

Compatibility of Elastomers in Neat Methanol Service

Elastomers and rubber compounds are widely used in methanol service as O-rings, gaskets, packing, and sealing materials to prevent leakage of methanol liquid and vapors into the surrounding environment. As originally used, the term “rubber” described materials that occurred naturally in nature. The term “elastomer” designated synthetically produced polymers characterized by their elastic properties. The terms are essentially interchangeable in current usage. This bulletin uses the term “elastomer” to indicate synthetic and natural compounds.



Elastomer performance is limited by temperature, pressure, and compatibility of the polymer sealing material with chemical properties of the contained fluid. These limitations are important considerations in meeting toxic fluid leakage issues addressed in Chapter VIII of the American Society of Mechanical Engineers

Process Piping Code, B31.3, and complying with fugitive emission regulations.

Elastomer applications typically assume several functional types: O-rings, gaskets, gland seals, and packings. Each functional type requires compounding and forming the polymer into a characteristic geometry necessary to satisfy the function. O-rings are solid circular rings; gaskets are cut from flat material; seals are often composite configurations of polymer and alloys or thermal plastics; packings are typically circular or rectangular ropes. Sealing applications are compressors, pumps, piping connections, valves, and instrumentation elements where the polymers are subject to static or flowing service over a wide range of temperatures and pressures. Operating conditions can be constant, fluctuating or cyclical. Polymers that are suitable for one type of service (e.g., O-rings, gaskets, seals or packing) may not be suitable for any another service in spite of the fact that they are exposed to the same chemical. Temperature and pressure are major determinates in selecting elastomers for a particular service.

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Small Polar Fluid Molecules Can Be Aggressive to Polymers

Polymers are subject to several forms of deterioration in methanol sealing service. The first of these is swelling. Liquids with small polar molecules such as methanol can be aggressive in causing elastomer and rubber compound matrices to swell. Excessive swelling causes the polymer to burst within the confinement of O-ring grooves thereby creating a path for fluid leakage. If confining pressure is sufficiently high, failure can result in a small jet stream of methanol liquid that flashes to vapor.

Chemical attack is a second form of deterioration. Process fluids can chemically attack and destroy the integrity of the polymer, thus also creating a path for fluid leakage. Polymer failure in this case may result in a 'leak before break' type of failure mode.

A third, and potentially the most hazardous deterioration mechanism can occur by explosive decomposition (ED). Explosive decomposition subjects sealed joints to abrupt, unexpected, catastrophic containment failure. Explosive decomposition occurs when liquid process fluid vaporizes upon decompression, thereby transmitting abrupt pressure, temperature, and flow fluctuation transients across the sealing surface into the plant working environment, and possibly upstream and downstream from the point of failure through equipment and piping works. Fluid movement across the sealing surface can disrupt positioning of the gasket or O-ring thereby increasing leak rate. Explosive decomposition essentially blows the sealing polymer out of the gap between the sealing surfaces. Pressure classes above 600 lbs require ED resistant O-rings: i.e., O-rings that are tested in conditions representing the actual fluid, fluid pressure, and fluid temperature (refer to NORSOK M-710). The most important criteria for explosive decomposition resistant O-rings are shore-hardness greater than 90, and cross section less than 7 mm.



Each deterioration mechanism dictates application limits of a particular polymer in a particular service.

In spite of gains during the past 20 years, elastomer gaskets in piping connections, and O-ring components in valves are the single most significant limiting factor on process system "operating window." Polymer O-rings provide excellent sealing performance at low cost; however, strength, pliability, and resilience characteristics required for proper

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sealing need to be maintained throughout the entire operating window, including abnormal operating conditions.

At low temperature, elastomers harden, become less resilient and lose shape memory. Undesirable experience causes some operators to avoid using elastomers in applications below a design temperature of -4°F (-20°C). The upper temperature limit of elastomers in methanol service is determined by the chemical characteristics of the elastomer relative to those of methanol. As operating temperature increases, chemically similar elastomers are affected more than elastomers that are chemically dissimilar to methanol. Because the rate of elastomer degradation increases as temperature increases, establishing a realistic temperature limit is vitally important in setting operating temperature window. Operating a piping works outside a selected elastomer's sealing capability subjects the entire piping works to losing its containment capability.

It is prudent to verify sealing limitations with the seal manufacturer, and to restrict temperature to an upper limit of 250-300°F (120 and 150°C) and a lower limit of -4°F (-20°C), depending on piping pressure class.

Description of Elastomer Sealant Materials

Elastomer types are referenced using standard designations and acronyms listed in ASTM D-1418 and ISO 1629 international standards. A brief description of selected elastomer and thermoplastics characteristics are provided below. A more complete listing of material grades is available at www.prepol.com.

FEP/PFA (Fluoroethylene Propylene-Perfluoroalkoxy)



This type of elastomer is a chemically modified fluorocarbon copolymer (fluoropolymer) that resembles plastic more than it does rubber. These polymers are extremely resilient and show excellent chemical resistance. Mechanical properties are good, even at high temperatures, and they have non-stick characteristics with moderate abrasion resistance. The published continuous exposure temperature range is from -148 to 360°F (-100 to 200°C) for FEP and -148 to 482°F (-100 to 250°C) for PFA. Typical applications are door seals and sealing systems in diaphragm pumps, cryogenic plants, sealed filter units, corrosive

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fluid plants and relief and emergency valves and pneumatics. Fluoropolymers can be used to encapsulate other elastomers to produce composite seals. Virgin Teflon FEP is considered an excellent choice for flange gaskets in methanol service.

FFKM/FFPM (Perfluoroelastomer)

FFKMs exhibit outstanding high temperature properties and as a rubber form of PTFE, they are the most chemically resistant elastomer available. FFKMs are superior to FKM elastomers, showing continuous dry-heat resistance to 500°F (260°C) with extended performance to 626°F for high temperature grades. They show excellent resistance to a majority of chemicals that attack other elastomers, and have good long-term high temperature compression set resistance. Applications are sealing systems in oil refineries, pharmaceutical plants, aerospace applications and chemical plants. Perfluoroelastomer shows little or no effect from methanol exposure.

FVMQ (Fluorosilicone)

FVMQ elastomers are modified silicone rubbers, which have many of the properties associated with silicone rubber, but show improved oil and fuel resistance. Typical properties are resistance to ozone, oxygen, weathering, and non-adhesive characteristics. Service temperature range is wide and chemical reactivity is low. Tensile strength, tear resistance and abrasion resistance are poor, and gas permeability is high. Elastomer shows little or no effect from methanol exposure.

IR (Polyisoprene)

IR is a synthetic version of natural rubber with similar strength and applications. Low temperature performance exceeds that of rubber with inferior performance at normal temperatures.

NBR (Nitrile or Acrylonitrile Butadiene)

Properties of this copolymer can be adjusted by changing the ratio of acrylonitrile and butadiene. Nitrile rubber can be classified as three types based on the acrylonitrile (ACN) content (low, medium, and high). Resistance to aromatic hydrocarbons is higher as ACN content increases. Low ACN content favors low temperature flexibility. The

Materials Selection for Neat Methanol Service (cont.)

most commonly specified, and the best overall balance for most applications is “medium nitrile.” General characteristics of NBRs are resistance to attack by aliphatic hydrocarbon oils, fuels, and greases, very low gas permeability, improved heat ageing and ozone resistance, improved tensile and abrasion strength, hardness, density, and low compress set. Applications are gaskets, seals, hoses, and cable jacketing in hydraulic/pneumatic systems and oil/hydrocarbon bases environments. NBR experiences some effects from methanol exposure with some loss of physical properties and some swelling.

HNBR (Hydrogenated Nitrile)

HNBR elastomers are a saturated version of NBR with superior heat resistance. These materials have excellent wear resistance, high tensile strength, high hot-tear resistance, low compression set, and good ozone and weathering resistance. Applications are in oil-fields, and automotive. HNBR experiences some effects from methanol exposure with some loss of physical properties and some swelling. Performance in methanol exposure is similar to that of NBR.

NR (Natural Rubber)



Natural rubber has high tensile strength, abrasion resistance resilience, tear strength, and low hysteresis with the best long-range elasticity. Main applications are tires, vibration mounts, springs, and bearings. Natural rubber is considered compatible with methanol.

PPO (Polyphenylene ether resin and polystyrene)

Noryl, a registered trademark of Saudi Basic Industries Corporation (SABIC) SABIC Innovative Plastics IP B.V. family of polymers, is a homogeneous mixture of two polymers, polyphenylene ether (PPE) resin and polystyrene. These materials combine the inherent benefits of PPE (high heat resistance, good electrical resistance, and excellent hydrolytic stability). Like most amorphous thermoplastics, the Noryl is sensitive to environmental stress cracking when in contact with organic liquids. Gasoline, Kerosine, and methylene chloride can initiate brittle fracture and product failure. Published information ranks compatibility with methanol as “good.”

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PTFE (Polytetrafluoroethylene)

PTFE is an inert thermoplastic, not an elastomer. It is used as a back-up ring for bearings and non-stick requirements, or in composite elastomer seals.

VMQ/PVMQ (Silicone)

Silicones have good resistance to ozone and weathering, good compression set at high temperatures, and a low level of combustible components. Tensile strength is poor, low tear and abrasion resistance, and high gas permeability. Uses are typically biomedical.

Chemical Compatibility

All types of elastomers are susceptible to chemical attack of varying degrees. Compatibility of elastomers in a particular environment is a function of polymer chemical structure and its formulation. Effects of incompatibility depend on the form of chemical attack and the temperature at which effects occur. Temperature accelerates the rate of attack.

Physical effects are evidenced as any or several of the following:

- embrittlement and hardening
- softening and tackiness
- swelling
- shrinkage (loss of volume).

All of these effects compromise sealing ability. It is important avoid choosing an elastomer that may experience explosive decompression in the intended service.



The most common effect is swelling, due either to solubility effects between the process fluid and the polymer, or chemical attack resulting in change in an elastomer's polarity. Volume increase due to swelling may be reversible, however, the effects on polymer properties may not be reversible. If a gasket, O-ring, or other shape is known to have changed dimension, then assume that the item is no longer fit-for-service.

Determine the cause for the change, and either select a more appropriate material, or modify fluid process conditions.

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Polymer terminology can be confusing unless some attention is given to the manner in which elastomers and rubber compounds are classified. The most important types fall within the five following groups based on the structure of their main carbon chains and atomic species present within the main chains. Physical properties such as heat resistance, cold flexibility, and methanol compatibility are similar within each group, but are specific to each material. Group designations, ASTM D-1418 abbreviations, and methanol compatibility rankings of materials most commonly used for O-rings, gaskets, bellows, and other sealing applications are summarized below.

- A = very good suitability. Elastomer shows little or no effect from chemical exposure. Little effect is shown on functional performance with little or no deterioration of physical properties. Chemical resistance is rated as “very good.”
 - B = good suitability. Polymer shows some effects from exposure with some loss in physical properties. There is some chemical swelling.
 - C = Limited suitability. Polymer exhibits significant swell and loss of physical properties as a result of exposure. Additional testing is recommended.
 - U = unsuitable. The elastomer is not suitable for application in the indicated media.
 - - = insufficient data. There is not sufficient data to rate service performance in neat methanol.
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- **‘M’ Group:** saturated carbon molecules in main macro-molecule chain
 - Polyacrylate Rubber- ACM = “C” compatibility rating
 - Ethylene Acrylate Rubber- AEM (ISO 1629, there is no ASTM designation) = information is insufficient to provide a compatibility rating
 - Chlorosulfonated Polyethylene Rubber-CSM
 - Ethylene Propylene Diene Rubber- EPDM = “A” compatibility rating
 - Ethylene Propylene Rubber- EPM = “A” compatibility rating for static and dynamic service
 - Fluorocarbon Rubber- FKM (Restifluor® 500) = “A” compatibility rating
FKM (other) = “C” compatibility rating
 - Perfluoro Rubber- FFKM (Isolast®) = “A” compatibility rating
 - **‘O’ Group:** saturated carbon molecules in main macro-molecule chain with oxygen molecules in the main macro-molecule chain
 - Epichlorohydrin Rubber- CO
 - Epichlorohydrin Copolymer Rubber- ECO
 - **‘R’ Group:** unsaturated hydrogen carbon chain
 - Chloroprene Rubber- CR = “B” compatibility rating
 - Butyl Rubber- IIR = “B” compatibility rating

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- Nitrile Butadiene Rubber- NBR = “B” compatibility rating
- Natural Rubber- NR = “B+” compatibility rating
- Styrene Butadiene Rubber- SBR
- Hydrogenated Nitrile Butadiene Rubber- HNBR = “B” compatibility rating
- **‘Q’ Group:** unsaturated hydrogen carbon chain with silicone in the main chain
 - Fluorosilicone Rubber- FVMQ = “A” compatibility rating
 - Methyl Vinyl Silicone Rubber- VMQ = “B” compatibility rating
- **‘U’ Group:** unsaturated hydrogen carbon chain with oxygen and nitrogen in the main chain.
 - Polyester Urethane- AU = “U” compatibility rating
 - Polyether Urethane- EU = “U” compatibility rating

Ratings in Table 1 are based on volume swell data, which has been compiled from published literature, laboratory tests, actual field experience and informed judgments from published sources. Neither Methanol Institute nor the bulletin author is responsible for accuracy of the indicated rankings.

Information on compatibility should be used only as a general guide in the selection of the most suitable material for your specific application. Users must assure themselves that the selected material has been appropriately and adequately tested and that the supplied parts will be safe and functional in the intended application.

TABLE 1.
Examples of Elastomer/Sealant Materials Considered for Various Applications in Methanol Service

A = excellent, recommended, resistance under normal conditions
 B = good, but conditional under some conditions, consult supplier, consider modifying process parameters
 C = poor, not recommended, investigate alternate materials
 D = not recommended, investigate alternate materials
 - = insufficient information to provide a rating

This table lists the chemical compatibility of various elastomer materials commonly used for o-ring and neat methanol. This data has been compiled from literature published by various material suppliers. Rankings are given as background information only. In any given case, factors such as concentration, temperature, degree of agitation and presence of impurities influence the rate of degradation. The user, through their own testing and evaluation, must determine the suitability of the material for their application.

Elastomers (ISO 1629 / ASTM D 1418) & Synthetic Rubbers (DIN/ISO 1629 / ASTM D 1418)	Application	Trade Name or Identifier	Compatibility Ranking
ACM (Polyacrylic or Polyacrylate M Group Rubber)	O-rings Gaskets	Noxtite®; Hytemp®; Nipol AR® ISCA rubber group B (Iso 2230:2002) low susceptibility to deterioration by aging:	D

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Elastomers (ISO 1629 / ASTM D 1418) & Synthetic Rubbers (DIN/ISO 1629 / ASTM D 1418)	Application	Trade Name or Identifier	Compatibility Ranking
		7+ 3 yrs	
AEM (Ethylene Acrylic M Group Rubber)	O-rings Gaskets	Vamac®	A
AU (Polyester urethane or polyurethane rubber)	O-rings Gaskets	Adiprene®; Millathane®; Vibrathane®; Vulkolan® ASTM D-2000 Classification BG ISCA rubber group A (ISO 2230-2002) moderate susceptibility to deterioration by aging: 5+2 yrs	D D
BR (Polybutadiene or Butadiene Rubber)	Tubing & hoses; flexible connectors ; gaskets; bellows	ISCA group A (ISO 2230:2002) moderate susceptibility to deterioration by aging: 5+2 yrs	A
BIIR (Bromo-Isobutene-Isoprene or Bromobutyl Rubber)		ISCA rubber group B (ISO 2230:2002) low susceptibility to deterioration by aging: 7+3 yrs	A
CO (Epichlorohydrin Group O Rubber)	O-rings Gaskets	ISCA rubber group B (ISO 2230:2002) low susceptibility to deterioration by aging: 7+3 yrs	B
CIIR (Chloro-Isobutene-Isoprene or Chlorobutyl Rubber)		ISCA rubber group B (ISO 2230:2002) low susceptibility to deterioration by aging: 5+2 yrs	D

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Elastomers (ISO 1629 / ASTM D 1418) & Synthetic Rubbers (DIN/ISO 1629 / ASTM D 1418)	Application	Trade Name or Identifier	Compatibility Ranking
CM Chloropolyethylene or Chlorinated Polyethylene)		ISCA rubber group C (ISO 2230:2002) highly resistant to deterioration by aging: 10+5 yrs	A
CR (Chloroprene Group R Rubber)	Tubing & hoses; flexible connectors ; gaskets; bellows	Neoprene®; Baypren®; Butacholor® ASTM D-2000 Classification BC ISCA rubber group B (ISO 2230:2002) low susceptibility to deterioration by aging: 7+3 yrs	A A A
CSM (Chlorosulphonylpolyethylene or Chlorosulphonatedpolyethylene M Group Rubber)	Tubing & hoses; flexible connectors ; gaskets; bellows	Hypalon® ISCA rubber group C (ISO 2230:2002) highly resistant to deterioration by aging: 10+5 yrs	A static only A
CSPE (Chlorosulfonated polyethylene)		Hypalon® registered trade mark of DuPont	A
ECO (Epichlorohydrin Group O Copolymer Rubber)		Hydrin®, Herclor®, Gechron® ISCA rubber group B (Iso 2230:2002) low susceptibility to deterioration by aging: 7+3 yrs	B
EPDM (Ethylene-Propylene-Diene Group M Rubber)	O-rings; Tubing & hoses; flexible	Dutral®; Nordel®; Royalene®; Vistalon®; Buna EP®; Keltan® ASTM D-2000 Classification DA	A A A A

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Elastomers (ISO 1629 / ASTM D 1418) & Synthetic Rubbers (DIN/ISO 1629 / ASTM D 1418)	Application	Trade Name or Identifier	Compatibility Ranking
	connectors ; gaskets; bellows	ISCA rubber group C (ISO 2230:2002) highly resistant to deterioration by aging: 10+5 yrs	
EPM (Ethylene Propylene Group M Rubber)	Tubing & hoses; flexible connectors ; gaskets; bellows		A
EU (Polyether urethane or polyurethane rubber)	O-rings Gaskets	ISCA rubber group A (ISO 2230-2002) moderate susceptibility to deterioration by aging: 5+2 yrs	D D
FEP / PFA (Fluoroethylene Propylene-Perfluoroalkoxy)	O-rings Gaskets		A
FEPM or TFE/P (Tetrafluoroethylene / Propylene)	O-rings Gaskets		A
FFKM (Perfluoroelastomer Elastomer Group M Rubber)	O-rings Gaskets	Kalrez®; Zalak®; Chemraz®; Perlast® Best heat resistance of all elastomers	A
FFPM (Perfluoro Group M Rubber)			A
FKM /FPM (Fluoroelastomer	Tubing & hoses;	Viton®; Dyneon®; Aflas®; Fluorel® ASTM D-2000 Classification HK	A/D A

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Elastomers (ISO 1629 / ASTM D 1418) & Synthetic Rubbers (DIN/ISO 1629 / ASTM D 1418)	Application	Trade Name or Identifier	Compatibility Ranking
Perfluoroalkyl or Fluorocarbon Group M Rubber)	flexible connectors ; gaskets; bellows	ISCA rubber group C (ISO 2230:2002) highly resistant to deterioration by aging: 10+5 yrs	A A
FMVQ /FVMQ (Fluorosilicone Group Q Rubber)	O-rings gaskets	FSE®; Silastic®; Sylon® ASTM D-2000 Classification FK	B; static only A A
HNBR (Hydrogenated Nitrile Butadiene Group R Rubber)	O-rings gaskets	Therban®; Zetpol® ISCA rubber group B (ISO 2230:2002) low susceptibility to deterioration by aging: 7+3 yrs	A+/B
IR (Polyisoprene or synthetic rubber)	Tubing & hoses; flexible connectors ; gaskets; bellows	ISCA rubber group A (ISO 2230-2002) moderate susceptibility to deterioration by aging: 5 + 2 yrs	A
IIR (Butyl Group R Rubber)	Tubing & hoses; flexible connectors ; gaskets; bellows	Esso Butyl® ASTM D-2000 Classification AA ISCA rubber group B (ISO 2230:2002) low susceptibility to deterioration by aging: 7+3 yrs	A A A
MQ (Silicone elastomer)		ISCA rubber group C (ISO 2230:2002) highly resistant to deterioration by aging: 10+5 yrs	A
NR	Tubing &		A

Materials Selection for Neat Methanol Service (cont.)

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Elastomers (ISO 1629 / ASTM D 1418) & Synthetic Rubbers (DIN/ISO 1629 / ASTM D 1418)	Application	Trade Name or Identifier	Compatibility Ranking
(Polyisoprene Rubber or Natural Rubber)	hoses; flexible connectors ; gaskets; bellows	ASTM D-2000 Classification AA ISCA rubber group A (ISO 2230-2002) moderate susceptibility to deterioration by aging: 5+2 yrs	A
NBR (Nitrile or Acrylonitrile Butadiene Group R Rubber)	Pressure Sensors Transmitters Wetted O-Rings; Tubing & hoses; flexible connectors ; gaskets; bellows	Europrene®; Krynac®; Nipol N®; Perbunan NT®; Breon®; Buna-N® ISCA rubber group B (Iso 2230:2002) low susceptibility to deterioration by aging: 7+3 yrs	B/A A/B A A
NBR/PVC (Acrylonitrile-Butadiene & Poly or Nitrile PVC)		ISCA rubber group B (Iso 2230:2002) low susceptibility to deterioration by aging: 7+3 yrs	B
PPO (polyphenylene oxide and styrene)	O-rings gaskets	Noryl® SABIC Innovative Plastics IP B.V.	A
PPS (polyphenylene sulfide)	Pumps: housing, vanes, impellers &	Ryton® Chevron Phillips Chemical Company Ryton PPS is expected to be suitable for extensive exposure to methanol even at elevated temperatures, retaining at least 50% of original mechanical strength and	A

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Elastomers (ISO 1629 / ASTM D 1418) & Synthetic Rubbers (DIN/ISO 1629 / ASTM D 1418)	Application	Trade Name or Identifier	Compatibility Ranking
	shafts Ball valves: seats & seals	exhibiting < 3% swell after exposure of 1 year at 200°F (93°C)	
PTFE (Polytetrafluoroethylene)	O-rings gaskets		A
PVDF (polyvinylidene fluoride)		Kynar® Arkema, Inc. Waste water drain systems aqueous methanol solns	A+
PVQ (Silicone elastomer)	O-rings Gaskets	ISCA rubber group C (ISO 2230:2002) highly resistant to deterioration by aging: 10+5 yrs	A B
PVMQ (Silicone elastomer)	O-rings gaskets	ISCA rubber group C (ISO 2230:2002) highly resistant to deterioration by aging: 10+5 yrs	A B
Q (Silicone elastomer)	O-rings Gaskets	ISCA rubber group C (ISO 2230:2002) highly resistant to deterioration by aging: 10+5 yrs	A B
RFE/P Tetrafluoroethelene propylene	O-rings gaskets	Aflas® Asahi Glass Co.	A
SBR (Styrene-Butadiene Group R Rubber)	Tubing & hoses; flexible connectors ; gaskets; bellows	Burna S®; Europrene® ASTM D-2000 Classification AA ISCA rubber group A (ISO 2230-2002) moderate susceptibility to deterioration by aging: 5+2 yrs	A A A
VMQ/Si	Tubing &	Elastosil®; Elastoseal®; Rhodorsil®;	B/A

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Elastomers (ISO 1629 / ASTM D 1418) & Synthetic Rubbers (DIN/ISO 1629 / ASTM D 1418)	Application	Trade Name or Identifier	Compatibility Ranking
(Methyl Vinyl Silicone Group Q Rubber)	hoses; flexible connectors; gaskets; bellows	Silastic®; Silopren®; SILPLUS®; Elastosil Wacker® ASTM D-2000 Classification GE/FE ISCA rubber group C (ISO 2230:2002) highly resistant to deterioration by aging: 10+5 yrs	static only A A
XNBR (Carboxylic-Acrylonitrile-Butadiene or Carboxylated Rubber)		Buna-N®, Butacril®, Paracil®, Perbunan®, Krynac®, Europrene-N®, Nipol® ISCA rubber group B (Iso 2230:2002) low susceptibility to deterioration by aging: 7+3 yrs	A/B

Rankings presented in Table 1 make it apparent that choosing elastomer materials is neither simple nor straightforward. There is a wide variety of choices, and depending on specifics of compounding, compatibility can range from very good (A) to limited suitability (C). Considerable care must be exercised in selecting an optimum elastomer or rubber compound.

Materials Selection for Neat Methanol Service (cont.)

Information Sources

General Information

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