

Material Selection Criteria for Elastomeric Rotary Propeller Seals for Marine Applications

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Abstract

The aim of this article is to search for technically feasible alternatives for the fluoro-elastomer material used for Propeller Shaft Seals in marine shipping transport. The shipping industry is vital to our economy and prosperity in the EU/EEA. The shipping industry today is responsible for transporting and delivering more than 80% of global trade, by volume roughly 11 billion tons annually. A backbone of global trade and the most efficient way of transportation of large volumes with high weights, compared to land and air routes.

Elastomeric Propeller Shaft Seals (made out of fluoropolymer rubber) separate oily environments in ships from the (sea) water, in order **to avoid environmental spillage of oil into the sea** and vice versa. The propeller shaft is supported by white metal sliding bearings, fixed in the stern tube. These bearings function within an oil bath; the elastomeric rubber sealings are used to seal the oil bath. Since 2013, the **environmentally allowed oils/lubricants** have changed from mineral oils to **primarily ester-based oils**. Sealing is achieved by a series of 5 or more seals in line. Stationary circular lip seals fixed in the stern-tube, slip along the rotating screw shaft. Heat is evolved in the lip contact, which increases the temperature to **130 °C -150 °C**.

In the past the seals were manufactured from NBR (nitrile) rubber. Ships were commonly significantly smaller, approximately 1,500 TEU (Twenty foot Equivalent container Units) per vessel in 1970 compared to nowadays 24,000 TEU. Propeller speeds were also lower. Since the 1960's, after the development of FKM (fluor-elastomer) for aerospace and airplane applications, **FKM came into use for sealing in the maritime sector as the one and only rubber-material**. It was able to cope with the **stringent requirements of temperature, oil- and water-resistance in combination with the required safe performance duration of minimum 5 years** (the scheduled dockings for major maintenance overhauls of ship vessels) to avoid leakage of the seals, with consequential risk for the environment and to avoid the need to dock the vessels unplanned for seals replacement. The performance requirements for the use of these seals in marine vessels are detailed in this article, as the basis for the search for alternatives for FKM. FKM derives its high endurance from the fluor-carbon (F-C) bond that outperforms all other elastomeric materials. At the same time FKM has the required material features, such as mechanical and abrasion properties, and the resistance to acids and steam generated from the ester-type oils in combination with the high temperatures encountered by the seals. **FKM is by far the highest temperature resistant elastomer, with excellent material properties and water/oil resistance with a duration of at least 5 years; there is no alternative rubber material available which can match its properties to meet the required high performance standards for the safe use of these**

seals in the marine transport sector. Experience over the past decades shows that no alternatives exist that match the combination of characteristics required to substitute FKM. Replacing FKM in propeller shaft seals is hardly realistic and will require at least many years of research.

Key words: Maritime industry, Stern seals, Temperature resistance, oil resistance

I. Introduction

Aim of this article is to review whether there are technically feasible alternative materials for the fluoro-elastomer material in Propeller Shaft Seals used in large container vessels. The shipping industry is vital in the world economy. It is responsible for transporting and delivering more than 80% of global trade¹, by volume roughly amounting to 11 billion tons annually (year 2022). Around 77% of goods that are imported/exported to and from the European Union are transported by sea², proving to be a backbone of global trade and the most efficient way of transportation of large volumes with high weight compared to land and air routes³. A vital element of the container vessel is the propulsion system (see **figures 1a and 1b**).



Figure 1a: Propulsion system of a vessel. Courtesy of AEGIR Marine BV.

Most engine-propelled ships derive thrust from a propeller or screw. The shaft driving the propeller and transmitting its thrust to the hull of the ship rotates within a metal tube, is called the propeller shaft. This propeller shaft, is supported by white metal sliding bearings, carried in the stern tube.

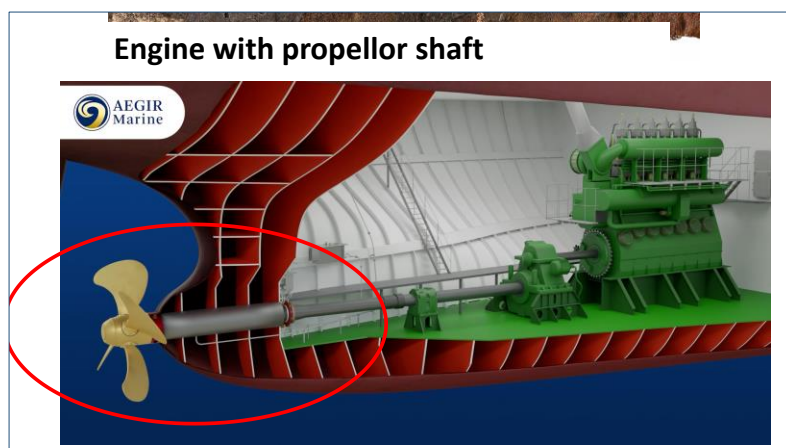


Figure 1b: Overview of the propulsion system of a ship. Courtesy of AEGIR Marine BV.

The stern tube extends to the stern-outside of the ship. Within this tube the propeller shaft while rotating is supported by white metal sliding bearings. These white metal sliding bearings function within an oil bath; the elastomeric rubber sealings are used to seal against leakage and spill of the oil bath to the environment and function also to guarantee the hull integrity.

A major part of the tube is flooded with lubricating oil, except for the outer stern side which is in contact with (sea-) water. To guarantee appropriate separation between the oil and water environments and to prevent leakage of oil into the water and the environment, a set of rotary lip seals is employed in combination with a series of compartments establishing a gradual transition from the under-water pressure to the oil pressure within the ship's stern tube⁴. This system of seals is schematically shown in **figure 2**.

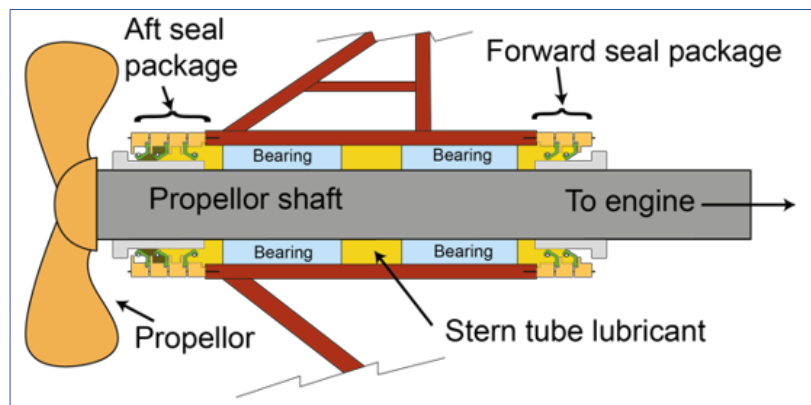


Figure 2: Concept of a ships propeller shaft rotating carried within the stern tube with rubber seals installed. Courtesy of Ref. [4]. Not on scale.

The seals are typically made of an annular-shaped elastomer material (i.e. rubber rings) in order to accommodate vibrations in the rotary shaft and any wear of the stationary seals in contact with the rotating propeller shaft. Depending on the construction of the shaft/tube combination, the transition from oil-filled at the engine-side to the water at the stern-side encompasses a set of compartments or chambers.

On the engine side the chamber is fully oil-filled, and at the propeller side the chamber is water-filled, with intermediate chambers filled with leaking water/oil combinations, from which the leaked oil/water combination can be drained if required on a regular basis: see **figure 3**.

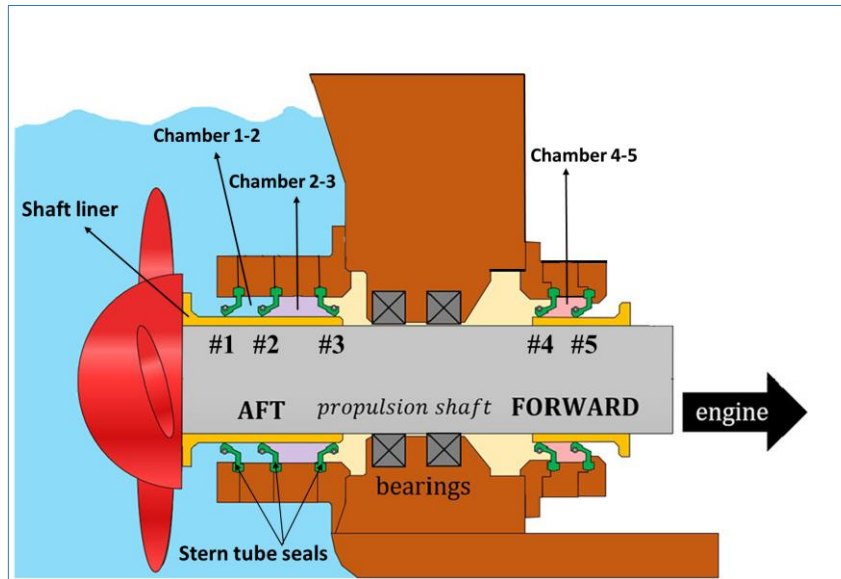


Figure 3: Stern tube chambers. Courtesy of AEGIR Marine BV.

It dictates the need for the **rubber seals to be resistant to oil-environments as well as (sea-)water-environment, which in terms of properties are two conflicting requirements for rubbers.**

During the last decades, the requirements for seals have risen drastically. The rotational velocity of the shaft relative to the stationary seal varies from zero to approximately 8 m/s (linear speed) for the largest ships whilst operating at the highest rotation speed. Over time ships have increased significantly in size. To give an example. Could a container vessel transport in 1970 approximately 1,500 TEU (Twenty foot Equivalent Units), nowadays a container vessel transports 24,000 TEU. And also the diameters of the propeller-shafts as well as the rotation speeds of the shafts increased the last decades. The corresponding linear rotational speed therefore has increased as well. The performance requirements of the seal materials have kept pace with these developments.

The stationary rubber seal in contact with the rotating propeller shaft is subject to friction and consequent heat evolution in the seal/shaft contact⁵. The replacement of such seals is a time consuming major overhaul, requiring docking of the ship. It is therefore in the interest of the ship-owner and the environment to reduce the need for replacement of the seals to a minimum. Typically, docking takes place once every five years, meaning that the safety and durability of the seals for - at the least - that period is required. **Due to increasing and conflicting requirements such as high temperatures and oil and water resistance, the selection of the most appropriate material for the seals from the perspective of long perseverance is a point of major concern and a serious challenge,** as detailed in the present review paper.

II. Rotary Propeller Seals for Marine Applications

The design of rotary propeller seals is based on an elementary concept of elastomeric lip seals⁵⁻⁷, as shown in **figure 4**. The fact that the lip is hinged and with the circumferential Garter spring position the seal is in concept asymmetrical. In practice this results in the need to fit the seal correctly to avoid leakage, and/or to avoid unreliable performance results. The contact edge with the shaft is formed at the intersection of two conical surfaces and defining the respective sealing angles (α and β in **figure 4**) is at the discretion of the designer.

There are limits which are dictated by manufacturing and performance criteria but within these, variations will be found when examining seals from various supplies^{8,9}. The contact between lip and shaft can be approximated from a simple geometric analysis which indicates that for a specific amount of radial wear, the cotangent of the angle β in **Figure 4** defines the wear. With a small angle the wear is increased by misalignment of the housing and any eccentricity of the propeller shaft. As a consequence of these factors, most modern designs have angles with the shaft of the order of 20° or more in the fitted state, and some may be up to 40° . The other angle α is determined by the need to have enough rubber at the contact to impart rigidity. Typically, the included angle forming the elastomer contact is between 90° and 120° . Since the diameter at the lip contact is smaller than the propeller shaft diameter, the deformation of the elastomer, which includes both bending and tension, causes a sealing force, which is complemented and stabilized by the force from the circumferential Garter spring.

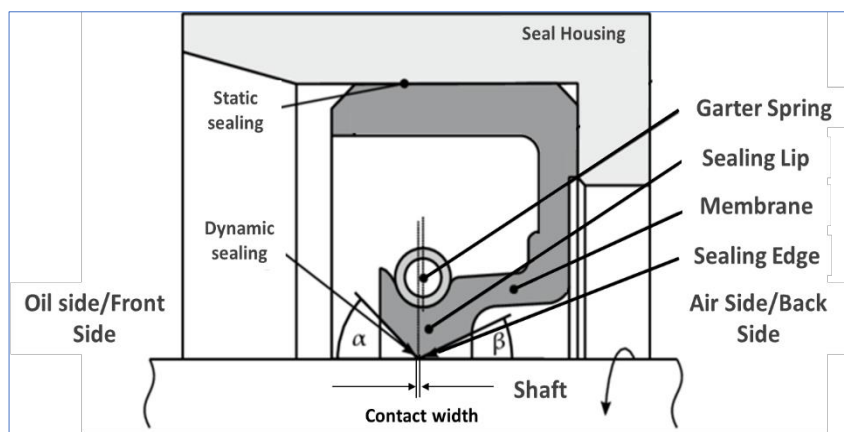


Figure 4: Typical cross-section of an elastomeric rotary shaft lip seal with Garter spring¹⁰. Air Side/Back Side may also be the Water Side.

Additionally, the pressure difference between the two sides of the seal translates into an extra radial component to the sealing force. The total value of the sealing force is known as the radial load. The contribution from the elastomer depends on its modulus or stiffness, the sectional shape of the lip, and the interference with the shaft, with each of these parameters being adjustable within limits. Garter springs are fitted not only to apply the load, but also to compensate for permanent deformation, creep and wear which elastomers undergo when subjected to permanent strain, and friction, augmented by heat.

For a newly produced seal, the sealing edge is sharp. After mounting the rubber seal on the shaft the sealing load causes the contact to flatten and the contact patch has a width of about

0.5 to 2.0 mm¹¹. Rotation of the shaft subsequently abrades the elastomer to form a wider contact band, which may vary considerably in size depending on the type of rubber and compound formulation used. The surface finish of the rotary shaft does have an influence on the amount of (potential) wear¹². The size of the contact band stabilizes after a short period, which indicates that an intermediate coherent lubricant film is formed between the seal lip and the shaft^{13,14}. Direct measurements and values calculated from frictional results indicate that this film is of the order of 1 µm thick. It is difficult to perform highly accurate direct measurements, because the surface structure of the elastomer often has a similar roughness as the shaft. Various base elastomers or the same elastomer with alternative filler systems give different film thicknesses and consequently different frictional results, which highlights the complexity.

There is a certain pumping action of the seal lip due to surface tension effects, which in steady state are counterbalanced by capillary forces determined by seal angles, film thickness and also the surface tension⁹. Under operational conditions, this results in hydrodynamic lift of the seal-tip leading to the lubricating film. The build-up of a lubricant film is also due to the surface roughness asperities on the elastomer which are exposed or formed during bedding-in and the macroscopic waviness of the sealing surface. The presence of a full lubricant film implies that the friction force is based on the viscosity of the fluid. As the shaft-speed increases, the heat generated in the contact causes a rise in the underlip temperature which for a hydrocarbon-based lubricant results in a reduction of the viscosity. A second influence is the variation in the film thickness, which is a function of lubricant viscosity and speed of the shaft, the governing principle being the need for the hydrodynamic lift to balance the sealing force. The very thin film gives rise to high shear rates and, hence the temperature under the lip can be substantially higher than that in the bulk fluid. Whilst there are disadvantages to the hydrodynamic formation of the thin lubricant films, they are also an integral part of the sealing mechanism. For example, if a lubricant film with an excessive thickness develops, it will usually lead to leakage.

Where the foregoing basically applies to the rotary shaft seals in direct contact with the oil-side of the construction, similar phenomena apply for the (sea-)water side, where a thin water-film is present between the seal and the shaft. This highlights the need to consider the operation of the seals under study in the present document, in contact with both types of fluids.

III. Typical Rotary Propeller Seal Configurations

Figure 5 shows a typical configuration of a five-fold sealing system for rotary propeller seals, creating four chambers. From left to right: one chamber filled with a water/oil mixture and three oil-filled chambers. As all seals operate under the same mechanical conditions and the segregation of the oily and water environments are not clearly defined, all seals are made out of the same rubbery material.

This construction aims to minimize the migration of oil into the sea water and -environment and of water into the oil. The intermediate chambers are operating under a slight overpressure to prevent excessive leakage of water and or oil underneath the seal lips via the hydrodynamic films, as discussed in the previous paragraph.

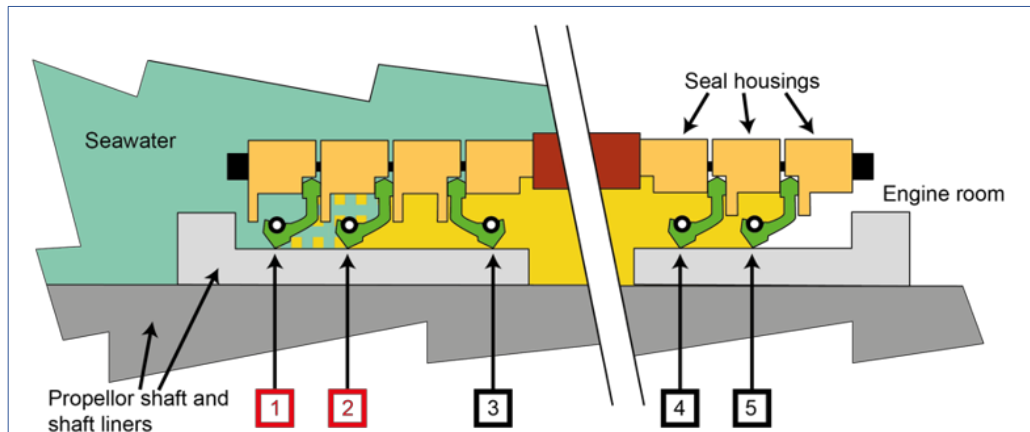


Figure 5: Typical example of a rotary seal configuration with 5 seals and an oil/water filled chamber⁴.

Other configurations with more seals are also employed, as well as configurations where air-chambers are present and where leaked water and oil are collected in one of the chambers.

Figure 6 shows a close-up of a seal.

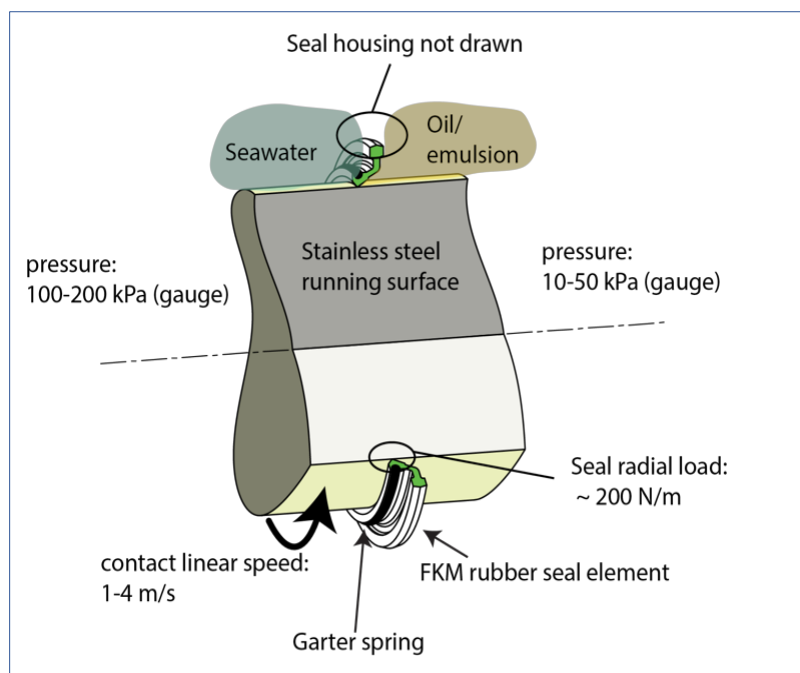


Figure 6: 3D-picture of an FKM-rubber rotary seal element running on a stainless steel propeller shaft⁴.

IV. Performance Requirements

On basis of the 5 years standard maintenance overhauls schedule for ships and corresponding expected high performance of the seals, the following rubber-related requirements may be formulated for the use of these seals in the marine transport sector:

1. A high continuous use temperature (minimum of 130 °C), well above the maximum temperatures which may occur during operation of the seals, during at least 5 years;
2. Long-term chemical resistance towards oil: limited or preferably no swell;
3. Long-term chemical resistance towards (salt-)water;
4. Sufficient mechanical properties: tensile and tear strengths, fatigue strength, abrasion resistance;
5. A static modulus (or alternatively hardness), sufficient to carry the axial force exerted by the Garter spring;
6. Low compression set (permanent deformation under compression or creep) at room temperature, at 0 °C and at operating temperatures for various durations;
7. Brittleness temperature in marine applications ≤ -5 °C.

In order to specify these requirements in more detail:

Continuous use temperature

Firstly, the maximum permitted temperature for continuous use of a rubber (e.g. an elastomer) cannot be taken in isolation, without a link to its service conditions. The load and duration of loading, whether the temperature is continuous or cycles intermittently and the action of surrounding media (oil and (sea-)water in the present case), in air or in anaerobic conditions, all play a decisive role. But **most importantly, the duration at which the heat acts plays a key role when it comes to the upper temperature limit required in practice.** Various industries employ different criteria to define the capacity to withstand the highest achievable temperatures, from e.g. **22,000 hours** continuous temperature load for the cable industry, to 1000 hours frequently used in the automotive industry. Hence there is no clearly defined concept of continuous use temperature and consequently different figures are found in literature. Clearly, **the longer the exposure to high temperature, the lower the corresponding continuous use temperature.** For the rotary stern tube seals to last for 5 years (minimum), equally 44,000 hours and assuming approximately 50% operational time of the propeller shaft, it is most appropriate **to adhere to a duration of 22,000 hours active use** and use the 22,000 hours continuous use temperature data.

Figure 7 shows the measured temperature development versus the linear shaft speed (m/s) during constant operation of both seal #1, i.e. the one closest to the (sea-)water, and seal #2 which operates in the water/oil transition stage as shown in **Figure 5**. All data were collected in four-fold with thermocouples mounted maximum 1 mm from the contact between the seal-lip and rotating shaft. Measurements were done at three speeds, maximum 6.1 (m/s) due to equipment limitations. On the other hand, for large vessels sailing at full speed the linear speed may reach 8 (m/s), well above the limitation of the experimental set-up. However, all data points develop in more-or-less a linear manner vs. the rotational shaft speed. For that reason it seems reasonable to expect that the temperatures at 8 m/s corresponding to the largest vessels can be obtained by extrapolation **to result in avg. 130°C for seal #2.** And

because of the fact that the temperature sensors are away from the actual contact by +/- 1 mm, it is reasonable to expect that the actual temperature is still a bit higher due to heat leakage to the rubber-mass around the lip-contact. Seal #1 operates at a lower temperature because of its direct contact with the water-side, whilst the operational temperatures for seals # 3, 4 and 5 are comparable to those of seal #2.

To conclude: the data do demonstrate the high temperature requirement (130 °C to 150 °C) for the rubber seals, to be seen in relation to the need to perform well for a long duration of 5 years.

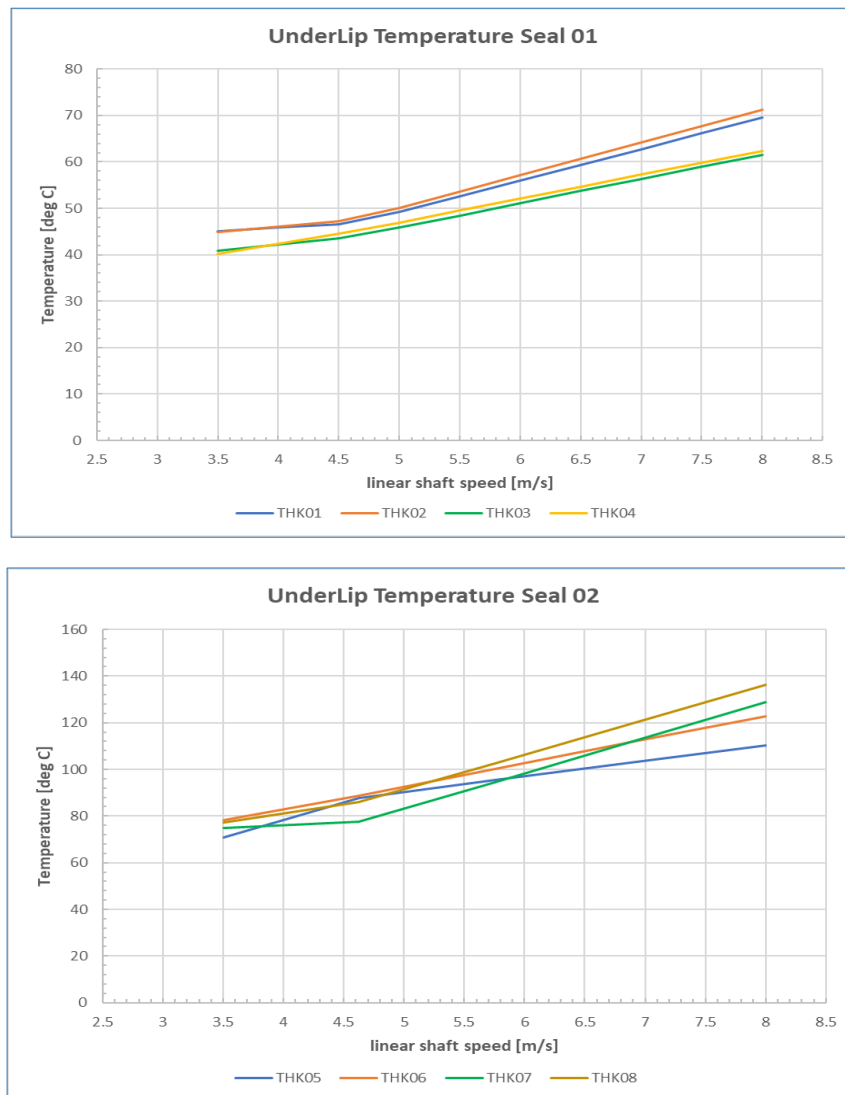


Figure 7: Seal lip temperatures (°C) vs. linear shaft speed (m/s) measured for seals #1 and #2 (ref. Figure 5) in the lips at max. 1 mm from the contact with the rotating shaft. Each measurement is an average of 4 measurement points. By courtesy of AEGIR-Marine B.V., the Netherlands.

Swelling

The second main performance requirement for the seal pertains to the **tendency of rubbers in general to substantially swell when in contact with liquid media with a close or similar polarity or solubility parameter**^{15,16}. As rubbers are basically crosslinked liquids, they want to

enter in solution, which is prevented by the crosslinks. A very significant amount of swelling may take place, depending on the degree of crosslinking and the viscosity of the liquid medium. The resistance of rubbers to swell in contact with oil is commonly measured by immersing the rubber at elevated temperature, depending on the rubber type e.g. for a duration of 70 hrs as given in **Figure 8**. In addition to the maximum permitted temperature, also the duration of contact with the liquid medium is an important factor in the present context, i.e. 44.000 hrs for 5 years, or 22.000 hrs at 50% operation of the vessels. The heat resistances or max. continuous use temperatures for the various elastomers are given in **Figure 8** for 1000hrs continuous use, as commonly specified by the automotive industry. As an empirical rule, each increase in exposure time by a factor of 2 (two) lowers the continuous use temperature by 10°C. To reach 44.000 or 22.000hrs continuous use, 4 - 5 steps of factors of 2 are needed relative to 1000 hrs.

This corresponds to a **decrease of appr. 45°C continuous use** temperature relative to the values presented in **Figure 8**, for all rubbers given.

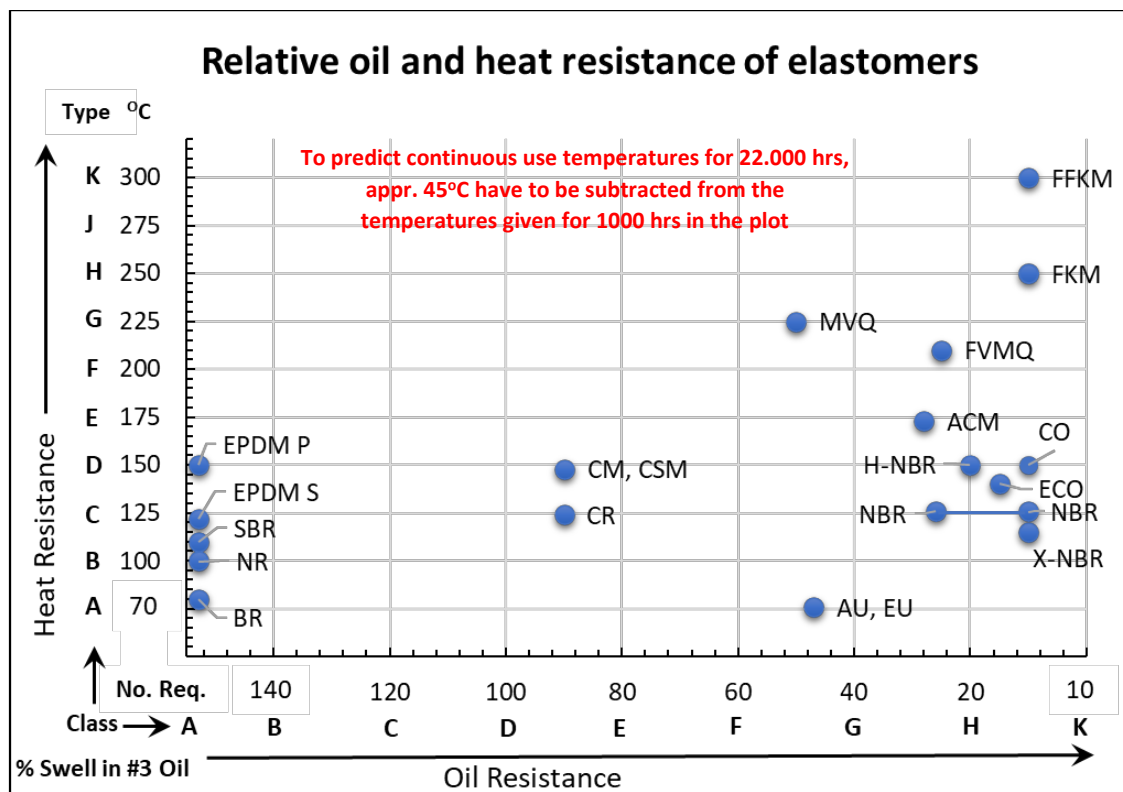


Figure 8: Continuous use/service temperature vs. Volume swell in ASTM-oil type 3, for various rubber types for automotive applications^{17,18}: 1000 hr continuous use. **To predict continuous use temperatures for 22.000 hrs, appr. 45°C have to be subtracted from the temperatures given for 1000 hrs in the figure.** Oil-swell test for low volume increase rubber was done at 150 °C, others at 70 °C. For clarification of abbreviations, see text.

In practice, the **balance between continuous service temperature¹⁹ and the oil-swell resistance** is the first selection criterium for rubber-types to be used in specific applications. Figure 8 provides such a comprehensive overview of practically all rubber types, where the used ASTM-oil type 3, also known as ASTM Industry Reference Material, IRM 3 is a reasonable

representative for most mineral-based oil types²⁰ For further details on the oil types used in stern tubes in contact with seals, see the next paragraph. **To conclude: in relation to rotary marine propeller shaft seals in permanent contact with oil, the types of rubbers located at the very low volume increase side (the right hand side of Figure 8) are clearly most relevant.** Their abbreviations stand for: NBR - acrylonitrile/butadiene rubber with high acrylonitrile content, shortly “nitrile rubber”; X-NBR – carboxylated nitrile rubber; CO and ECO – epichlorohydrine rubber; and FKM – fluor rubber.

Mechanical properties

Key functional mechanical properties for rubbers in seal applications include the tensile strength, tear strength, fatigue strength and abrasion resistance. These parameters should be related to the mechanical load during operation, as well as compared to alternative rubbers. The static modulus (or, alternatively, and directly related to the modulus, the hardness of the rubber) should be high enough to carry the load of the Garter spring and the effects of counter-pressure of the oil without major deformation.

The compression set of a rubber, defined as the change in thickness under a specific load and duration of loading, at low, room and high temperatures is a sort of creep-test. A sample of predefined dimensions is commonly held under 25% compression during a predefined time period and at set temperature. After release of the load on the sample, the amount of deformation to which the sample recovers compared to its original thickness, within 30 minutes is registered. The remaining deformation relative to the imposed deformation of 25%, expressed in percentage, is called the Compression Set²¹. **The lower the remaining deformation, the better. For proper understanding: if the sample returns to its original thickness with zero deformation remaining, the Compression Set is 0%: the best achievable. Worst is 100%, when the sample does not return at all.** It is important to perform this test at various temperatures, especially at low and high temperatures. For instance, if the rubber tends to crystallize at low temperature, it will have a very negative effect on compression set. At elevated temperature the compression set parameter provides an indication for ageing phenomena taking place during the compression exposure.

The brittleness temperature marks the point where the rubber, coming from deep-cooling to – 70 °C whilst heating up slowly, recovers its elastic rubbery properties, i.e. returning from the glassy or brittle state. It is an important performance criterion for rotary shaft seals²². **To conclude: for proper functioning, rubbery behavior is required along the temperature range, from low, freezing temperatures to the elevated temperatures occurring at the seal tip in contact with the propeller shaft (as previously discussed, over 130 °C).**

V. Oil types employed in Marine Applications

Governmental regulations limit the use of oils and lubricants in applications where there is a risk of environmental damage. In December 2013, the use of Environmentally Acceptable Lubricants (EALs) became mandatory in large ships sailing within the coastal waters of the USA by the Environmental Protection Agency (EPA)²³. The German Blue Angel, the European Eco-label²⁴, and the American Vessel General Permit (VGP) are the most well-known labelling programs for EALs. A lubricant can only have the label of an EAL if it meets the requirements

of the VGP: when it is biodegradable, non-bio accumulative and minimally toxic. As a consequence, a large range of lubricants tailored to comply with these criteria have been introduced in the marine lubricants world.

The American VGP 2013 allows four kinds of base oils for the formulation of EALs: Hydraulic oil Environmental Triglycerides (HETG) types; Hydraulic oil Environmental Ester Synthetic (HEES); Hydraulic oil Environmental Polyglycol (HEPG) and Poly- α -olefins PAO or HPER)²⁵. It is the responsibility of the oil product manufacturers to meet the EPA's EAL definition.

The HETG are lubricants obtained from plants and animal fats. Their quick aging when exposed to water and heat makes them unsuitable for hydraulic systems. The strict European Eco-Label program restricts the content of a high fraction of natural esters or synthetic from the renewable resources in the formulation of marine lubricants²⁵.

The second and third classes HEES and HEPG are produced by esterification of carboxylic acids and alcohols, mainly glycerol. These base oils can be specially tailored to the application by selecting the proper acids and alcohols and therefore are the obvious choice for most ship owners.

The fourth class, PAOs obtained from polymerization of α -olefins, are basically non-polar in nature and are often mixed with esters, acting as carriers of polar additives to increase the additive solubility. There is an ongoing discussion as to whether or not PAO's are actually EALs, since they do not meet any renewable source standards and only the low viscosity types are somewhat biodegradable.

However, the synthetic ester-based oils (HEES and HEPG) are susceptible to hydrolysis and regenerate acids at higher temperatures. These acids may attack the sealing ring, especially when mixtures or emulsions of oil and water build up in any of the chambers in the sealing system or in the stern tube. **Consequently, the lifetime of the lip-type sealing system may decrease due to this aggressive mixture of oil and hot water or steam.**

VI. Material selection for Marine Rotary Propeller Seals on Basis of Performance Requirements

Basically only **four elastomers need further consideration** for application in marine rotary stern seals, as detailed above and shown in **Figure 8**, based on the balance between continuous use and oil resistance requirements:

- **NBR** - acrylonitrile/butadiene rubber with high acrylonitrile content, shortly "nitrile rubber";
- **X-NBR** – carboxylated nitrile rubber, a special grade of NBR, vulcanizable with zinc-oxide, not relevant in the present context;
- **CO and ECO** – epichlorohydrine rubber are property-wise largely comparable with NBR, but distinctly higher priced; and
- **FKM** – fluor rubber. FFKM, perfluorinated fluor rubber, is extremely highly priced and only used for the highest achievable temperatures: a step too far in the context of the

present propeller shaft seals. **To conclude:** because of the beforementioned, **the following discussion focusses on nitrile rubber NBR and fluoro-elastomer FKM.** Table 1 provides an overview of typical properties obtained for NBR with low and high ACN-content, and FKM.^{17, 26, 27}

NBR is a random copolymer of butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) and acrylonitrile (ACN) ($\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$), wherein the ACN is a highly polar monomer which provides the oil-resistance vs. the butadiene phase, which has no oil resistance. NBR is commercially available in a variety of ACN-contents ranging from typically 18 to 51 wt%. The lower the ACN-content, the higher the butadiene-level and consequently the lower the oil resistance, which is accompanied by a lower glass transition temperature, which does enhance the dynamic rubbery properties at low temperatures. The range of oil-resistance for NBR marked in **Figure 8** covers both types, where the utmost left point corresponds to the high ACN variants with the poorest dynamic properties. The glass transition temperature by itself cannot be taken as a measure for dynamic properties in comparison with other rubbers. In particular the fact that the glass

Table 1: Comparison of typical elastomeric properties between NBR and FKM.

Property	Standard	NBR Low ACN	NBR High ACN	FKM	Ref.
Low temp. glass trans. TR-10 (°C)	ISO 2921	-28	-10	-13	17, 26
Tensile strength *)	ISO 37	M/H	M/H	M/H	17
Resistance to tear *)	ISO 34-A	M	M	M	17
Resistance to abrasion *)	DIN 53516	M/H	M/H	H	17
Compression set at -20°C / 70 hr (%)	ISO 815	40	45	50	17
Compression set at Room temp. / 168 hr (%)	ISO 815	8	8	18	17
Compression set at + 120°C / 70 hr (%)	ISO 815	50	55	20	17
Compression set at + 200°C / 22 hr (%)	ISO 815	-	-	17	27
Continuous use working temp. (°C)**)		80 - 110	85 - 120	180 - 250	17, 27
Max. Working temp., short duration		125	125	250	17
Swelling after 70 h in ASTM oil #3 (%)	ISO 1817	5 (100 °C)	25 (100 °C)	2 (150 °C)	17

*) M: medium; H: high, acc. to common rubber standards.

**) Highest temperatures typically apply to 1000 h continuous use; lowest temperatures typically apply to 10.000 h continuous use.

transition temperature for the high ACN NBR is practically the same as typically for FKM, does not have predictive value for the dynamic properties of FKM. It basically means that both types of rubber become glass-like brittle at about the same sub-zero temperature of -10 °C.

FKM was developed by the DuPont Company in 1957, in response to the extreme performance sealing needs in the aerospace industry. The type of FKM under consideration here for marine lip seals is a random copolymer of vinylidene fluoride ($\text{CH}_2=\text{CF}_2$) and tetra fluor ethylene ($\text{CF}_2=\text{CF}_2$) which is vulcanized or crosslinked with a peroxide curing system. **Most conspicuous for FKM in comparison to NBR is the continuous service temperature, which is approximately 100 °C higher, compared under same test-conditions. It highlights the unique range of temperatures for FKM (180 °C) relative to NBR (85 °C).** Another important performance criterium for FKM vs. NBR is its very high abrasion resistance, particularly in relation to its expected performance of min. 5 years dictated by the scheduled regular maintenance overhaul dockings for ship vessels.

In ECHA Annex XV Restriction Report, Proposal for a Restriction for Per- and polyfluoroalkyl substances (PFASs)²⁸, page 351, Table E.114, the statement is made that NBR and CR (Polychloroprene or shortly Neoprene) are generally suitable for water-lubricated bearings in stern tube seals for marine vessels, though at the cost of inferior friction and wear characteristics compared to PTFE (PolyTetraFluoro Ethylene or shortly Teflon). The use of CR is highly unlikely because CR is positioned on the scale of Oil Resistance in **Figure 8** right in between oil- and water-resistant: basically not compatible with either medium, at least not for sufficiently long time.

The high temperature range for both rubbers quoted to be + 150 °C does apply for short durations of just a few hours at most, to be compared with the highest continuous use working temperature of 120 °C for NBR for automotive continuous use of 1000 h. In the past, NBR was widely employed for stern tube seals, however with the advent of FKM it was essentially fully replaced in response to the ever increasing requirements by larger ships. In terms of time-temperature application range, FKM clearly stands out as the best performing of all available elastomer/rubber types, as demonstrated in **Figure 8**, and confirmed in ECHA Table E.114 by a lifetime of NBR of approx. 10% of fluorocarbon and above 100 °C even lower.

For a comprehensive overview of the eventual other alternatives for FKM with reference to the performance criteria mentioned: see **Table 2**.

To conclude: comparing the mechanical properties for high-ACN NBR and FKM, they seem roughly comparable, where FKM positively stands out on the compression set at +120 °C, again on basis of its much higher temperature resistance in combination with durability and thus safety (see in this context also the issue on blister-formation, mentioned below).

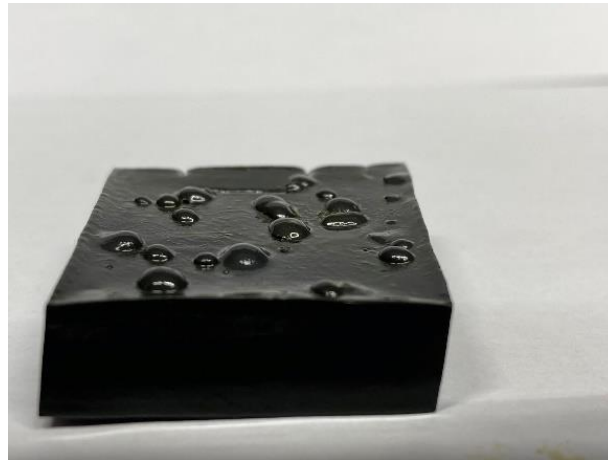
Substance FKM-Fluoroelastomers	
A potential alternative substance for FKM for use as seals and/or in sealing applications in marine shipping; must fulfil – at least - the following cumulative requirements: a) continuous high temperature as from 130 °C and much higher degrees; b) long-term chemical resistance to oil; c) long-term chemical resistance to (salt)-water; d) sufficient mechanical properties: such as tensile and tear strengths, fatigue strength, abrasion resistance; e) sufficient static modulus or hardness to carry axial force exerted by the Garter spring; f) low compression set at different temperatures between 0 °C and operating temperatures for various durations; g) brittleness temperature in marine applications ≤ -5 °C; and h) need to perform safely for a duration of 5 years (dry-docking)	
Potential Alternative substance	Suitable alternative?
H-NBR	No, because H-NBR does not fulfil requirement(s) a), b), c) and h).
FVMQ	No, because it fails severely on c) and d), and so on h).
ACM	No, because it fails on a), d), g) and h).
High CAN NBR	No, because it fails on a), d), g) and h).

Table 2: Overview potential alternatives for FKM for use as seals and/or in sealing applications in marine shipping.

VII. Blister-formation

A common failure mechanism in seals is the formation of small blisters on one or both sides of the contact of the seal lip with the shaft, **Figure 9**. These blisters are most commonly found on seals that are in contact with sea water. The phenomenon has been extensively studied and occurs on both elastomers used for rotary propeller seals, however it is more common on NBR than on FKM^{29,30}. For NBR the formation of a blister requires a temperature at the lip-contact of 130 °C for a longer duration.

Under these conditions, NBR shows excessive hardening and subsequent blister formation at either side of the contact. **Blister formation was originally one of the major factors in the**



switch from NBR to FKM once the latter became available as an alternative material.

***Figure 9:** Example of blisters alongside the seal lip of a NBR-seal.*

The root cause of these blisters remains a point of discussion in the scientific literature in spite of all research devoted to this phenomenon. The most comprehensive study of the phenomena was reported by Fr. Schultz³¹, who refers to a combination of factors, which each individually or jointly may cause the blisters to develop:

- Dynamic load and, as a consequence, fatigue by which small cracks are formed. These are filled with oil or water by capillary forces due to the pressure under the lip. These subsequently grow to a visual size whilst volatile enclosures in the rubber evaporate when operating at a persistent high temperature. Additives included in the oil for reasons of viscosity control and thermal stabilisation, in particular amine-containing compounds. Apparently, oils without additives lead to very little or no blister-formation.
- Also by this author²⁹ the pivotal role of misalignment and the resulting variable loads.
- Contact of at least one side of the seal with air, in combination with high temperatures. This points obviously to oxidative ageing.
- Starvation of the lubricant film under the lip as a result of insufficient transport.
- To this listing has to be added the much more aggressive nature of the present EAL-oils, which were still not in focus at the time of the Schultz study³¹.

While all these failure mechanisms occur with NBR and to some extent with FKM as well, it is well understood that FKM outperforms NBR on these critical aspects because of its far better thermal stability. FKM seals are overall chemically far more resistant than NBR seals. Table 3 provides detailed test results for compatibility of a selection of EALs with NBR and FKM.

***Table 3:** Compatibilities of various oil-types with NBR and FKM, with further classification as VGP EAL compliancy. By courtesy of Lagersmit³².*

Company name	Product name	Viscosity [cSt @ 40°C]	NBR * compatible	FKM compatible	VGP EAL compliant ***
Castrol	Biostat 68	70	*	✓	
	Biostat 100	103	*	✓	✓
	Biostat 150	144	*	✓	
	Biostat 220	207	*	✓	
Chevron	Clarity synth. EA Gear Oil 100	100	X	✓	✓
	Clarity synth. EA hydraulic Oil 46	46	X	✓	✓
	Clarity synth. EA Hydraulic Oil 68	68	X	✓	✓
ExxonMobil	SHC Aware ST 100	100	*	✓	✓
	SHC Aware ST 220	220	*	✓	✓
Fuchs	Plantosyn 68 HVI	68	X	✓	✓
	Plantogear 100 S	100	X	✓	✓
	Plantogear 150 S	150	*	✓	✓
Gulf Oil Marine	GulfSea BD Sterntube Oil 68	68	*	✓	✓
	GulfSea BD Sterntube Oil 100	100	*	✓	✓
	GulfSea BD Sterntube Oil 220	220	*	✓	✓
Klüber	Klüberbio RM2-150	150	X	✓	✓
	Klüberbio EG2-68	68	X	✓	✓
	Klüberbio EG2-100	100	X	✓	✓
Shell	Shell Naturelle S4 Gear Fluid 68	68	X	✓	✓
	Shell Naturelle S4 Gear Fluid 100	100	X	✓	✓

Terresolve	Envirologic 200	68	X	✓	✓
	Envirologic 210	100	X	✓	✓
	Envirologic 3046	46	X	✓	✓
	Envirologic 3068	68	X	✓	✓
Total	Biohydran TMP 100	100	*	✓	✓
	Bioneptan 100	100	**	✓	✓
	Bioneptan 150	150	**	✓ **	
	Bioneptan 220	220	**	✓ **	
Vickers	Hydrox Bio 68	68	*	✓	✓
	Hydrox Bio 100	100	*	✓	✓
	Hydrox Bio 220	220	*	✓	✓
	Biogear XP 68	68	X	✓	✓

Notes:

EALs can chemically affect the sealing rings by hydrolysis. Especially when emulsions are built up in the oil chamber of the sealing system or in the stern tube, these bio-oils interact with the water present and tend to break down. The lifetime of any lip-type sealing system can decrease due to this aggressive mixture. FKM seals are chemically more resistant than NBR seals

* NBR compatibility was tested with clean oil. Hydrolysis and higher operating temperatures than 40 °C may limit the life-time of NBR lip seals.

VIII. End-of-life disposal

In the context of the recent proposal of ECHA to impose a restriction on the production and use of PFAS (Per- and Polyfluoralkyl substances), published on 07.02.2023, the question of disposal of end-of-life articles is a major point of concern because of their extremely high persistence and accumulation in nature²⁸.

During docking and overhaul of ship vessels, the stern tube seals are commonly one-by-one replaced by new ones, recovering as many used seals as installed new ones. Apart from the seal lips which have been in continuous contact with the propeller shaft during extended use, most part of the seals have only been in contact with oil, (sea-water) or a mixture of both. The lip-contact represents only a minor part of the seal. The FKM by nature not being compatible with oil nor with water will not have absorbed relevant quantities of either one. In fact, the

seals represent a rather pure material, apart from contaminations which may have adhered to the surface, but can be removed easily by proper cleaning.

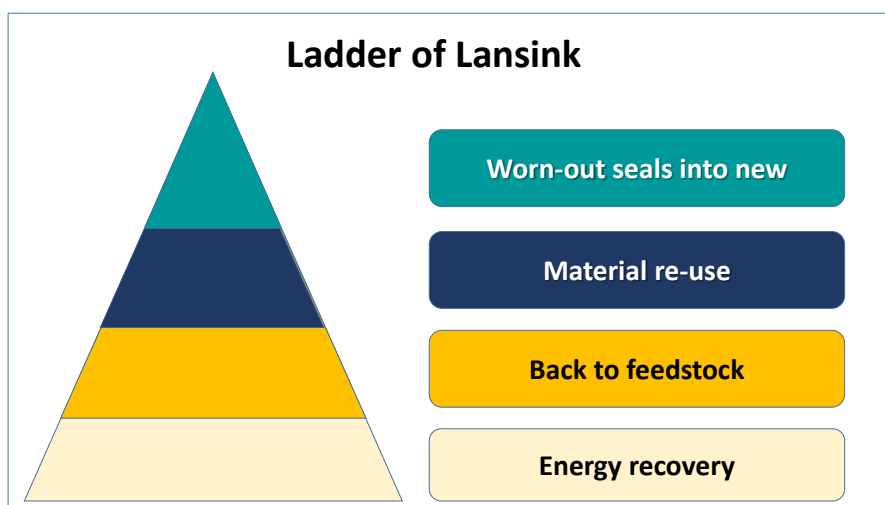


Figure 10: Ladder of Lansink.³³

The various ways to discard waste can best be portrayed in terms of the so-called ladder of Lansink³³, **Figure 10**, listing the hierarchy in waste management for end-of-life seals from high to low:

- Prevention
- Re-use of articles into new
- Recycling by material reuse
- Back to feedstock
- Energy recovery by burning/incineration
- Disposal

Disposal on a landfill: is not considered as a feasible option to consider by virtue of the primary objective of the ECHA restriction proposal: to prevent the extremely high persistence and accumulation in nature of PFASs and so of FKM.

Incineration with Energy recovery: At the present moment in time, most worn-out seals are burned /incinerated: the lowest step on the ladder above. There have been various studies as to the conditions necessary in waste incinerators, demonstrating that at sufficiently high >850°C oven temperature the combustion products are practically only HF (hydrogen fluoride) and CO₂ (Carbondioxide)^{34,35}. Minor to trace amounts of low molecular PFASs may still be traced in the CO₂ recovery. According to Bakker et al.³⁴ all waste incineration plants in the Netherlands fulfill on average the requirement of an incineration temperature > 850 °C. No statement is made about the feasibility of energy recovery, although the amount of energy to be recovered in municipal and industrial waste ovens by burning the relatively low amounts of FKM is negligibly small.

The company AEGIR Marine in the Netherlands has recently -implemented a circular collection system for wasted seals to be collected and returned to their homebase in the Netherlands.

From thereon they will be kept separate to be burned under controlled conditions as depicted above. Under implementation.

Back to feedstock: On basis of their compound composition the rotary propeller seals consist for appr. 70 – 80 wt% out of FKM elastomer and for appr. 30 – 20 wt% of N990 carbon black. N990 carbon black has no practical value as reinforcing filler because of its largest primary particle size in the whole range of reinforcing and non-reinforcing carbon blacks¹⁷. Its main role in the compound is for cost savings and as a pigment to stabilize the material against UV-attack (not an issue in the present context). Where the FKM cannot be recovered without the rupture of the crosslinks (see later under devulcanization) the only back to feedstock option is pyrolysis of the rubber. Pyrolysis at temperatures around 600-700°C to result in a vapour-phase, oil-phase and a solid phase called carbon black, is a back to feedstock option catching much attention these days. Particularly for tire-waste. The carbon black phase consists of reinforcing carbon black to be re-used in the production phase of the tire compounds. It also includes pyrolyzed remains of the elastomers, with additionally mineral fillers and remnants of the vulcanization ingredients³⁶.

As FKM compounds contain practically no carbon black, except some quantities of N990 black, any pyrolysis remnants are per definition low-molecular weight PFASs and as such this technology for back to feedstock does not lend itself for small size fluoroelastomer consumers, but rather for a large scale operation at e.g. fluoro-polymer producers, where the low-molecular weight PFASs could immediately be re-used for renewed polymer synthesis; if at all feasible.

Material reuse: Grinding towards sub-millimeter powder and mixing it into virgin rubber compounds is often employed for FKM. The smaller the ground particles, the less damaging for the mechanical properties. Commonly appr. 5% powder can be accommodated in virgin material with limited loss in properties. Some people quote amounts till 15%. It is most commonly employed for FKM with production waste.

As seals are replaced on a one-to-one basis much higher quantities of re-grind should be feasible than 5% to accommodate this route for recycling of used seals. Furthermore, on 30 August 2022, the European Commission published a proposal to restrict the placing on the market of microplastics, including where they are added in mixtures. Microplastics are defined here as < 5mm. The restriction will be adopted under the REACH Regulation, which establishes the EU chemicals framework. According to this recent proposal from ECHA there will be a ban on microplastics production and use. Consequently, grinding used rubber to particles smaller than 1 mm and adding them to virgin rubber may soon come under scrutiny³⁷. It does not seem a feasible solution for the long term.

Recycling as an option for worn out seals into new: Reclaim/devulcanization. Apart from reclaiming which is a devulcanization technology developed in the second world war for Natural Rubber and still employed in large quantities, reclaiming or rather devulcanization of synthetic rubbers, to include FKM is still in its infancy. For a status-report see ref.³⁸. The devulcanization technology has proven itself for Natural- and EPDM-rubbers and is in the development stage for the other rubbers employed in tyres: SBR, BR and IIR (Butyl) rubbers, under supervision of Assoc. Prof. Dr. W.K. Dierkes of the University of Twente, Enschede, the

Netherlands³⁸. To extent this technology to FKM requires a totally new approach, because of the special unique nature of fluoro-polymers. At present discussions are underway between a consortium of companies under leadership of AEGIRMarine in the Netherlands, to join forces with the University of Twente to screen the feasibility of devulcanization for FKM. This will aim at the highest step of the ladder of Lansink with substantially increased percentages of re-use than the 5-15% for grinding, preferably approximately 50%. Special attention has to be paid to avoid the risk of formation of low-molecular PFASs as by-products!

To conclude: there remain basically two feasible options on the long term to dispose of used end-of-life seals, which are incineration at sufficiently high temperature and reclaim/devulcanization, the latter still in its infancy needing extensive research and development efforts.

IX. Conclusions: no suitable alternative for FKM, extensive R&D needed

Elastomeric Rotary Propeller Seal Systems for Marine Applications typically consist of a series of circular seals in a row, allowing for a gradual transition from oil in the inside of the stern tube to (sea-)water outside the hull of the ship. Material selection of the appropriate elastomer for such seals is a potential choice between NBR (nitrile-rubber) and FKM (fluoro-rubber).

Over the years, the increase in size and tonnage of ships has resulted in a growth of thrust, and lead to larger and faster rotating screw shafts within the stationary seals. Due to the inevitable and functionally necessary contact force and resultant friction between the seal lip and the propeller shaft, **the temperature of the seal contact steadily increased and can be up to a minimum of approximately 130°C. This temperature greatly surpasses the maximum allowable temperature for NBR of 85°C to enable proper and safe operation for (at least) 5 years before requiring replacement during a ship's scheduled overhaul.** This has gradually resulted in a switch away from NBR, and at present FKM is used almost exclusively as this elastomer permits a substantially elevated **continuous** use temperature, of 100°C extra. **Furthermore, FKM is better resistant and inert to oils, surfactants and (sea-)water.** This is increasingly important as according to recent American and European legislation, the use of Environmentally Acceptable Lubricants based on esters of carboxylic acids is mandated for stern tube purposes. These EALs are more aggressive to the rubber seals than purely mineral oils, as these tend to decompose by saponification under the generation of organic acids in contact with hot water or steam at the high temperatures occurring under the lips. **Also in this respect FKM cannot be substituted by NBR. The root cause of the much better properties of FKM over NBR is based on the fluoro-carbon bond prevailing in FKM: Table 4.**

At this moment in time **incineration of end-of-life seals at high enough temperatures >850 °C is practically the only way to deal with proper disposal.** Efforts are being undertaken to see whether reclaim/devulcanization can replace this way of disposal in order to achieve an acceptably higher proportion of re-use of the still valuable FKM.

Experiences over the past decades show that no alternatives exists that match the combination of characteristics required to substitute FKM. Replacing FKM in propeller shaft seals is practically not realistic and will require at least many years of research.

Table 4: Typical Bond-dissociation temperatures and bond energies of some typical chemical bonds in relevant vulcanised elastomers¹⁵.

	Chemical Bond	T _{diss} in °C	E _{diss} in kJ/mol
1	$\text{— CF}_2 \text{—} \overset{\text{—}}{\underset{\text{—}}{\text{C}}} \text{— CF}_2 \text{—}$	500	400
2	$\text{H}_3\text{C—} \overset{\text{—}}{\underset{\text{—}}{\text{C}}} \text{— F}$		445
3	$\text{— CH}_2 \text{—} \overset{\text{—}}{\underset{\text{—}}{\text{C}}} \text{— CH}_2 \text{—}$	400	320
4	$\text{H}_3\text{C—} \overset{\text{—}}{\underset{\text{—}}{\text{C}}} \text{— H}$		420
5	$\text{— CH}_2 \text{—} \overset{\text{—}}{\underset{\text{—}}{\text{C}}} \text{— CH}_2 \text{— CH = CH —}$	390	300
6	$\text{— CH}_2 = \text{CH — CH}_2 \text{—} \overset{\text{—}}{\underset{\text{—}}{\text{C}}} \text{— H}$		320
7	$\text{— C — S —} \overset{\text{—}}{\underset{\text{—}}{\text{C}}} \text{— S — C —}$	320	270
8	$\text{— C —} \overset{\text{—}}{\underset{\text{—}}{\text{C}}} \text{— S}_x \text{— C —}$ X ≥ 3	~ 160	120

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Resumes

Resume prof. dr. ir. J.W.M. Noordermeer



Jacques Noordermeer is professor (em) in Elastomer Technology and Engineering at the University of Twente, Enschede, the Netherlands. After completing his study biochemistry (cum laude) he obtained his PhD at the Delft University of Technology. He worked as a post-doctoral research associate at the Rheology Research Center of the University of Wisconsin, Madison, Wis. USA. After working several years as Director R&D in the industry in the field of rubber development, he specialized in elastomer technology applications. As of 1995 he worked as professor in Rubber Technology at the University of Twente, Enschede, the Netherlands.

In 1999 he was recipient of the Technical Award of the IISRP: Institute of Synthetic Rubber Producers. In 2000 he was awarded with the Original Contribution Award of the 157th meeting of the Rubber Division of the American Chemical Society, Dallas, Texas.

In 2005/2006 he received the Gold medal of the International Rubber Conference Organization (IRCO).

In 2010 he was recipient of the George Staffort Whitby Award of the American Chemical Society, Rubber Division.

In 2011 he was awarded as Dutch Master of Materials. In 2014 he received the Original Contribution Award of the 184th meeting of the Rubber Division of the American Chemical Society, Cleveland.

In 2019 he was honored as Officer in the Royal Dutch Order of Oranje Nassau for professional and societal merits.

In 2019 he received a Honorary Doctorate Degree in Polymer Technology of the Prince of Songkla University, Hat Yai, Thailand.

Currently Jacques Noordermeer has several professional memberships:

- 1975 – present: Member of the Sigma Xi, The Scientific Research Society, USA;
- 1982 – present: Member of the American Chemical Society, Rubber Division;
- 1982 – present: Member of the Dutch Association of Rubber and Plastics Technologists VKRT;
- 1986 – present: Member of the Board of the International Rubber Conference Organizing Committee, on behalf of the Netherlands;
- 2000 – present: Board Member of the Dutch Natural Rubber Foundation.

Resumes

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Marc Masen is associate professor in Tribology and Mechanical Engineering Design at Imperial College London.

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