

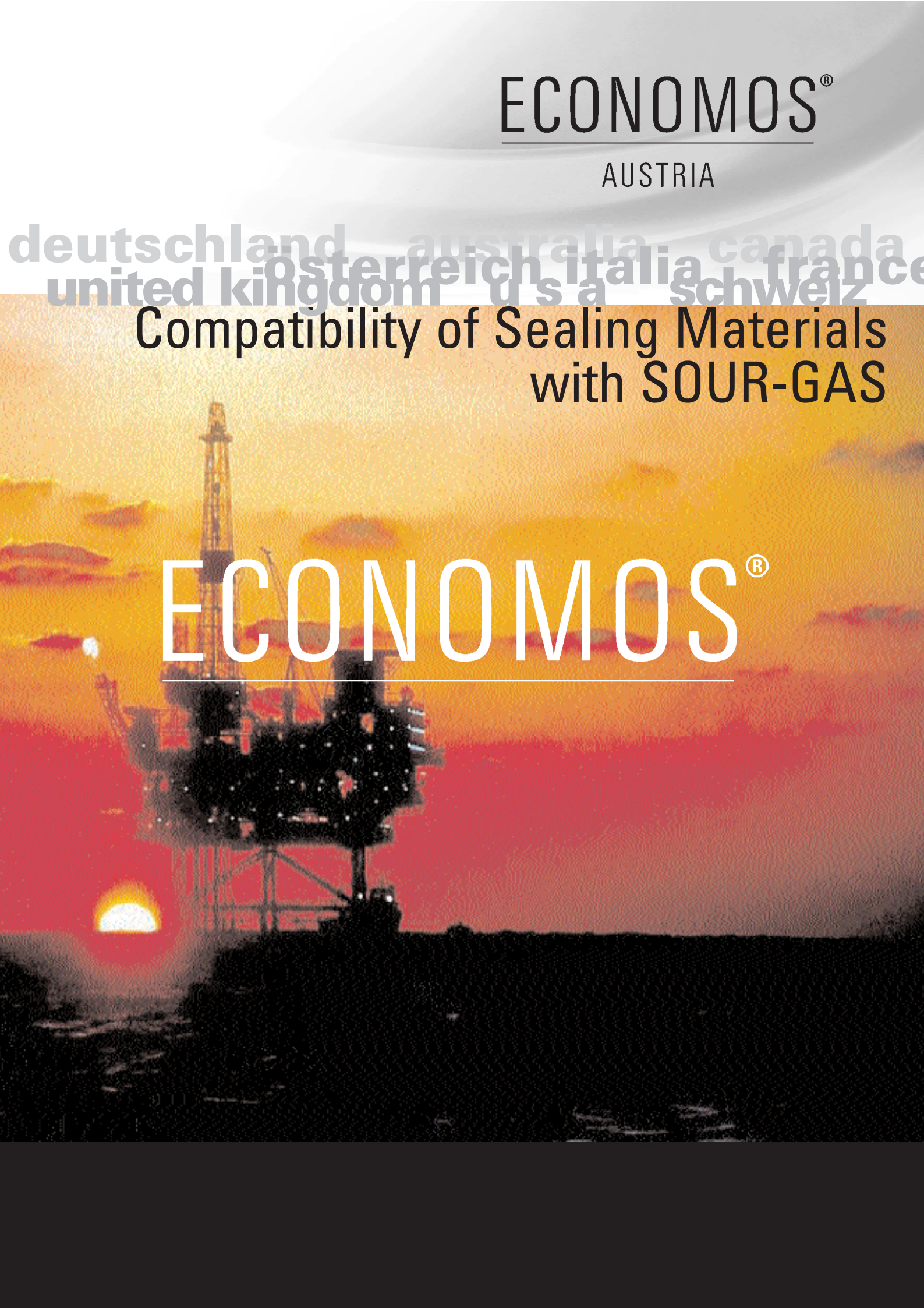
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Compatibility of Sealing Materials with SOUR-GAS

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New Materials

Compatibility of Sealing Materials with Sour Gas

Th. Schwarz, ECONOMOS Austria GmbH

Elastomeric sealing elements intended for use in oil-field operations are required to function in a wide range of fluids, temperatures and pressures. A failure of elastomeric seals can lead to defects or even total standstill of oilfield machinery or plant which can cause high costs or danger to human life and the environment. Therefore the selection of oil-field environment resistant sealing materials is of vital importance.

Besides the main components such as crude oil, natural gas and various well fluids, sour gas (hydrogen sulphide) is a very critical and hostile ingredient of oil-field environments. Hydrogen sulphide (H₂S) is not only problematic for its toxicity and corroding properties, but also for its aggressiveness against elastomeric seals. Therefore this paper deals with the sour gas compatibility of elastomeric sealing materials for the oil-field environment.

1. Introduction

Elastomeric seals which are working in oil-field environments, e.g. in off-shore exploration, refineries or transportation of crude oil or natural gas, can suffer severe stresses such as high pressure and mechanical forces, a broad temperature range and a wide variety of chemicals. The immersion in these chemicals in combination with high temperatures and mechanical stresses causes physical and chemical effects to elastomers and thermoplastics, especially during long-term exposure. These effects can

lead to a deterioration of the sealing materials. The hostile environments that elastomers must resist in service are aromatic and naphthenic hydrocarbons, corrosion inhibitors, acids and other drilling fluids, sea water, carbon dioxide, etc. and last but not least hydrogen sulphide (H₂S), which is - in combination with methane and carbon dioxide - usually called sourgas. Normally crude oil and natural gas can include different concentrations of hydrogen sulphide; in some areas the concentration can increase up to an amount of 16 % and more [1].

Hydrogen sulphide is not only known for its corroding effects on metals but also for physical and chemical effects to elastomeric materials, high swelling and chemical deterioration for example to fluorocarbon rubbers (FPM, FKM) which are often used in oil-field operations.

Therefore the resistance of elastomeric seals, which are used in oil-field operations and off-shore exploration, such as sealing systems for packers, blowout preventers, Xmas trees, surface well-head equipment, subsurface safety valves and so on is of the utmost interest.

Such sealing elements are mostly manufactured of properly formulated nitrile rubbers (NBR), hydrogenated nitriles (HNBR) and fluorocarbon rubbers (FPM, FKM). Sometimes special elastomers of the group of tetrafluorethylene-propylene rubbers (TFE/P) and perfluorocarbon rubbers (FFKM) are used.

NBR elastomers can be used up to a maximum temperature of 212 °F and have a limited resistance against sour gas [2, 3]. In comparison to pure nitriles HNBR elastomers have a good stability to sour gas containing environments [2, 4] and are able to resist temperatures up to 302 °F. For a temperature range up to 392 °F fluorocarbon elastomers are the most suitable materials and are considered as sourgas resistant, if they are properly formulated [5].

Material	Standard	Unit	H-Ecopur™	Ecorubber-H™	HNBR/T	Ecorubber 2™ (FPM 1)	FPM 2
Abbreviation	--	--	TPU/YAU	HNBR	HNBR	FPM	FPM
Colour	--	--	red	black	black	brown	black
Hardness	DIN 53505	Shore A	95	83	80	88	78
100%-modulus	DIN 53504	N/mm ²	15	10	11	11	11
Tensile strength	DIN 53504	N/mm ²	58	21	17	13	18
Elongation at break	DIN 53504	%	410	240	150	130	160
Compression Set 100 °C / 24h	DIN 53517	%	30	20	16	--	--
Compression Set 175 °C / 24h	DIN 53517	%	--	--	--	8	8
max. working temperature	--	°C	110	150	150	200	200
min. working temperature	--	°C	-20	-25	-35	-20	-20

Table 1: Test Materials

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There is no detailed information about the use of polyurethane elastomers (TPU, YAU) in the technical literature. This class of sealing materials due to its superior extrusion and abrasion resistance, is of major interest for sealing applications. Since there exist also chemical and hydrolysis resistant grades of polyurethanes [6, 7], the use of this material is also of interest to the gas and oil exploration industry. In the meantime we have experience with rod seals, piston seals and wipers which are working in Downhole Completion Tools and Drilling Tools, packings for Subsea Gate Valves and U-cups as static seals for Subsea Connectors, all made of hydrolysis resistant polyurethane.

This paper is concerned with the compatibility with sour gas of one member of the polyurethane group in comparison to elastomers based on HNBR and FPM.

2. Research

2.1. Materials

The tests were performed on a thermoplastic polyurethane elastomer (TPU), two grades of HNBR and

two grades of FPM. The materials are specified in table 1.

H-ECOPUR is a mineral oil and hydrolysis resistant polyurethane with a very small compression set, ECORUBBER-H is an hydrogenated nitrile rubber with standard cold flexibility, whereas HNBR/T is an hydrogenated nitrile rubber with improved cold flexibility. Both fluorocarbon rubbers are copolymers and differ regarding hardness and the fillers.

2.2. Immersion tests

The immersion tests were performed at the Institute of Petroleum Engineering, Technical University of Clausthal, Germany. The materials were immersed in two different sour gas environments; the composition of the environments are in accordance with the reference gas phases of the NORSOK-Standard M-CR-710 (environment 1: 5% H₂S, 10% CO₂, 85% CH₄; environment 2: 1% H₂S, 10% CO₂ and 89% CH₄). The samples were immersed at a temperature of 176 °F and a pressure of 1.450 psi in an autoclave over a period of 6 weeks (1000 hours), the polyurethane samples were also tested after one and 3 weeks. The release of pressure occurred not in sudden bursts and therefore we cannot talk of conditions which usually cause explosive decompression.

The measurements of change of hardness, weight and volume and the optical control of the test specimens were done immediately after removing the samples from the autoclave by the Institute of Petroleum Engineering. The tensile testing and a second testing of hardness were done after storing the samples for three months at room temperature in the laboratory of ECONOMOS Austria. This second test describes the chemical effects of the immersion to the elastomer but, because physical effects like volume change are largely reversible, they do not influence the three months results.

3. Results and discussion

The volume change of H-ECOPUR in sour gas for both environments is shown in figure 1.

H-ECOPUR suffers a very small volume change in both atmospheres; the swelling rate in the higher concentrated sour gas atmospheres is approximately one percent higher compared to the low-concentrated atmosphere. Furthermore there is no change of hardness over the whole immersion period. Another proof of the good resistance of H-ECOPUR against sour gas is shown by the results of the tensile tests (Fig. 2).

There is no sign of chemical deterioration of the material in both atmospheres over the whole period of 1000 hours. The intermediate decrease of tensile strength and elongation at break of the material

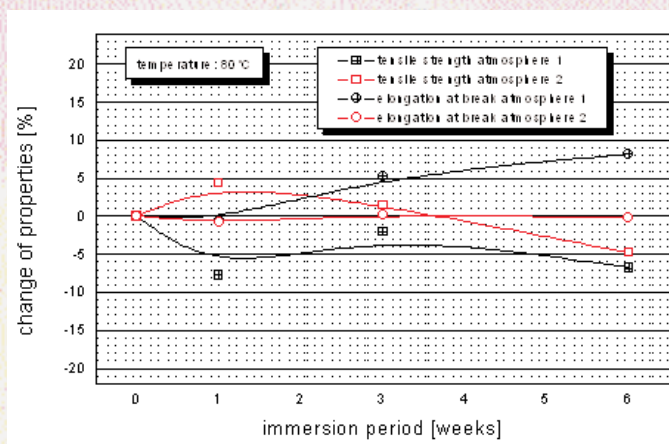


Fig. 2: Change of tensile strength and elongation at break of H-ECOPUR in sour gas over an immersion period of 6 weeks ($T = 176\text{ }^{\circ}\text{F}$, $p = 1.450\text{ psi}$)

in atmosphere 1 after 168 hours can be explained by changes in the morphology of the crystalline and paracrystalline domains of this segmented polymer [8].

The following charts show a comparison of the sour gas compatibility of the hydrogenated nitrile rubbers and the fluoroelastomers in comparison to H-ECOPUR. The swelling behaviour and the change of hardness of the materials after an immersion period of 1000 hours is demonstrated in Fig. 3 and 4.

Compared to the special grade of polyurethane elastomer the volume change of the nitriles is three times higher and that one of the fluorocarbon rubber 4 times higher. As expected the volume change of H-ECOPUR and the fluorocarbon elastomers increases with increasing hydrogen sulphide content, whereas the HNBR elastomers show an inverse behaviour. Besides the volume change the immersion in sour gas results in a destruction of the material structure, what can be seen in the formation of gas bubbles and blisters after removing the test

specimens of the autoclave (Fig. 5). The blisters remain in the material

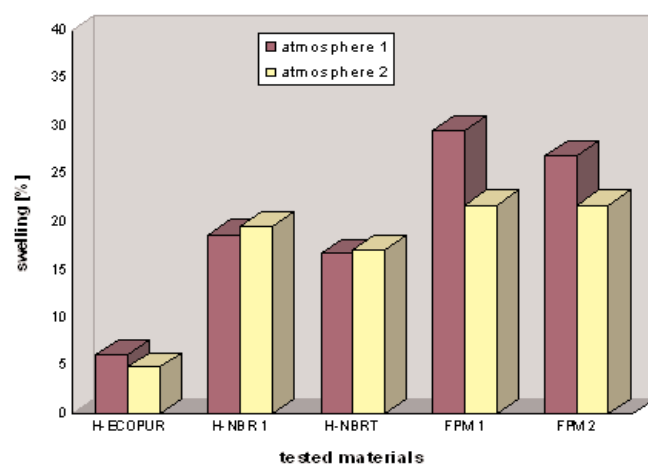


Fig. 3: Volume change of sealing materials after an immersion period of 6 weeks in sour gas environments ($T = 176\text{ }^{\circ}\text{F}$, $p = 1.450\text{ psi}$).

in the shape of cracks / splits, when the gas has migrated out of the material (Fig. 6).

ECORUBBER-H: no blisters but a few small bubbles < 3 mm diameter; HNBR/T: many big blisters up to 20 mm diameter; FPM 1 and 2:

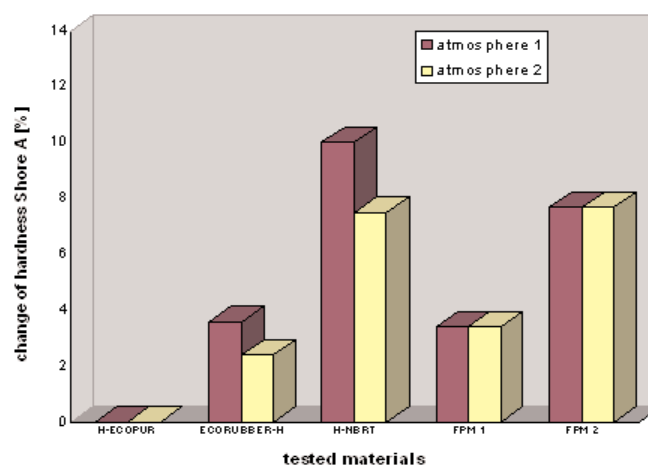


Fig. 4: Change of Shore A hardness of sealing materials in sour gas environments after an immersion period of 6 weeks ($T = 176\text{ }^{\circ}\text{F}$, $p = 1.450\text{ psi}$).

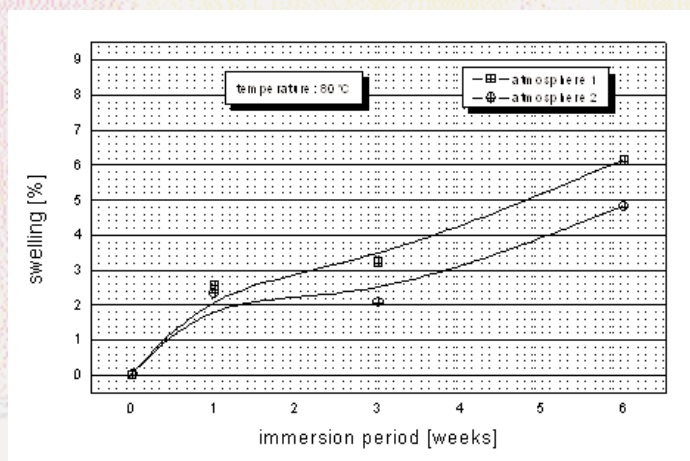


Fig. 1: Volume change of H-ECOPUR in sour gas environments at a temperature of $176\text{ }^{\circ}\text{F}$ and a pressure of 1.450 psi .

medium and big blisters up to 20 mm diameter), the measurement was repeated with the "blister-free" specimens after 3 months.

These measurements demonstrate that all of the materials except H-ECOPUR have suffered more or less chemical deterioration by the immersion in sour gas. The fluorocarbon elastomers show an increase of hardness between 3 Shore A

the materials, the effect of the sour gas immersion to the different materials can be seen very clear (Fig. 7 and 8).

The superior resistance of H-ECOPUR in comparison to the other materials is clearly demonstrated with the whole retention of the tensile properties over the whole immersion period. Relating to the other elastomers, ECORUBBER-H

has a higher stability against sour gas which results in a 25 % loss of elongation at break whereas the deep-temperature modification HNBR/T and both fluorocarbon rubbers have suffered a dramatic loss of tensile strength and elongation at break up to 70 %. This means that these three materials are not suitable to work under conditions which are similar to the test parameters, i.e. high-concentrated sour gas environments.



Fig. 5: Formation of blisters in HNBR/T after immersion in environment 2 for 6 weeks at 176 °F and 1.450 psi.



Fig. 6: Microscopic photography of cracks in a fluorocarbon rubber FPM 2 (thickness: 2 mm)

(FPM 1) and 6 to 7 Shore A (FPM 2); the increase of hardness of the HNBR elastomers depends on the atmosphere. The higher concentrated atmosphere 1 causes - in comparison to the volume change - a higher increase of hardness (3 Shore A of HNBR 1 and 8 Shore A of HNBR/T) as the lower-concentrated atmosphere 2 (appr. 1,5 Shore A of HNBR 1 and 6 Shore A of HNBR(T).

Looking to the tensile properties of

polyurethane elastomer (H-ECOPURTM) and elastomers of the group of hydrogenated nitrile rubbers (HNBR) and fluorocarbon rubbers (FPM, FKM), which are usually used in such aggressive environments. The immersion of the mate-

fluorocarbon rubbers and a deep-temperature version of a hydrogenated nitrile rubber have suffered severe chemical deterioration. Only one HNBR grade (ECORUBBER-H) has also shown an acceptable ageing behaviour.

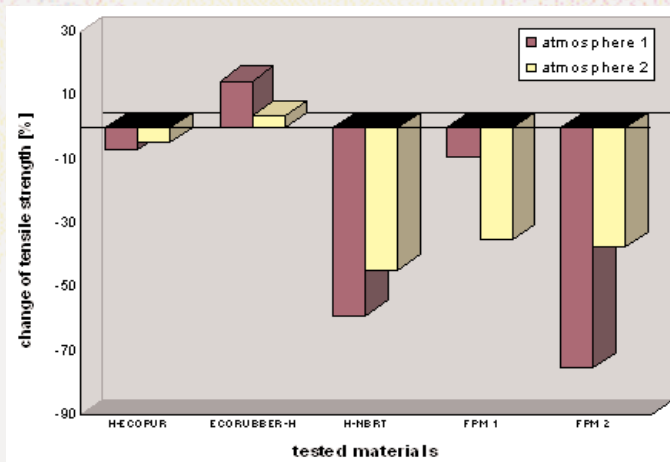


Fig. 7: Change of tensile strength of sealing materials after immersion in different sour gas atmospheres after 6 weeks (T= 176 °F, p= 1.450 psi).

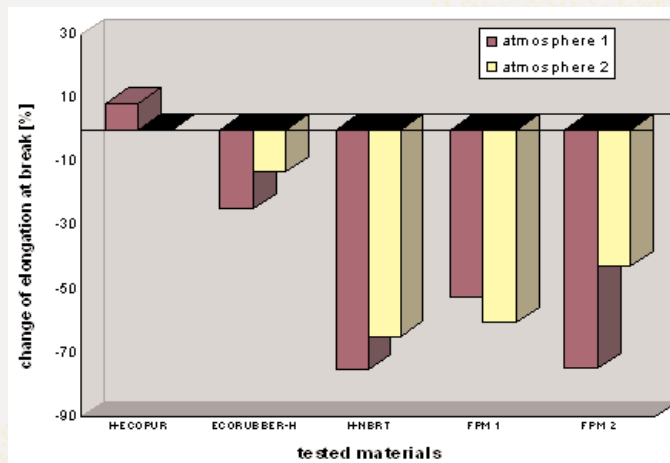


Fig. 8: Change of elongation at break of sealing materials after immersion in different sour gas atmospheres after 6 weeks (T= 176 °F, p= 1.450 psi).

rials occurred at a temperature of 176 °F and a pressure of 1.450 psi in two sour gas environments (mixtures of methane, carbon dioxide and hydrogen sulphide) with a hydrogen sulphide content of 1 % and 5 %.

The surprising result of the investigations was that the special polyurethane elastomer H-ECOPUR displays a superior resistance against sour gas environments compared to the other materials. This superior compatibility appears with a small volume change and no change of hardness and tensile strength over the whole immersion period, whereas both

These results prove that special formulations of polyurethane elastomers, are a most interesting material class for sealing applications because of their superior wear properties and excellent extrusion resistance, and are an excellent solution for sealing elements for use in sour gas environments.

Dr. Thomas Schwarz is technical director of ECONOMOS Austria GmbH, Austria

... please refer to the bibliography on the next page ...

Summary and outlook

This work was concerned with the compatibility of various elastomers with different concentrated sour gas environments. The investigations were performed on a special, hydrolysis-resistant thermoplastic

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