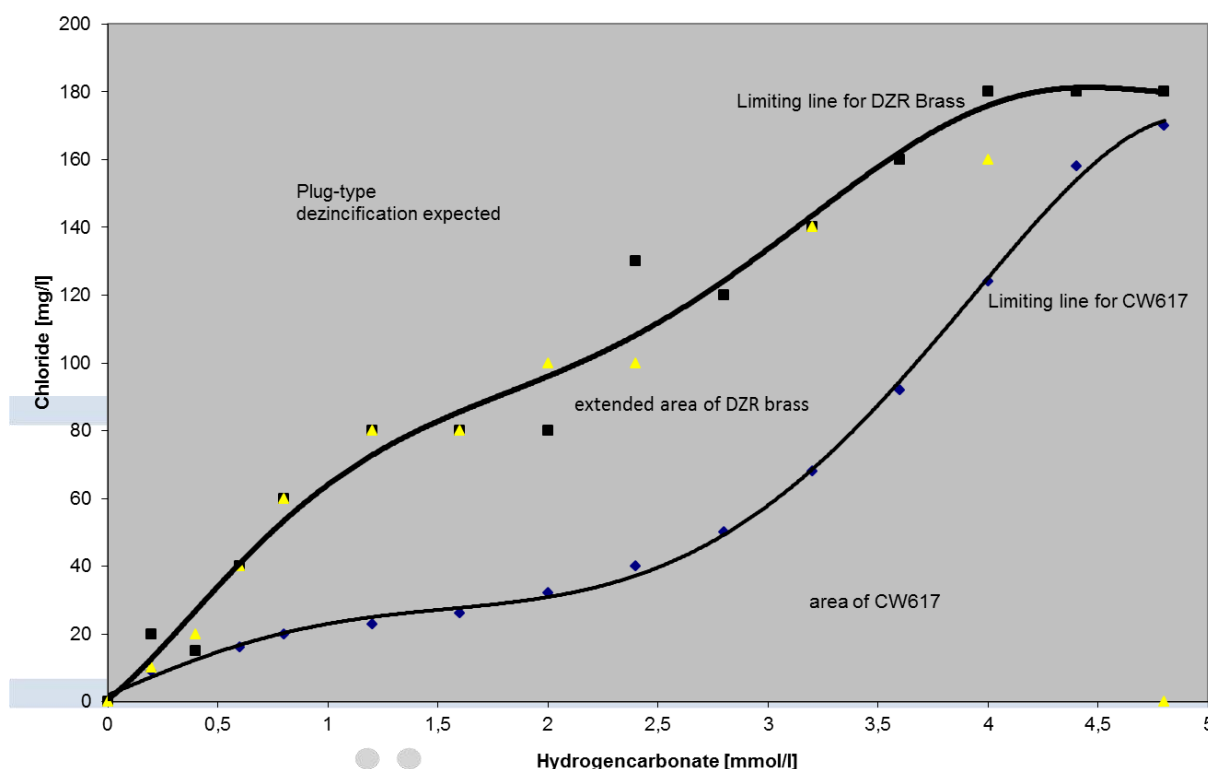


Fig. 1: Turner diagram with limit range curves of two different brass qualities: the upper curve stands for a dezincification-resistant brass (DZR); above this curve, the dezincification of this more stable material also occurs. The lower curve stands for a free-cutting brass (CW 617N = similar to the now impermissible designation Ms 58), below this curve there is no dezincification for both materials (Figure: Material consultant Dr. Peter Dierschke).

3. Damage Pattern

3.1 Description of the Damage Pattern and Problematic Areas

Damage caused by autoxidation often has a diverse appearance. Elastomeric materials can soften, crack (see **Fig. 2**), become sticky or shiny due to this mechanism. These characteristics can occur on the same gasket in different areas. In extreme cases of autoxidation, complete depolymerization of the gasket may occur, meaning decomposition to the extent of carbon black. A preliminary stage before complete depolymerization is the appearance of shiny areas, which are often accompanied by local softening. These glossy areas are reminiscent of a partially melted thermoplastic (see **Figs. 4 and 5**), although a three-dimensional elastomer cannot be melted.

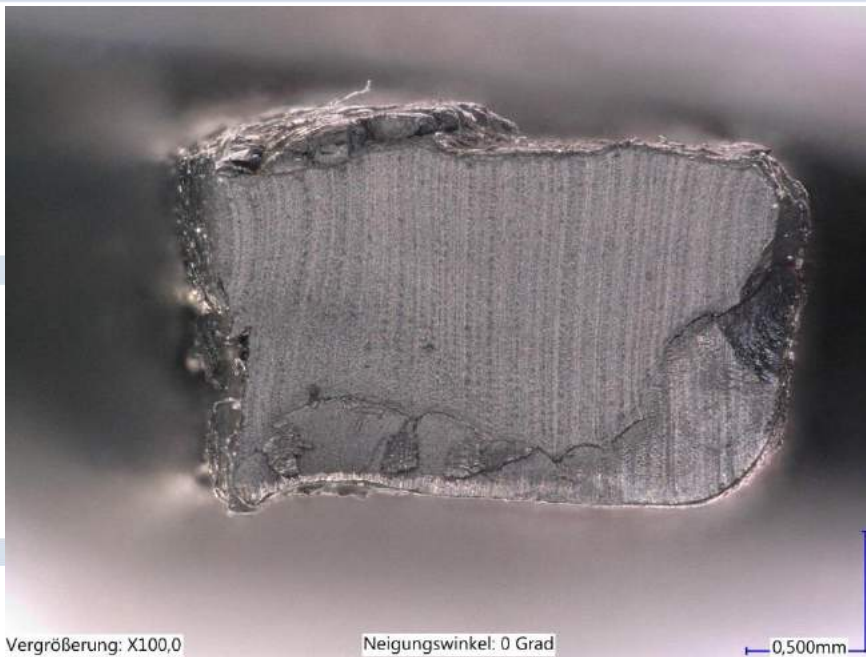
Autoxidation can occur after long exposure to heavy metals or fluids containing heavy metals and after higher temperatures on the entire seal. The damage is often found both in the contact area with brass housing parts (in hot water sanitary installations) and on the fluid side (see **Fig. 5**).



Vergößerung: X100,0
Neigungswinkel: 0 Grad

0,500mm

Fig. 2: EPDM O-ring, peroxidically cross-linked after use in a monitored endurance test for a water fitting (cause of damage: dezincification of brass, cyclic temperature changes from 25°C to 95°C in water, test duration 4500 h)



Vergößerung: X100,0

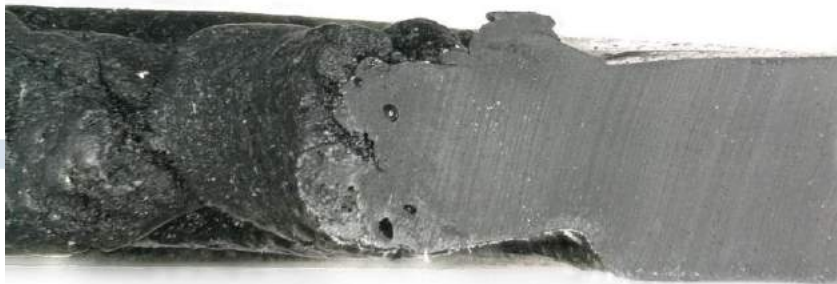
Neigungswinkel: 0 Grad

0,500mm

Fig. 3: Cross section of the O-ring from Fig. 2, the autoxidative damage occurred mainly in the marginal areas, the core is not yet depolymerized.



Fig. 4: An elastomer damaged by autoxidation (peroxidically cross-linked EPDM), which has clearly fused areas in the interior of the sealing ring, similar to a thermoplastic or TPE.



OR

Fig. 5: Seal from Fig. 4 in cross-section: On the left, the damaged area is clearly visible, which had contact with rubber poisons. The area on the right is still completely intact since it was protected by the housing.

The following three microscope images of one and the same O-ring show that different damage patterns can occur on a seal during autoxidation.



Fig. 6: EPDM O-ring after autoxidation in the installed state, permanently deformed and with a sooty surface



Fig. 7: Opposite surface of the EPDM O-ring from Fig. 6, the white areas are probably lime deposits.

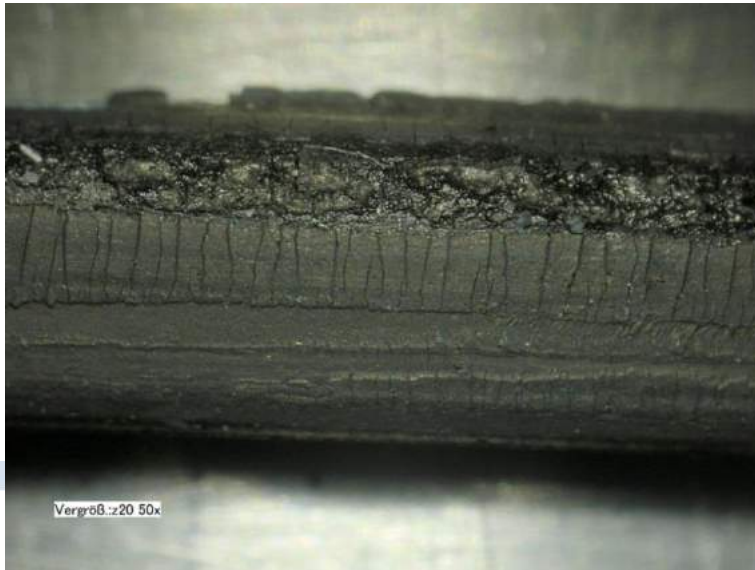


Fig. 8: Top view of removed EPDM O-ring from Fig. 6, the apparently fused areas in the upper area are clearly visible. These were in contact with water, in which the rubber toxin was dissolved. The side with the fine cracks is the contact surface towards the housing.

3.2 Effects of the Damage

Autoxidative damage in the area of hot water applications leads to leaks and leakages, which must be avoided in any case.

Higher manganese contact can almost completely destroy natural rubber components.

3.3 Differentiation from Similar Types of Damage

The chemical corrosion of strong cleaning agents (with chlorine) causes sooty surfaces on certain elastomers. This type of damage can resemble autoxidative aging.

To distinguish these similar damages from each other, it is necessary to trace the use of the seal and apply exclusion criteria.

If it is still not possible to make a clear statement using this method, a REM EDX analysis of the damaged surfaces is also advisable. If copper ions are then found in the damaged area, autoxidation can be assumed.

4. Prevention Measures

During the production of compounds, contact with critical heavy metals must be avoided. In addition, it must also be ensured that the sum of all compound constituents contains critical substances below the recommended maximum percentages.

During application, contact with the critical heavy metals described above must be avoided both in terms of construction and application. If it cannot be avoided, then special materials (e.g. D(Z)R brass) and elastomer types more resistant to autoxidation must be used. Antioxidants that act against autoxidation can also be used for autoxidation accelerated by heavy metals. However, there are also additional compound ingredients which have a special effect against rubber poisons (e.g. DNPD), e.g. which for the most part inactivate the effect of

copper and manganese compounds. "The positive influence of antioxidants against rubber poisons is at least partly due to a complex binding (chelation) of the harmful ion".²⁰

The subject of autoxidation must also be taken into account in the field of materials testing so that artificial aging is not unintentionally accelerated by rubber poisons and thus falsified. For example, the ISO 188 standard on hot-air aging of elastomers prohibits the use of copper and its alloys in the area of the furnace chamber.²¹

5. Practical Tips (Testing Possibilities / Standard Recommendations)

Since there is no national or international standard for testing resistance to rubber poisons, the O-Ring Prüflabor Richter has developed an internal laboratory test procedure. This only deals with the element copper, since the copper compatibility of EPDM in hot water applications in the field of autoxidation is currently the most frequent question for seal users.

The elastomer specimen (finished part or test plate section) is pressed between a glass and copper plate with a pre-defined percentage value and stored in hot air for a certain period of time. If the large-area bonding of the elastomer to the copper plate, as defined in the test instructions, occurs and there is a large deviation in hardness, the elastomer is unsuitable for critical applications with copper contact.



Fig. 9: Remains of a large-area bonding of a test specimen to a copper plate: Such an elastomer is considered susceptible to autoxidation.

6. Other

²⁰ SEEBERGER, D.: Alterung und Alterungsschutzmittel (Antioxidantien) (=Kap. 7.4) in: HOFMANN, Werner und GUPTA, Heinz (Hrsg.): Handbuch der Kautschuk-Technologie, Ratingen, 2001, Kap. 7, S.83

²¹ vgl. International Standard ISO 188: ISO 188: Rubber, vulcanized or thermoplastic — Accelerated ageing and heat resistance tests, Fifth Edition: 2011-10-01, S.2, Unterabschnitt 4.1.1

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Special thanks to Dr. rer. nat. Peter Dierschke of the "Materials Consultancy Dr. Peter Dierschke"²² in Titz for the technical support in the section dezincification and providing a Turner Diagram.

The logo consists of a large, light gray circle on the left, followed by the word "RING" in a bold, light gray, sans-serif font.

The word "PRÜFLABOR" is written in a large, bold, light gray, sans-serif font.

The word "RICHTER" is written in a large, bold, light gray, sans-serif font.

²² <https://gfkorr.de/Forschung/Experten/Dierschke.html>