Bulletin on Testing of Oilfield Elastomers — A Tutorial

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SECTION 1
SCOPE

1.1 This document is a tutorial for the evaluation of elastomer test samples or actual elastomeric seal members intended for use in the oil and gas industry. In earlier times, most of the oil and gas production was from sweet, low pressure wells and oilfield equipment manufacturers could supply low durometer nitrile rubber for seal members and the customers could depend on the seal with reliability. With time, these oil reserves have been depleted and the search for oil and gas has led to the development of deep, high pressure reservoirs and/or sour (H_2S), corrosive oil resources. In a prospective application, the customer and the oilfield equipment manufacturer may not really be sure of the performance of the seal materials and members in the equipment. Many tests exist which evaluate the performance of a seal material or member. It is the intent of this document to review testing criteria, environments, evaluation procedures, guidelines for comparisons, and effects of other considerations on the evaluation of elastomeric seal materials and members.

SECTION 2
DISCLAIMER

2.1 It is the intent of this document to outline several tests which can be conducted to attempt to predict the performance of elastomeric seal materials and members in related environments. It is not within the scope of this document to either offer any correlation between the data obtained from a screening test and the actual service performance of the seal member or to present any pass/fail criteria. In the oil and gas industry the relationship between elastomer screening test conditions and actual service conditions is only approximate, at best. Consequently, the correlation between the results of any screening tests and actual service life or performance is also approximate. It has been shown that the gross effects observed in the screening tests *may* identify possible problems in field applications. The extent of the correlation has not been recognized or quantified.

SECTION 3
REFERENCES

3.1 Terminology. The following terms, definitions, expressions, abbreviations, etc., are commonly used in the oilfield seal technology and in this bulletin but also apply to the design of seals, elastomers, and pressure-holding devices in general. There is no attempt to give detailed explanations or derivation of the terms; instead a concise description of the common terminology is given. Additional lists of terms can be found in other API or ASTM publications such as API Spec 6A or in "Glossary of Oilfield Production Terminology," 1st ed., Jan. 1988, or ASTM D1566 in Volume 9.01 of the Current Annual Book of ASTM Standards.

ACS — American Chemical Society.

AFLAS — See fluoroelastomer.

ANTIEXTRUSION DEVICE — Plastic, metal, wire, etc., rings and packings used to block the extrusion of the elastomer seal.

ASTM — American Society for Testing and Materials.

BUNA-N — Trademark for acrylonitrile butadiene elastomer (NBR). Other trademark names are KRYNAC, HYCAR, PERBUNA, CHEMIGUM and PARACRIL.

BUTTON — A cylindrical shaped, standardized size rubber specimen or pellet used for testing physical and chemical properties.

COMPOUND — The thorough mixture of raw rubber or elastomer with other ingredients and additives which will allow the base material to be molded and cured in order to optimize its physical, thermal, mechanical, and chemical resistance properties.

COMPRESSION SET — The residual deformation of a material after removal of the compressive stress.

CURE — The act of vulcanization.

DUMBBELL — A dog bone shaped flat specimen of rubber used for testing of physical and chemical properties.

ELASTOMER — This term is used synonymously with rubber, particularly synthetic rubber; generally a nonmetallic material which resists deformation, up to a point, and has the ability to recover its original shape after the deforming force is removed. See RUBBER.

ERG — Energy Rubber Group.

EXPLOSIVE DECOMPRESSION — A type of seal failure manifested by gas bubbles, blisters, cracks, etc., on the surface of a seal or internally in a seal which has been exposed to high gas pressure and then subjected to a rapid release of pressure.

EXTRUSION (Processing) — One of the methods to form rubber and plastic materials into usable shapes, such as gaskets, seals, etc.

EXTRUSION — One of the common modes of failure of seals. This usually refers to the flow of rubber seal particles into the gap between a piston and cylinder.

FIELD — In this text: the oilfield.

FLUOROELASTOMER — Fluorine-containing elastomer: Common examples are trademarked VITON, FLUOREL, KALREZ, CHEMRAZ, and AFLAS.

GAS DEFUSION — Gas penetration through a seal material, usually under high pressures; see EXPLOSIVE DECOMPRESSION.

HNBR — Hydrogenated acrylonitrile butadiene elastomer or HSN.

HSN — See HNBR.

KALREZ — See fluoroelastomer.

MODULUS — The ratio of stress to strain; in the rubber industry modulus refers to the tensile stress of rubber compounds at 100 percent, 200 percent, etc., stretch. Consequently the rubber strength values are usually given at 100 percent MODULUS, 200 percent MODULUS, respectively.

NACE — National Association of Corrosion Engineers.

NBR — Standard abbreviation of nitrile rubber (acrylonitrile-butadiene).

NITRILE — See NBR.

OIL AND GAS INDUSTRY — In this bulletin, the name is used in reference to the exploration and production of natural gas, crude oil, and geothermal products.

PACKING — A deformable material which is generally less flexible than homogeneous rubber seals and energized by squeezing or compressing it by mechanical means; usually located in a stuffing box.

P_c — Critical pressure.

POLYMER — A broad group of high molecular weight materials which includes rubber, elastomers, and plastics.

PLASTIC (Packing) — Various soft materials used to inject behind or around a certain type of seal and thereby to hydraulically energize it. The plastic itself is usually not intended to be a sealant.

PLASTICS — Synthetic, moldable, castable, pliable material with some elastic properties. In seal technology, plastics are often used for backup rings and antiextrusion devices.

RUBBER — Natural or synthetic, pliable material with elastic, and springy properties, often stretchable to several times its original length, and with the ability to recover the original length. Rubber is always used in a mixture with other ingredients in order to make it moldable and to improve its mechanical properties; see ELASTOMER, also COMPOUND.

SEAL — A device that prevents the leakage of fluids (liquid or gas) from a pressure vessel. Seal material may be elastomer, metal, plastic, or a composition of several materials.

DYNAMIC SEAL — A seal where there is any one of several possible modes of relative motion between the sealing surfaces: lateral, rotary, etc.

FACE SEAL — A static seal between two surfaces.

ROTARY SEAL — A type of dynamic seal where the relative motion is circular.

STATIC SEAL — A seal where there is no relative motion between the seal and the sealing surface. The seal may be energized by compression in the vertical or radial direction.

SOUR — The presence of hydrogen sulfide (H_2S) in natural gas or crude oil.

SWEET — The well product contains no H_2S; see SOUR.

T_c — Critical temperature.

T_g — Glass transition temperature; below this point rubber becomes rigid, glass-like material.

VITON — See fluoroelastomer.

VOLUME FILL — (Also seal/gland occupancy ratio) is the ratio of seal volume to available seal groove volume, often expressed in terms of percentage.

VULCANIZATION — The crosslinking of molecules of the raw rubber material; an irreversible thermochemical process that takes place during and/or after molding, extruding, casting of raw rubber compounds.

XNBR — Carboxylated nitrile.

3.2 Reference Documents.

"Specification for Wellhead and Christmas Tree Equipment," API Specification 6A, 16th Ed., Washington, DC., 1989.

API Glossary of Oilfield Production Terminology, (Definitions and Abbreviations, 1st Edition, January 1988.

ASTM D395-STM for Rubber Property, Compression Set.

ASTM D412-STM for Rubber Properties in Tension.

ASTM D471-STM for Rubber Property — Effect of Liquids.

ASTM D1329-STM for Evaluating Rubber Property — Retraction at Lower Temperatures (TR Test).

ASTM D1414-STM for Rubber O-rings.

ASTM D1415-STM for Rubber Property — International Hardness.

ASTM 1566 — Standard Terminology Relating to Rubber.

ASTM D2240 — Rubber Property, Durometer Hardness.

ASTM D4483 — Standard Practice for Rubber — Determining Precision for Test Method Standards.

NACE — TM0187-87 — Evaluating Elastomeric Materials in Sour Gas Environments.

NACE — Proposed Test Method, Evaluating Elastomeric Materials in Carbon Dioxide Decompression Environments.

ACS Rubber Division, Paper No. 83 — "A User's Approach to Qualification of Dynamic Seals for Sour Gas," October 1988.

ACS Rubber Division, Paper No. 44 — "Swelling of Some Oilfield Elastomers in Carbon Dioxide, Hydrogen Sulfide and Methane at Pressures to 28 MPa, October 1983.

Underwriters Laboratory Inc., "UL 746B Standard for Polymeric Materials — Long Term Property Evaluations," 4th Ed., 1991.

SECTION 4
ENVIRONMENT

4.1 Introduction. Oilfield equipment can be exposed to a wide variety of environments. In one instance, it is expected to work within the full range of chemical, thermal and pressure conditions in order to drill, produce, process, and transport the products of gas and oil wells. In the second instance, it is expected to perform reliably in any geographical or seasonal locale of the world — from the Tropics to the Arctic.

The performance-limiting components of oilfield equipment are usually the seals and packings. The materials of construction of nonmetallic seals are generally lower strength and less resistant to the environmental factors that the metallic portion of the wellheads, valves, etc. Consequently, understanding the environmental factors is of utmost importance before the material selection, the design, and the testing procedures of the sealing mechanisms are undertaken.

4.2. Chemical Environment. The following list contains the most common fluids, both liquids and gases, found in the oilfield. It should be noted that the effect of all chemicals is dependent on the concentrations, temperature and other conditions. The effect of multiple chemicals and their reaction products is beyond the scope of this listing. However, the design engineer and the end user should be wary of the complexities of this possibility and should consult a chemist who is expert in this field.

Primary Chemicals (Fluids — Drilling, Completion and Produced).

Crude Oil
Natural Gas
Hydrocarbon Condensates
Brine (Produced)

Hydrogen Sulfide
Carbon Dioxide
Steam (Geothermal)
Drilling Fluids — Oil- and Water-Based
Packer Fluids — Brines, Acidic Zinc Brines, Corrosion Inhibitors, Biocides, etc.

Secondary Chemicals (Fluids — Testing, Cleaning, Conditioning, Treatment).

Diesel and Arctic Diesel Fuel
Motor Oil
Jet Fuel
Water — Fresh, Salt, Steam
Corrosion Inhibitors — Water and hydrocarbon carrier
Solvents — Kerosene, Methanol, Highly Aromatic, Trichloroethene, etc.
Hydraulic Fluids
Acids — Inorganic and Organic
Scale Inhibitors

4.3. Temperature Conditions. Thermal conditions can be steady state, transient, cyclic or a combination of all three. High temperatures can have a significant impact on the life of an elastomeric element. These effects can either be thermal-chemical and/or thermal-mechanical. The higher the temperatures and the longer the time of high temperature exposure, the more likely the seal element will be degraded. However, seals can tolerate short-term excursions at considerably elevated temperatures beyond their published service temperature rating, providing that the mechanical property limitations are not exceeded at that temperature.

Seals at low temperatures become stiff and brittle and their sealing capability may be severely reduced as the temperature approaches the glass transition (T_g) of the elastomeric material. This latter effect is reversible and raising the temperature of the seal sufficiently above its T_g will cause the seal to function normally.

TABLE 4.3
TEMPERATURE RATINGS

Temperature Classification	Operating Range [Degrees Fahrenheit (°F)] Min.		Max.
K	-75	to	180
L	-50	to	180
P	-20	to	180
R	Room Temperature		
S	0	to	150
T	0	to	180
U	0	to	250
X*	0	to	350
Y*	0	to	650

*Appendix G of Spec 6A.

The following list shows the temperature classifications generally recognized by the Industry:

Standard: Majority of wellheads: 0°F to +250°F

High Temperature: +250°F to +350°F

Arctic: Ambient Temperatures: -75°F to -20°F
Flowing Temperatures: as high as +180°F

Geothermal and Steam Injection: as high as 650°F

The 16th Edition of API 6A Specifications and Appendix G recognizes the temperature classifications shown in Table 4.3.

4.4 Pressure Conditions. The following pressure listing is traditionally used in the drilling and production segment of the oil and gas industry:

Low to Moderate Pressure	up to 5000 psi
High Pressure	greater than 10,000 psi

Pressure can be exerted on the seal gradually, incrementally or suddenly; in a constant or cyclical manner. Higher pressure may mean shorter seal life. A sudden drop of gas pressure can be very destructive to a seal by a phenomenon known as explosive decompression. Pressure-energized seals designed for high pressure applications can sometimes leak at low pressures. One practice to avoid this is to use two sets of seals — one for high pressure and one for low pressure sealing. A small, measurable leak can be related to the permeability of the elastomeric material. Consequently, the leak rate of a well-designed seal is in the molecular scale and is usually not discernible with conventional leak detection devices.

4.5 Seal Function. Seals can be static or dynamic (moving) types. If dynamic, the abrasion resistance and the coefficient of friction between the seal and the mating surfaces are very important properties. Seals can also be classified by the way that they are energized.

Pressure: The higher the pressure, the tighter they hold — within limits. Extrusion failure is the result of exceeding the limit. Piston and rod seals are examples. Higher modulus will improve the extrusion failure resistance of a seal to a large extent. Reduced gap clearances will generally alleviate seal extrusion failures.

Mechanically: Face seals, lockdown screw packings and some valve stem packings.

Plastic Injection: Energized by hydraulic means.

Extrusion resistance for an elastomer or a backup system is a very critical property for all seal systems at high pressures and temperatures. To be successful, back-up materials used in antiextrusion devices need to survive the pressure and temperature conditions with little or no yielding.

4.6 Time Duration. Elastomeric materials will deteriorate with time and this process can be accelerated under certain environmental conditions. The longer a seal is exposed to these conditions, the shorter will be its life expectancy. The higher the temperature and pressure and the more concentrated the attacking chemicals, such as hydrogen sulfide, the shorter the life expectancy. This relationship will be discussed more thoroughly in Section 5.2.3 on life prediction testing.

4.7 Storage Conditions. This subject is related to the one above on time duration, but it is primarily concerned with the protection of the seals before they are put into service. Exposure to UV radiation (sunlight), ozone and heat are the source of most storage problems. Proper packaging in a shielded plastic bag or wrap and stored out of the sun in a cool warehouse away from high voltage, ozone-producing equipment will assure a long storage life for the seal. In cold climates storage should be in a heated warehouse. Elastomers such as NBR are much more susceptible to storage degradation than the chemically resistant materials such as the fluoroelastomer seals. The latter frequently have a shelf life greater than 20 years.

SECTION 5
TESTING OPTIONS FOR EVALUATION

5.1 Immersion Testing in accordance with ASTM D471 Liquid/Gas Exposure.

5.1.1 Material Samples — O-rings or ASTM D-412 dumbbell samples.

5.1.2 Test Vessel — May be closed *or* open, depending if liquid or gas is used.

a. Gas — must be closed.

b. Liquid — may be closed or open, depends on liquid volatility and test temperature.

c. Mixtures of gas and liquid — closed vessel required.

5.1.3 Samples — Unconstrained or Constrained.

a. The use of unconstrained samples in an immersion test exposes 100 percent of the exterior surface of the samples to the test media. For screening tests to quickly determine the effect of test media on an elastomer, this technique is satisfactory. Stressed samples, such as bent loop specimens, may be included.

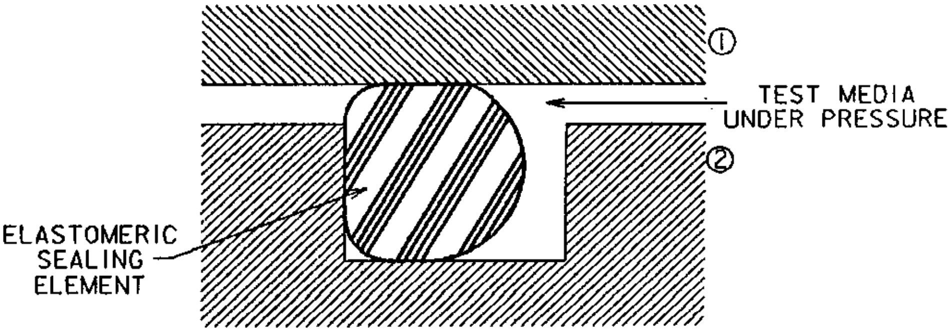
b. The use of constrained samples, or seals made from an elastomeric material in a seal gland simulates actual surface exposed to test media in service. This is considered a more realistic test simulation than the use of free sample immersions.

c. In either free or constrained immersion testing, the effects of the test media plus pressure and temperature can be studied. However, immersion testing will not quantify how long the elastomer will continue to function as a sealing element in the test media.

d. Typical immersion testing will determine changes in elastomer stress/strain characteristics, changes in hardness, volume (swelling), and compression set. Results of immersion testing do not answer the question of how suitable an elastomer sealing element is for a particular application.

5.2 Performance Testing

5.2.1 Static Testing is defined as a sealing element being exposed to the test media with constant or varying pressures *without* relative motion between the two fixed elements against which the seal acts. See Figure 5.2.1 below. Along with test media, pressure and temperature (high and/or low) are applied to the sealing element to verify or estimate performance.



NOTE: NO RELATIVE MOTION OCCURS BETWEEN ① AND ②

FIGURE 5.2.1
STATIC SEAL TESTING

5.2.2 Dynamic Testing is defined as testing a sealing element being exposed to the test media with constant or varying pressures *with* relative motion between the two fixed elements against which the seal acts. Along with test media, pressure and temperature (high and/or low) are applied to the sealing element to verify or estimate performance.

In both static and dynamic testing above, no attempt is generally made to accelerate the thermochemical degradation of the elastomeric sealing element. Sometimes elevated temperatures, high pressures, and high concentrations of corrosive media are used in an attempt to create an "excessive" environment or a worse case condition. However, unless the testing is conducted for an extremely long period of time, the life of the sealing element in the test media cannot be determined.

5.2.3 Life Prediction Testing — An objective of life prediction testing is to accelerate the thermochemical degradation of the seal element in a known test environment. This technique is based on the Arrhenius aging technique utilized for material evaluation in the nuclear industry and by the Underwriter Laboratories in life prediction testing. This is accomplished by elevating the temperature of the test environment. Elevated temperature testing is conducted until the sealing element fails to hold rated pressure in a test media simulating the service environment. Tests may be conducted in a static or dynamic environment. However, designing a dynamic life prediction test is much more difficult than a static test, but has been reported for a full-size seal system (Paper No. 83 ACS Rubber Div., October 1988).

Care must be exercised in designing the experiment so that thermomechanical failures (such as extrusion) are isolated and thermochemical failures (compression set, embrittlement) can be studied. Temperature selections are critical to prevent thermal degradation during a study of accelerated thermochemical degradation. The study of seal failure by thermomechanical means can also be pursued by examining the effects of extrusion gap and/or antiextrusion devices.

Life prediction tests should be performed on a sealing element made of the candidate elastomer.

While exposed to the test media, the sealing element made of the candidate elastomer is repeatedly cycled between atmospheric conditions and test pressure/elevated temperatures until a failure occurs. The time to failure is recorded along with the elevated test temperature. This test procedure is repeated with new specimens at several other elevated temperature, with the test pressure being constant. The data are collected according to the Arrhenius Equation:

$$\text{Log } t = \frac{Ea}{2.303R}\left(\frac{1}{T}\right) + \log C$$

Where

t = Time to Failure

T = Elevated Temperature, degrees Kelvin

R = Gas Constant

Ea = Activation Energy

C = Constant

The data points can then be plotted on semi-log graph paper with the vertical scale as time to failure and the horizontal scales as the reciprocal of the absolute temperature. A least squares regression analysis (best fit) is conducted and a line drawn to the specified service temperature. The validity of a straight line representing the elevated test data is based on Arrhenius aging technique and the occurrence of a zero order chemical reaction. In the analysis of the data using the least squares regression analysis, care

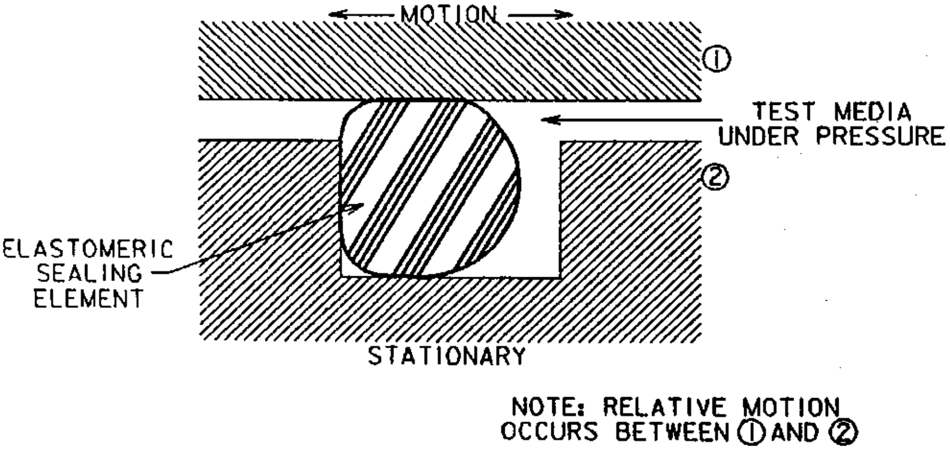


FIGURE 5.2.2
DYNAMIC SEAL TESTING

must be taken to assure a correlation coefficient of greater than 0.90 is achieved, which indicates that the data points approximate a straight line.

This life prediction technique gives an approximation to the question: "How long will the candidate elastomer last in a specified service environment?" Should extrusion failures occur, they may be controlled through the incorporation of antiextrusion devices. Thermochemical failures due to excessive compression set or embrittlement/cracking are the most frequent cause of failure of sealing elements used for long-term sealing (in the order of years).

Other life prediction methods, such as ZURHKOV or BUECHE exist but are not addressed in this document.

5.2.4 Explosive Decompression/Gas Rupture Testing. Exposure to pressurized gases can lead to explosive decompression damage of elastomeric sealing elements used in the oil and gas industry. The damage will occur after the pressure is rapidly released from a sealing element. Damage will usually show up as surface blisters and splits in the exposed surface of the sealing element. However, internal damage may also occur without external evidence. Of all the gases encountered, CO_2, CH_4, and N_2 are the major contributors to explosive decompression damage.

The effects of explosive decompression can be minimized by slowly reducing the applied pressure to ambient pressure. The slow release of pressure will allow the entrapped and dissolved gases to escape and minimize damage to the seal. The crucial portion of the pressure let-down leading to explosive decompression damage has been reported to be uncontrolled depressurization below 1000 psi. Uncontrolled depressurization down to 1000 psi produced little or no sample swelling or subsequent damage. (Paper No. 44, ACS Rubber Div., October 1983).

A number of factors influence an elastomeric sealing element's resistance to explosive decompression damage:

a. Elastomeric material mechanical properties

b. Seal/gland occupancy ratio

c. Temperature

d. Material processing variables leading to internal voids or defects

e. Gas/elastomer solubility

Testing materials for explosive decompression damage resistance can be accomplished in either a free or confined state. In *unconstrained state testing*, the complete outer surface of the elastomeric sample (O-ring or slab) or sealing element is exposed to the test gas in a pressurized test vessel. This is the most severe form of testing. In a NACE test for CO_2 testing, gas bottle pressure (up to 900 psi) has been shown to be sufficient to cause damage when the pressure is rapidly released. Matching the thickness of the field sample is very important for meaningful results: For example, a thin cross-section sample may pass the test, but a thicker sample of the same material may fail.

In *constrained testing*, the elastomeric sealing sample is confined to a gland or cavity. In this case, only a limited amount of surface area is exposed to the gas, and volumetric swell is limited by the confines of the gland.

In either of the above procedures, rapid release of pressure will cause the maximum amount of damage if a material is susceptible to explosive decompression damage. It should be reemphasized that explosive decompression damage only occurs when rapid depressurization is allowed to take place. Prior to decompression and while the sealing element is under pressure and confined to its gland or cavity, it may function satisfactorily. Damage is often not discovered until repressurization is attempted.

Explosive decompression testing can be incorporated into a life prediction test procedure.

SECTION 6
GUIDELINES FOR EVALUATION OF TEST RESULTS

6.1 Immersion testing results may give an indication of the functionality or suitability of a seal material within the limitations noted in Section 5.1.3. Evaluating the effects of property changes in a seal material after an immersion test requires a knowledge and understanding of the seal design and the potential consequence of the observed property changes taking place in the actual service. For example, a seal material may swell 100 percent in an unconstrained sample exposure, but in a tight gland, it may only be allowed to swell 25-30 percent. ASTM D471 and D1414 methods are used.

Caution should be used in evaluation of data from unstressed samples.

6.1.1 Hardness. This measures on a nonlinear scale, a sample's resistance to an indenting deformation. It is an indication of the elastic modulus at low strain. If an accurate measurement is obtained after immersion testing, a gross change in hardness is indicative of a change in elastic modulus or stiffness. ASTM D2240 and D1415 methods are used.

6.1.2 Volume Swell. An increase in volume is common after an immersion test. Decreases in volume indicate the loss of material from the sample. In many seals, only the slightest decrease in volume is tolerable.

Volume increases are more tolerable. Sample swell typically is a result of a physical process in which an equilibrium swell value is reached or it may be a result of a chemical process in which case equilibrium values may not easily be attained. A multipoint test is necessary to evaluate this situation.

Immersion tests permit an unconfined specimen to swell without external restraint. In service, seals confined in glands or housings may be restricted from swelling beyond the limits of the gland. If the swelling is strictly a physical process, this limited situation can be tolerated in actual use, depending upon the swollen materials response to stress. Some O-ring manufacturers recommend that if swelling beyond 20 percent is expected, the user is advised to adjust the gland volume and/or material selection.

6.1.3 Tensile Strength. Changes in tensile strength are a common method of evaluating material changes in the seal material. It is not uncommon to first observe an increase through a maximum followed by a decrease when observed versus exposure time. Tensile strength changes must be evaluated in conjunction with the tensile modulus and elongation changes. ASTM method D471, D412, or D1414 is used.

6.1.4 Tensile Modulus. Increases in stiffness and modulus are indicative of additional crosslink formation or plasticizer extraction. Reductions indicate softening because of swell or perhaps bond scission in the polymer or its crosslinks. Reduced modulus is associated with extrusion and explosive decompression problems. ASTM D471, D412, and D1414 are used.

6.1.5 Elongation at Break. Swell and softening may lead to elongation increases, and it is almost always accompanied by a decrease in modulus. Excessive crosslink formation can lead to embrittlement and is normally accompanied by modulus increases and elongation decreases. ASTM D471, D412, and D1414 are used.

6.1.6 Compression Set. This is a measure of a material's ability to recover from a compressive deformation after exposure. High set can lead to leakage by compression energized seals. A material may exhibit higher or lower compression set in a fluid relative to an air aging test depending on the interaction with the fluid. ASTM D395 and D1414 are used.

6.2 Use of Immersion Test Results is only one aspect of selecting a candidate for an elastomer seal application. In general, these results can only be expected to be helpful if all the ramifications and the consequences of changes in mechanical properties are considered. In many applications, some hardening of the seal is inconsequential. If the property changes due to immersion fail to meet specifications, then a fixture test should be considered.

6.3 Boundary Changes. The oil industry *has no specifications* for the retention of mechanical properties after immersion of seal materials in produced or treatment fluids.

The important point is that an agreement between the two parties must be reached on time, temperature, environment, and boundary conditions or limits based on the capability of the elastomer compound being used.

Acceptable boundary changes in mechanical properties will depend greatly on the original value of the property. Obviously, ±10 hardness points to a 95 Shore A elastomer is meaningless on the plus side, since the scale has a maximum value of 100. Likewise, if a seal material has an initial tensile value of 4500 psi and a recommended maximum change is -50 percent, then a 2250 psi residual tensile strength is still very respectable, but a 50 percent drop on a 1500 psi material would be substantial. Therefore, there can be no *general* hard and fast rules about acceptable changes. Finally, the technologist is usually comparing the results on several elastomer materials, and he/she is usually looking for the least change in each category and for a balance of residual properties.

6.4 Test Results may be used in two ways: First as a *customer qualification test* for the seal materials to be submitted in a bid proposal. For example, the customer may specify that the fluid-aged tensile properties (T_B, M_{100}, and E_B) of the candidate elastomer must not be less than 50 percent of the original values, the swell be no more than 40 percent, and the hardness not vary more than 5 points after 14 days at 300°F in using 5 percent H_2S/95 percent CH_4 1000 psi in diesel.

Secondly, for quality control purposes, to ensure the reproducibility of the production seals, the tool vendor will agree with the rubber molder just what changes are acceptable in the aged properties in some standard ASTM test oils or air oven aging. In addition to the properties cited above, compression set limits may also be established — less than 40 percent when the sample is aged for seven days at 250°F, for example.

SECTION 7
ENVIRONMENTAL SIMULATION

In designing any evaluation of elastomer seal materials, environmental simulation is a critical factor. An improperly simulated environment can lead to an erroneous evaluation of a material as acceptable with the consequence of catastrophic field failure.

In any environmental test procedure, proper consideration must be given to the composition and the phase behavior of the environmental models. Of particular importance is the stoichiometric ratio of the elastomer seal material and the chemicals in the model environment. That is, enough of the reacting gases or chemicals must be used so that there will be a sustained concentration throughout the duration of the test.

7.1 Chemical Environments.

7.1.1 Field Samples. It is generally recognized that the use of field samples of fluids (liquids and gases) for evaluating elastomers will afford the most valid test results. However, several factors deserve consideration:

Simulating a specific environment by the use of field samples can limit an evaluation's usefulness to that environment, similar environments, or those known by experience to be less severe.

The field sample may not accurately reflect the actual media to which the seal is to be exposed. For example, a sample taken after H_2S and water has been separated will not be the same environment that a given seal would be exposed to in service. When the exposure test is designed, the field sample must adequately represent the original service environment. This may require replacing separated constituents and/or increasing the amounts of trace corrosive chemicals (H_2S) in order to be sure they are present in sufficient quantity throughout the test period.

An analysis of the constituents of a field sample may be advisable for a thorough evaluation of the seal/environment system. This analysis is imperative if the test results are to be useful for elastomers in applications of a similar environment.

7.1.2 Model Liquids and Gases. Lacking the ability to obtain actual field samples, the environment must be simulated by the use of model fluids. In order to prepare model test fluids, the technologist must have at his disposal some knowledge of the qualitative and quantitative makeup of the actual service media. There is a tendency to eliminate minor constituents to simplify the makeup. This action would be incorrect if the minor constituents interact with the seal materials to be tested. For example, distilled water has been shown in some experiments to affect certain elastomers more than seawater and chemically treated seawater could have a more pronounced effect than straight seawater or distilled water. Again, this illustrates the need for care in reproducing the environmental model simulation.

Examples of fluids proposed for use to simulate the effects of crude oil are standard ASTM Oils 1, 2, and 3; standard ASTM Fuels A, B, and C; diesel fuel and Jet Fuel A. ASTM oils are standard fluids developed to simulate typical lubricating oils. The ASTM fuels simulate blends of hydrocarbon/aromatic gasolines. Diesel fuel varies dramatically from source to source because of its broad specification range. Jet A is a relatively tightly controlled aircraft turbine engine fuel and has been specified in API Spec 6A, Appendix F (Table F114.1). None of the above fluids, however, are very close to the varied compositions of crude oil from around the world. Therefore, the selection of any model test fluid will be arbitrary and is selected for its availability, reproducibility, and reasonably low viscosity.

The gases present in service are normally simulated by appropriate additions of H_2S, CO_2, of CH_4 to the test. The technologist must be careful to address the questions of phase behavior, solubility, and interactions of the gases and liquids with themselves, the test vessel, and the elastomer test samples. In a recent attempt to evaluate a proposed NACE sour liquid test method, it was determined that a mix of 95 percent straight chain hydrocarbons and 5 percent toluene would not dissolve sufficient H_2S to cause the expected embrittlement of a standard NBR elastomer. The conclusion was that the 20 percent H_2S gas mix at 1000 psi was not soluble in the 95/5 solvent mix. On the other hand, a 90/10 mix has been successfully used as the base hydrocarbon solvent mix for other sour liquid test procedures.

CAUTION: Aromatics used in test fluids can produce degradation of some elastomer compounds.

7.2 Physical Environments

7.2.1 Temperature and Pressure. These parameters must be discussed together because their effects are related. Elevated temperatures increase most chemical reactions rates — a principle which is useful in accelerating tests. However, elevated temperatures reduce the mechanical properties of elastomers. Care must be taken in selecting test temperatures to avoid exceeding the thermal stability or the heat resistance of the elastomers to be evaluated. Pressure and temperature also affect the concentration of gases, density of the test media, volatility, solubility, permeability, and reactivity of the combined test system. Add to this the fact that service conditions are seldom steady state and the problem of test design becomes even more difficult.

7.2.2 Dynamic. When seals are used in dynamic applications, it is often necessary to simulate the dynamics in a material evaluation. Static tests may not be valid. Simulating dynamics increases the complexity and cost of material evaluations. If the test environment is toxic, special care is required not to compromise safety.

Some of the elastomer properties of concern in dynamic service include coefficient of friction, swelling, resilience, fatigue, abrasion, and erosion. These properties are all affected by the temperature, pressure, and chemical changes that occur due to environmental reaction.

7.3 Worst Case Conditions. It is normally assumed when evaluating elastomers that testing under worst case conditions is desirable. If the test is valid, service performance is expected to exceed the test results affording an increased margin of safety. Typically, to ensure a worst case evaluation, it is common to increase reactant concentrations, temperature, pressures, and other parameters that increase reaction rates. Caution is required., however, to avoid designing an evaluation to severe that all materials fail the test. As noted, elastomers are often exposed to conditions more severe than actual service. The assumption is that failure mechanisms do not change, but are only accelerated.

7.4 Arctic or Cold Weather Applications. Several factors must be considered when seals are evaluated for low temperature service. Elastomers are stiffened by low temperature. A thousand fold increase in modulus can be observed by crossing through the glass transition temperature of an elastomer. At sufficiently low temperatures, many elastomers under stress take a 100 percent set in the stressed condition. Reversible embrittlement frequently occurs in cold seals. The chemical effects, fortunately, of most environments are reduced because of slower reaction rates.

One note of caution is that under arctic conditions, antifreeze-type products are sometimes used in the service environment to permit continued operation and they must be considered an important part of the environmental exposure simulation conditions.

The evaluation of elastomers for low temperature service can be conducted by extending the temperature range of tests to incorporate these effects.

7.5 Summary. Environmental simulation is complicated, but with care it is possible for many typical situations. Because of the broad range of conditions to which elastomers are subjected, it is necessary to conduct several tests. Elastomer technologists have struggled for some time trying to agree on a limited number of test environments. It appears that the use of several tests will continue to be necessary to conduct evaluations for specific application conditions.

SECTION 8
OTHER CONSIDERATIONS

The following items should be considered if test results are expected to be valid, reproducible, and to conform to ASTM D4483 (Standard Practice for Preparing Precision Statements for Standards Related to Rubber and Rubber Testing):

a. Availability of Standard Elastomer *"Control"* Compounds.

b. Reversible Changes/Compensating Effects.

c. Irreversible Changes.

d. Compatibility (Solubility) of phases (gases in liquids).

e. Stoichiometry.

f. Temperature Effects.

8.1 Availability of Standard Elastomer Control Compounds. Standard compounds featuring commonly used oilfield elastomers should be made to specific formulas and available from a common source. These would be used, first, to establish test method validity in terms of reproducibility, and secondly, as control samples in subsequent test programs to ensure that tests have been conducted under controlled conditions. The use of the control materials for comparison purposes cannot be stressed to highly. In addition to establishing the improvement (or lack of improvement) of the test material in the environment, the absolute results on the control elastomer indicate that the test method and conditions were correctly carried out.

8.2 Reversible Changes/Compensating Effects. Whether the changes in the sample properties are reversible will affect the final results. It is well known, for example, that certain physical changes are completely and totally reversible. One illustration is the change in elastomer properties above and below the glass transition. When the samples have been brought back up to a temperature above the T_g, test results indicate that the elastomers have not been damaged as a result of being frozen. Swelling is another example of a change that may be reversible, i.e., when the elastomer seal test coupon is removed from the media, the swelling fluid may diffuse out and the seal coupon recover to its size and properties. This recovery is generally time dependent and related to the following variables:

a. Volatility of Swelling Media

b. Test Temperature

c. Test Pressure

d. Cross-Sectional Thickness of Sample

e. Solubility of Media and Sample

f. Rate of Depressurization

In the case of gases and low boiling point liquids, these can easily be removed from elastomer samples of thin cross-section through evaporation once the elastomer is removed from the swelling media. However, it is not unusual to see large samples of rubber remain swollen for an extended period.

Carbon dioxide may diffuse from elastomers under standard temperature and pressure within approximately 24 hours, depending on cross-section and degree of solubility. It has been demonstrated that elastomer test pieces, which have been softened in CO_2 by 20 durometer points and lost 50 percent of strength, when tested immediately after removal from a pressure vessel will recover significantly within one hour and will recover almost completely within 24 hours. Thus, elapsed time after removal from immersion media and the commencement of the physical property testing becomes extremely important as far as test results are concerned. This has long been recognized and *some* procedures specify that the test pieces must come to constant weight after removal and before physical property measurements are made.

Liquids are more difficult to remove and may become, in effect, permanent plasticizers. Plasticizers, on the other hand, are often extracted from elastomers with the net effect leading to shrinkage instead of swelling. Extracted plasticizer may actually be replaced by the swelling medium and differing results can be expected until equilibrium has been achieved. Other compensating effects can be observed by the softening effects of solvent swell and embrittlement. Examples of embrittlement are those crosslinking reactions such as those obtained with NBR and H_2S or some fluorocarbons with amines.

8.3 Irreversible Changes. Elastomers can be and frequently are permanently affected by some reversible changes if the change occurs too rapidly and causes damage in the form of ruptures and splits in the elastomer matrix. This occurs during rapid pressure changes, which lead to the phenomenon defined as explosive decompression. Similar physical damage can result from internal heat buildup due to post curing, internal friction, or microwave heating.

Chemical changes in elastomers tend to be irreversible, whether they are temperature induced and associated with the polymer itself or reactions of the polymer with other chemicals. Examples of reactions with other chemicals are those associated with corrosion inhibitors, H_2S or air in oxidative degradation. These generally follow basic reaction kinetics and comply with the Arrhenius equation illustrated in 5.2.3.

The use of this procedure permits accelerated testing to determine data points for regression analysis and prediction of long-term results with a high degree of confidence if the correlation factor is at or near 1.0.

8.4 Compatibility of Phases. Other concerns in severe environment testing are with the critical temperatures and pressures of gases and the solubility and chemical reaction of these gases with the liquid phase. Pressurized mixed gases may not exist in the specified ratio as gases unless they are all above their respective critical temperatures. This is of concern for bottled gases to be added to autoclaves and for the gases in the autoclave. Critical properties for methane, CO_2, and H_2S, gases commonly used in severe environment testing, are:

	T_c	P_c	
	°C	atm	PSI (Approximate)
Methane	-82.1	45.8	675
CO_2	+31	72.9	1,075
H_2S	+100.4	88.9	1,300

Adding low pressure gas mixtures directly to autoclaves will be satisfactory only if the final test pressures are also relatively low and *enough of each gas is present to complete whatever chemical reactions take place with added liquids and test pieces.* Normal test temperatures will not raise the pressure by more than approximately a factor of two which is still below usual test pressures.

8.5 Stoichiometry. Low pressure gas mixtures may contain less than stoichiometric amounts of individual gases. A one-liter autoclave at STP would contain no more than 0.045 moles (1.5 grams) of pure H_2S and only a fraction of that if a gas mixture was used in the autoclave, the volume occupied by the liquid added, and the volume of any test fixtures (compression set). The issue of concern is how much H_2S is required to completely react with the several hundred grams of hydrocarbon present in the autoclave in the form of elastomer test coupons and liquid petroleum products. At 523°F (273°C) and 2,940 psi (200 atm), 4.5 moles (150 grams) of pure H_2S (100 times) would be present. For example, if diesel fuel is the test fluid being used, there would be more olefinic bonds reacting with the H_2S than in the elastomers being tested.

Extremely small amounts of H_2S are very detrimental to some rubber test pieces, and significantly different results are obtained if the gas at a low concentration is replenished during the test. Meaningful results may not be obtained if the supply of H_2S is not representative of the essentially inexhaustible quantities (zero order kinetics) found in service.

The effects from exposure to a gas phase-only environment versus a liquid phase immersion with gas overpressurization must also be studied. If the primary effect of the H_2S gas phase is embrittlement and that of the liquid phase is swelling, then the net compensating result could be only minor changes in the physical properties. On the other hand, combined effects sometimes appear to be synergistic.

8.6 Temperature Effects on The Properties of Elastomers. As a general phenomenon, elastomer mechanical properties change with temperature. Thermal expansion (or contraction), hardness, and flexibility are among the more significant properties that relate to seals and packers used in drilling and production equipment. Generally, rubber expands or shrinks about ten times as much as steel for the same change in temperature. When designing elastomers as sealing elements, the coefficient of thermal expansion must be considered to prevent seal gland (cavity) overfill and possible seal extrusion. On the other hand, thermal contraction during cool down will result in loss of sealing force and can potentially produce a leak of contained gas or fluid. Elevated temperatures/pressures accelerate chemical changes such as reversion, crosslinking, chain scission, etc., according to the Arrhenius principle. These are generally permanent and irreversible changes. Changes due to low temperatures are, however, physical rather than chemical and are generally completely and totally reversible. Two types of changes may occur at low temperature. Both cause increased stiffness in rubber compounds. Thermal stiffening is independent of time providing thermal equilibrium has been achieved and is common to all elastomers. The second is due to crystallization, which *is* time dependent and is a characteristic of only those elastomers which undergo crystallization. Although glass transition temperatures, as related to thermal stiffening, are reproducible to within ±2°C, values for compounds of various elastomers are highly dependent on compounding variables such as filler and plasticizer loading. On the other hand, crystallization occurs over a broad temperature range, but occurs most rapidly at a specific temperature for a given elastomer and may take days, weeks, or even months to complete. The rate of crystallization is also influenced by compounding variables including vulcanization chemicals, state of cure, and degree of stress. Highly crystallized elastomers are very stiff and leathery but not brittle.

SECTION 9
SUMMARY

In summary, the required range of severe testing environments is very broad. The effects on the elastomers can be, and frequently are, drastic. Because of the complexities of the environmental systems and required testing procedures, extreme differences in the results are quite possible. For this reason, the definitions of the environments to be used and the detailed methods of any autoclave testing procedure need to be defined and followed as precisely as possible.

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