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EFFECTS OF THERMAL CYCLING ON ELASTOMERS IN HIGH TEMPERATURE COOLANT

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ABSTRACT

In the past ten years diesel engine performance has significantly increased in terms of kilowatts/litre (kW/L). These higher power density outputs create higher thermal loads on the cooling system and associated seals.

While compatibility of elastomers in high temperature coolants has been studied and reported, the inevitable impact of thermal cycling on these elastomers is not well documented. This study examines the effects of thermal cycling in three general coolant categories on three different elastomers commonly considered for sealing hot engine coolants. The elastomers, by ASTM D1418 designation, are HNBR, FKM Type 2, and FEPM. The coolants are an organic acid technology (OAT) coolant, a propylene glycol premix coolant, and a corrosion inhibited de-ionized water.

Normal service applications are characterized by an indefinite number of shutdowns and startups. Testing was designed to simulate such service. Aging periods incorporated ongoing 24 hour cycles: a 16 hour period to heat up and operate at 150ºC, and an 8 hour period to cool off to ambient. O-rings, a common seal design, were subject to axial and radial deformation during testing. The o-rings' sealing attributes were examined after four, ten, twenty, and forty cycles.

Elastomeric properties were evaluated, before and after cyclical aging, in accordance with ASTM D1414-94 ("Standard Test Methods for Rubber "O-rings") and D412-06a ("Standard Test Methods for Vulcanized Rubber … - Tension"). Compressive stress relaxation (CSR) was evaluated using an in-house procedure, comporting with ASTM D6147-94.

HISTORY

During the past ten (10) years, diesel engine performance has significantly increased in terms of kilowatts/litre. Power and heat are interrelated so engine coolants might be subjected to 25% higher heat rejecting surfaces, often complicated by nucleate boiling. EPA Tier requirements, in some instances, have necessitated the use exhaust gas recycling (EGR). The gas temperature of 700˚C is reduced to 160ºC resulting in an additional thermal load to the engine coolant system. The result is a possible 25-35% increase in thermal load to be dissipated by the cooling system.[1]

Basic chemistry posits that heat accelerates reactions. Thus, the increased thermal load on coolants and the associated seals in conjunction with longer engine warranties is a precursor for warranty issues associated with marginal sealing materials. Warranty periods of 1.0 Mkm (mid-size engines), 1.6 Mkm (large-bore engines), 20,000 hours (stationary engines) and 9 year service requirement (locomotives) are not uncommon. Warranty problems associated with coolant seals are not uncommon either.

COOLANTS STUDIED

Three general categories of commercial heavy-duty ("HD") engine coolants were used as test media.

a. Organic Acid Technology Coolant ("OAT")
b. Propylene glycol 50/50 premix ("PG")
c. Deionized Water with Corrosion Inhibitors ("W/CI")

OAT and PG coolants are commonly used for on and off-road service. W/CI coolant is often found in HD diesels for locomotive service.

The coolants used are all alkaline. The OAT coolant is an ethylene-glycol based coolant stabilized with carboxylic acid complexes for long-life service with a pH of 8 or more. The

PG coolant is a propylene-glycol based coolant, pH of 9 or more, and is considered more environmentally acceptable. Finally, the W/CI coolant is stabilized with inorganic complexes to suppress corrosion, with a typical pH of 10 or more.

A 1,2-glycol can be easily cleaved under mild conditions. One mechanism is oxidative cleavage, catalyzed by a metal, into an aldehyde, ketone, or both.[2] In the actual glycol-based coolants, oxidation of the glycol forms glycol degradation organic acids such as glycolic, formic, oxalic etc.[3]

These coolants act as either aqueous and or non-aqueous electrolytes working in a system of various metals and insulators and as such can be modeled as a nucleophile or electron-pair donors (i.e. Lewis base).

ELASTOMERS STUDIED

A number of elastomers have been successfully used in the past at lower operating temperatures. Those materials and their ASTM D1418 designations are nitrile (NBR), silicone (VMQ), ethylene-propylene (EPDM), and fluoroelastomers (FKM-Type 1). However, at elevated temperatures and high pH these materials degrade quickly. The more severe operating environment and longer warranty requirements have warranted consideration and use of

a. Hydrogenated nitrile rubber (HNBR)
b. Vinylidenefluoride-tetrafluoroethylene-hexafluoropropylene rubber (FKM-Type 2)
c. Tetrafluoroethylene–propylene rubber (FEPM)

Elastomers are long-chain molecules polymerized from combinations of C_2 (ethylene), C_3 (methylethylene), and C_4 (butadiene) gases, with or without substitutions upon the carbon chain. This basic monomer structure is a good indicator of both thermal and chemical reactivity with adequate descriptions of possible chemical reactions in an introductory Organic Chemistry textbook.

Proprietary compounds of comparable modulus were examined. Relative changes in properties are reported to otherwise normalize inherent differences in the viscoelastic response of the base polymers.

HNBR:

Hydrogenated NBR is a copolymer of butadiene (which has been hydrogenated to a level ranging from 80% to 99%) and acrylonitrile. This process enhances heat stability of the butadiene component by removing double-bonded carbons. The acrylonitrile component (a substituted ethylene with a cyano group-CN) is a critical organic component imparting material properties such as oil resistance and strength. However, a fundamental reaction of nitrile is hydrolysis to a carboxylate in the presence of a base (supplied by the coolant) and heat (supplied by the engine). The end result is high swelling of the elastomer due to the water soluble characteristic of a carboxylate and loss in shear modulus.[4] The reaction typically becomes apparent after 1,200 hours at lower temperatures (125ºC) and can be duplicated in a lab after 1,000 hrs @ 135ºC.

FKM Type 2:

The FKM Type 2 fluoroelastomer is a terpolymer of vinylidenefluoride-tetrafluorethylene-hexafluoropropylene. The elastomer is primarily vinylidenefluoride, technically a 1,1-disubstituted ethylene (i.e. there are 2 fluorine atoms substituted on the first carbon). The hydrogen atoms adjacent to the fluorine atoms on this vinyl are very acidic and a strong base under mild conditions can readily abstract them leaving a carbon-carbon double bond and a hydrogen fluoride byproduct. The presence of tetrafluoroethylene greatly minimizes this tendency but does not eliminate it. Thus, measurements of fluoride ion released into the coolant are included in this study.

FEPM:

The most popular FEPM class elastomer is a copolymer of tetrafluoroethylene (a fully substituted monomer) and propylene (a non-substituted monomer). This elastomer exhibits remarkable stability in a high pH environment. The material is sometimes faulted for a relatively high temperature stiffening value (0ºC) but possesses a remarkably low brittle temperature (-58ºC).[5] Nevertheless, this attribute can be a limitation if a truly rubbery characteristic is required at below freezing temperatures. Notwithstanding, the FEPM elastomer has been widely used in HD diesel engine service, including power cylinder seals, for over ten (10) years.

TEST PROTOCOL

Specimens

O-rings are commonly used for sealing so test fixtures were designed to simulate conventional seal applications which include both radial and axial deformations. The o-ring aging fixtures were designed for AS568-214 standard dimension o-rings and deform the o-rings in either the radial or axial direction. Fixture SK2264, in figure 1, is used for radial deformation.

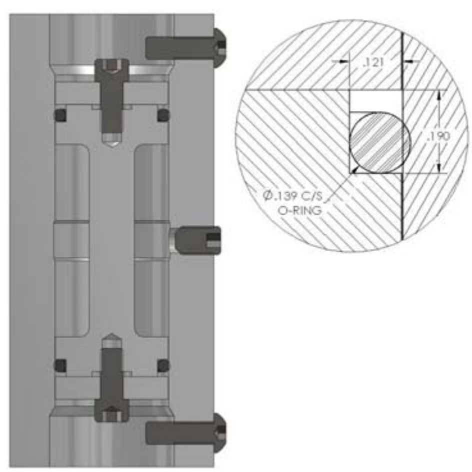

Figure 1 – SK2264, radial deflection of o-rings

Fixture SK2451, in figure 2, applies axial deformation to three separate specimens.

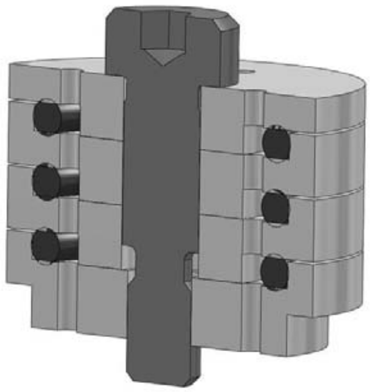

Figure 2 – SK2451, axial deflection of o-rings

AS568-225 o-rings are subject to axial deflection serving as cap seals in the aging vessel (see figure 4).

Test Methods

ASTM D1414 ("Standard Test Methods for Rubber O-rings") procedure was used to determine tensile strength and elongation of AS568-214 o-rings before and after aging.

ASTM D412 ("Vulcanized Rubber … - Tension") procedure was used to determine tensile strength, M25, and elongation of standard dumbbells before and after aging.

ASTM D2240-05, Type M indentor was used to measure hardness.

Compressive stress relaxation (CSR) data, comporting to ASTM D6147-94, was determined at 25% deformation using an in-house procedure. Fixture SK1303 (see figure 3) contains a .250 inch deflected sphere of the subject elastomer and can be mounted on a pressurized manifold with pressure gage. The fixture fits inside test vessel SK2451-V for aging in coolant.

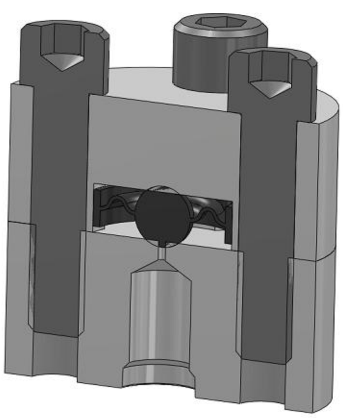

Figure 3 – SK1303 CSR fixture

The pH values and fluoride ion were measured using a Hanna Instruments (HI-3222) pH bench meter and a HI-4110 fluoride ion half-cell electrode according to established procedures.

Aging Cycles

To more closely simulate engine service the test chamber is programmed to run a twenty four (24) hour cycle, ramping from room temperature (RT) to 150ºC. After sixteen (16) hours elapsed time, power is shut off and the oven chamber is allowed to cool to ambient over the next eight (8) hours. This is considered one (1) cycle. Test data results are summarized for periods of 4, 10, 20, & 40 cycles.

Test Vessels

The gray iron test vessels (SK2451-V), in figure 4, are designed to develop specific sets of information. Test o-rings are either deformed 13% in the radial direction (see fixture SK2264) or 22% in the axial direction (see SK2451). Heat rejecting surfaces commonly create nucleate boiling so test fixtures were designed to isolate and age o-rings in either the saturated vapor (the top o-ring) and saturated liquid phase (the bottom o-ring) of the coolant.

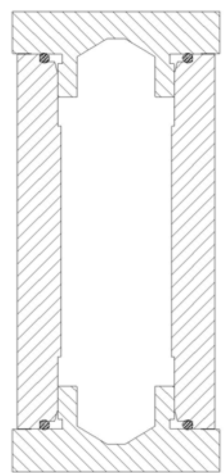

Figure 4 – SK2451-V Gray Iron aging vessel

The test vessels, SK2451-V and SK2264, are placed perpendicular in the chamber after being charged with 50ml and 30ml of coolant, respectively, and identified "top" and "bottom". The top seal is subject to a saturated vapor from within the vessel and dry-heat oxidative exposure from outside. The bottom seal is subjected to liquid coolant internally and oxidative exposure externally. Any unusual appearance of the o-ring, such as groove pitting, corrosion, staining, or leakage, is reported. D412 dumbbells were fully immersed in fluid during the aging process.

Baseline Data

Table 1 – D1414 Baseline Values (AS568-214 O-rings)

Baseline Data			
	FEPM	FKM	HNBR
Tensile Strength (Mpa)	17.1	8.4	18.7
Elongation (%)	133	173	155
Durometer (points)	77	72	67

Table 2 – D412 Baseline Values (D412 Dumbbells)

Baseline Data			
	FEPM	FKM	HNBR
Tensile Strength (Mpa)	21.7	17.2	23.8
Elongation (%)	139	252	270
Durometer (points)	82	75	73
M-25	3.23	1.69	1.48

RESULTS

Reported values are the calculated mean value unless indicated otherwise.

The reported percent change calculation is set forth in Equation 1.

Eq. (1) $$\%\,Change = \frac{Property\,Value_{aged} - Property\,Value_{original}}{Property\,Value_{original}}$$

The reported percent retained calculation is set forth in Equation 2.

Eq. (2) $$\%\,Retained = \frac{Property\,Value_{aged}}{Property\,Value_{original}}$$

When a material became incapable of evaluation due to degradation, the data series was terminated at that point.

Tensile Strength

The percent retained values in tensile strength (at break), per D1414, after aging in OAT, PG, and W/CI coolants are plotted for the AS568-214 o-rings in figures 5 though 7 respectively.

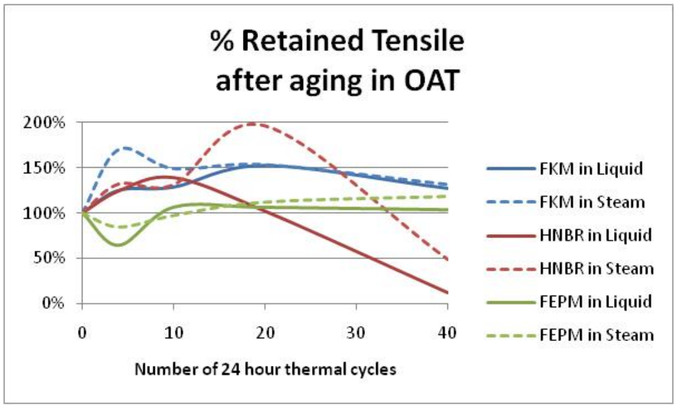

Fig 5 – D1414 Retained Tensile after aging in OAT

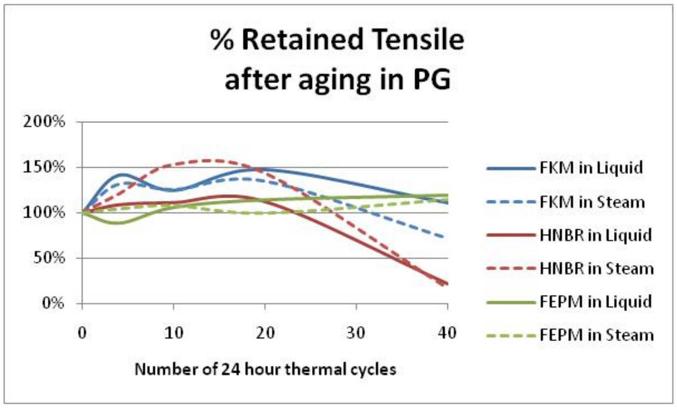

Fig 6 – D1414 Retained Tensile after aging in PG

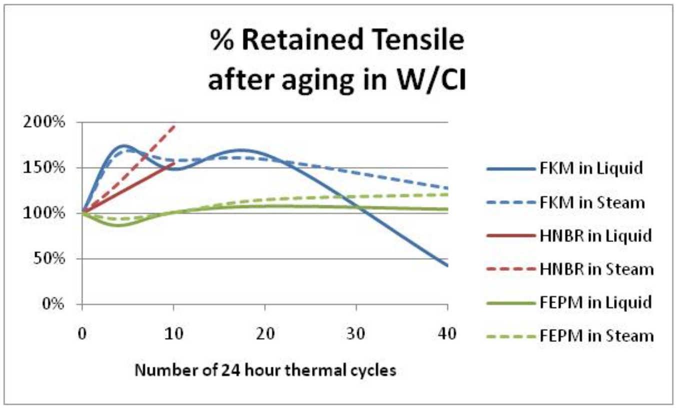

Fig 7 – D1414 Retained Tensile after aging in W/CI

FEPM exhibits the greatest stability in both the liquid and vapor phase of all three coolants as observed in figures 5 - 7.

The percent retained values in tensile strength (at break) after aging in OAT, PG, and W/CI coolants are plotted for the D412 dumbbells in figures 8 though 10 respectively.

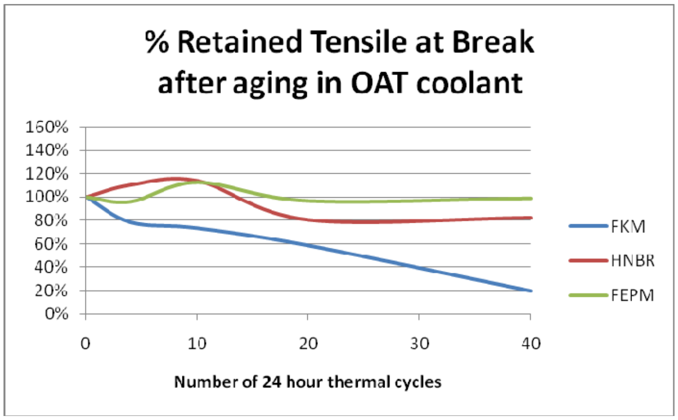

Fig 8 – D412 Retained Tensile in OAT

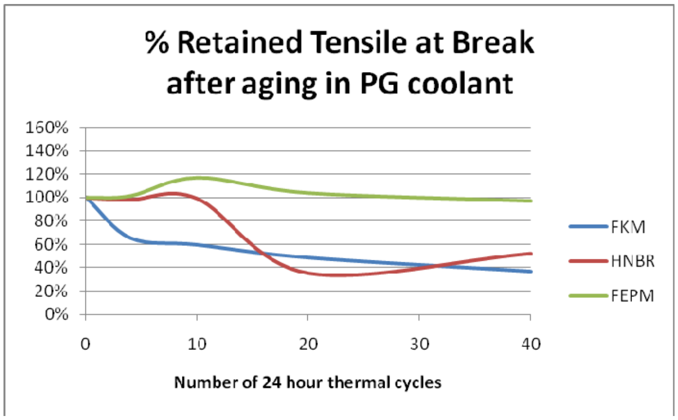

Fig 9 – D412 Retained Tensile in PG

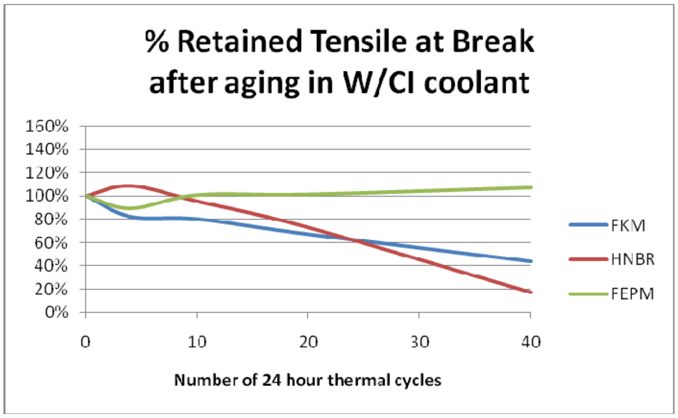

Fig 10 – D412 Retained Tensile in W/CI

The retention of tensile strength in the FEPM D412 dumbbells after aging in all three coolants exhibits greater stability than either FKM or HNBR. This observation coincides with the same observation made using the D1414 o-rings.

Elongation

The percent retained values in elongation (at break) after aging in OAT, PG, and W/CI coolants are plotted for the AS568-214 o-rings in figures 11 – 13 respectively.

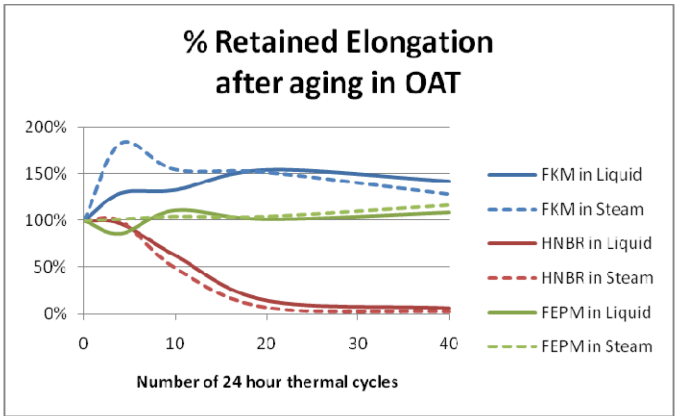

Fig 11 – D1414 Retained Elongation in OAT

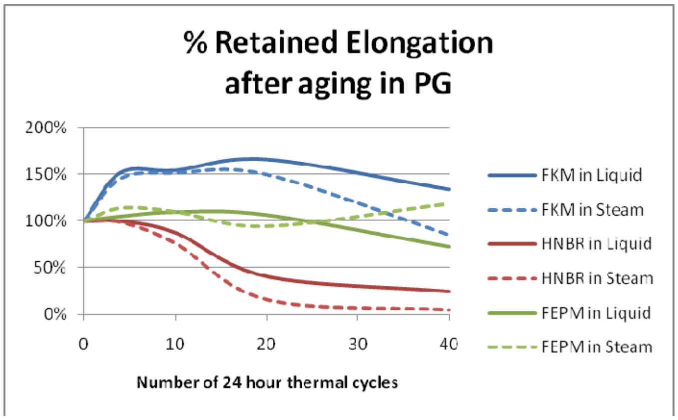

Fig 12 – D1414 Retained Elongation in PG

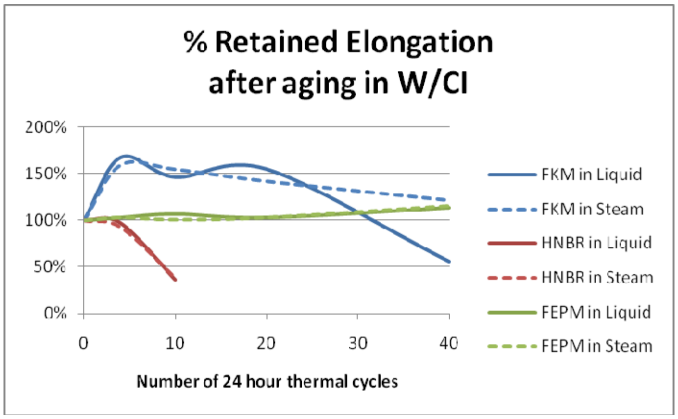

Fig 13 – D1414 Retained Elongation in W/CI

The retention of elongation in the FEPM D1414 o-rings, after aging in all three coolants, exhibits greater stability than either FKM or HNBR.

The percent retained values in elongation (at break) after aging in OAT, PG, and W/CI coolants are plotted for the D412 dumbbells in figures 14 – 16 respectively.

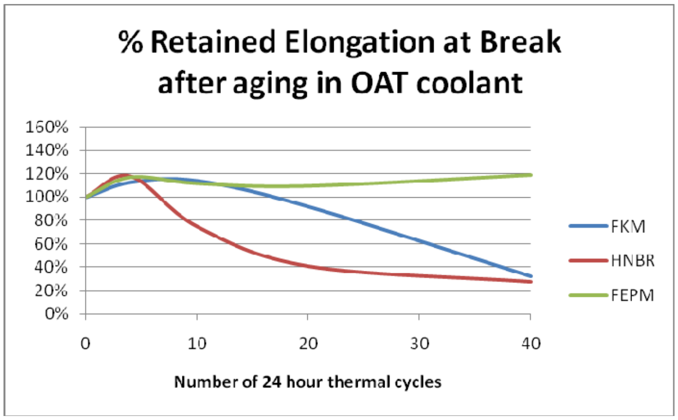

Fig 14 – D412 Retained Elongation in OAT

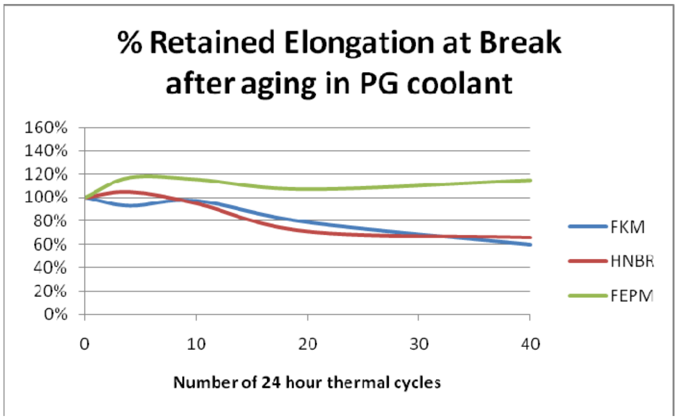

Fig 15 – D412 Retained Elongation in PG

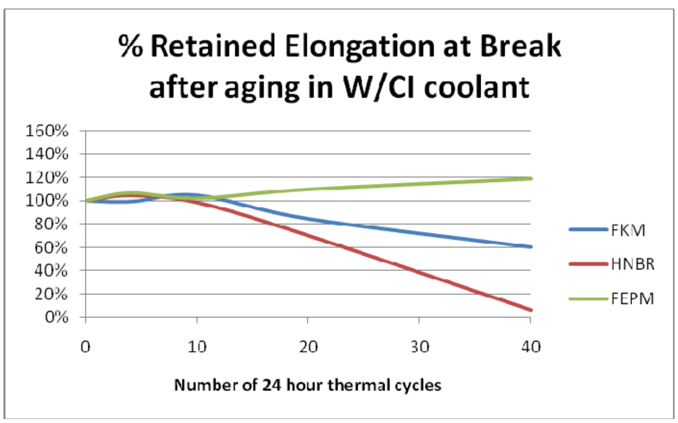

Fig 16 – D412 Retained Elongation in W/CI

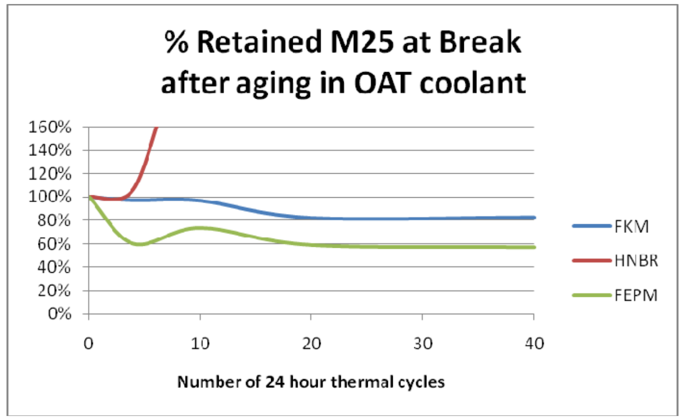

Fig 17 – D412 Retained M25 in OAT

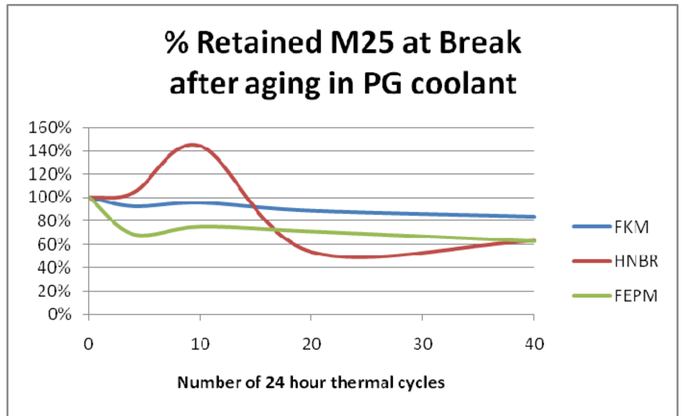

Fig 18 – D412 Retained M25 in PG

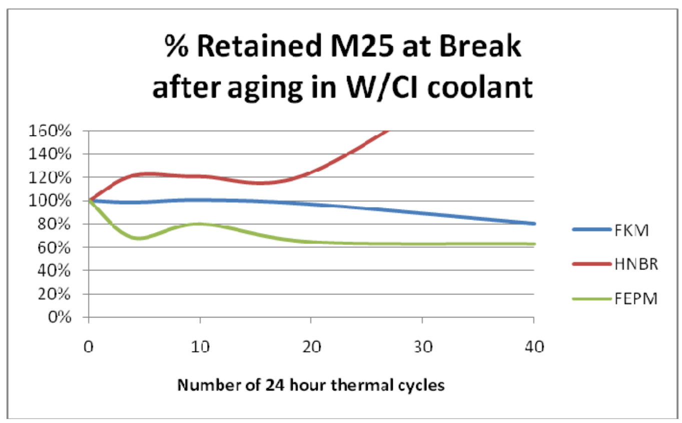

Fig 19 – D412 Retained M25 in W/CI

The retention of elongation in the FEPM D412 dumbbells after aging in all three coolants exhibits greater stability than either FKM or HNBR. This observation coincides with the same observation made using the D1414 o-rings.

M25 – Stress at 25% Elongation

The percent retention of stress at 25% strain (“M25”) after aging in OAT, PG, and W/CI coolants are plotted for the D412 dumbbells in figures 17 through 19 respectively.

The FKM D412 dumbbells exhibit the greatest stability while the HNBR appears remarkably unstable.

Compression Set

Radial compression set of the AS568-214 o-rings from fixture SK2264 is plotted for both steam phase and liquid phase exposure in figures 20 – 22.

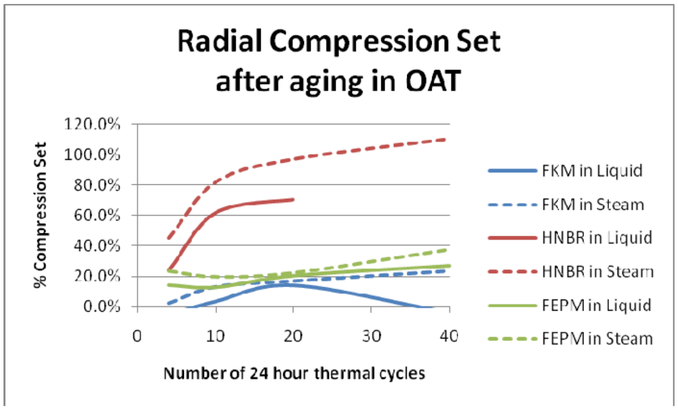

Fig 20 – Radial Compression Set in OAT

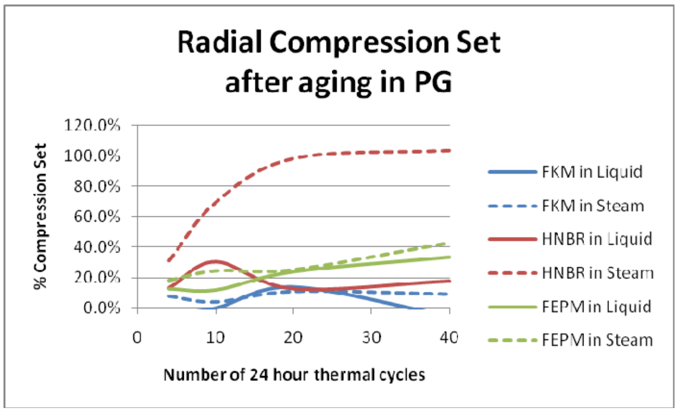

Fig 21 – Radial Compression Set in PG

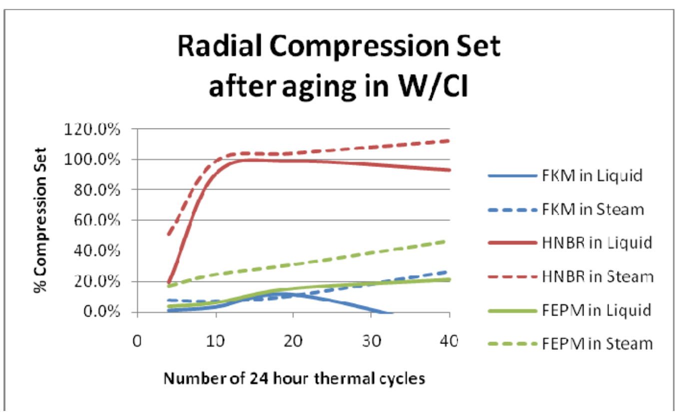

Fig 22 – Radial Compression Set in W/CI

Axial compression set of the AS568-214 o-rings from fixture SK2451 in the liquid phase is plotted in figures 23 – 25.

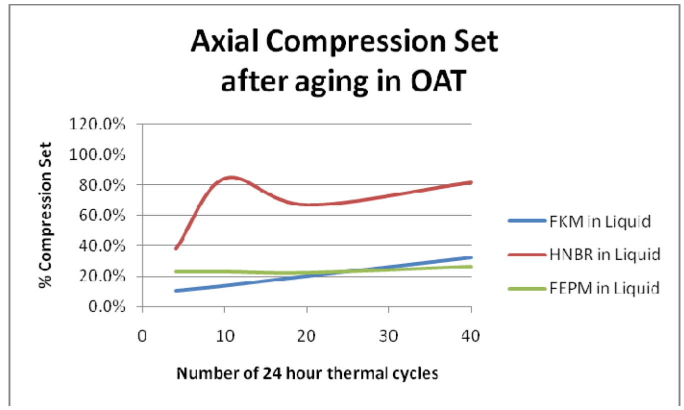

Fig 23 – Axial Compression Set in OAT

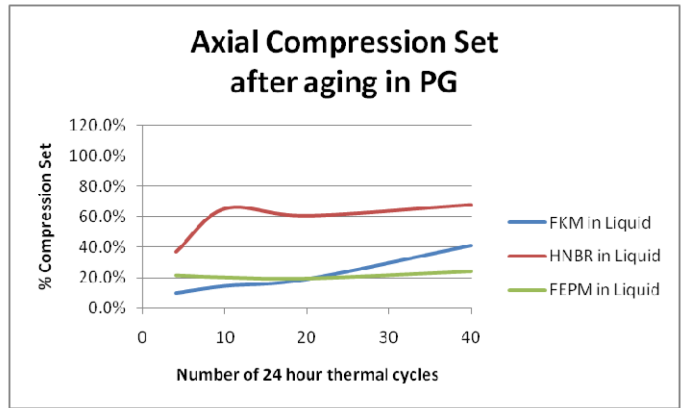

Fig 24 – Axial Compression Set in PG

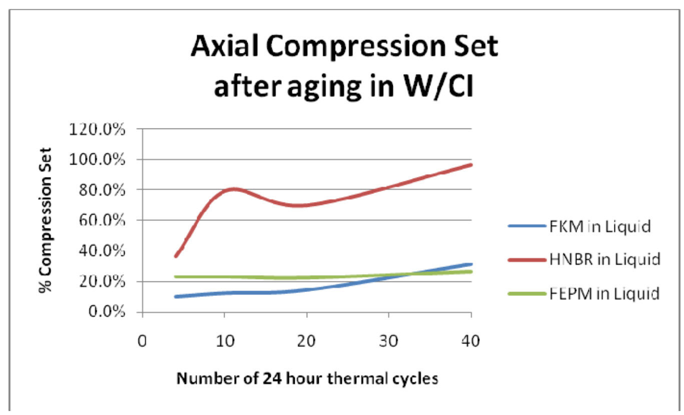

Fig 25 – Axial Compression Set in W/CI

Axial compression set of the AS568-225 cap o-rings from the vessel SK2451-V is reported for both dry/steam phase and dry/liquid phase exposure:

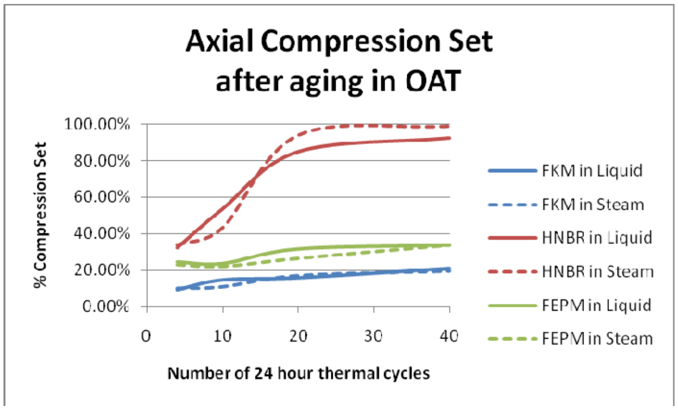

Fig 26 – Axial Compression Set in OAT

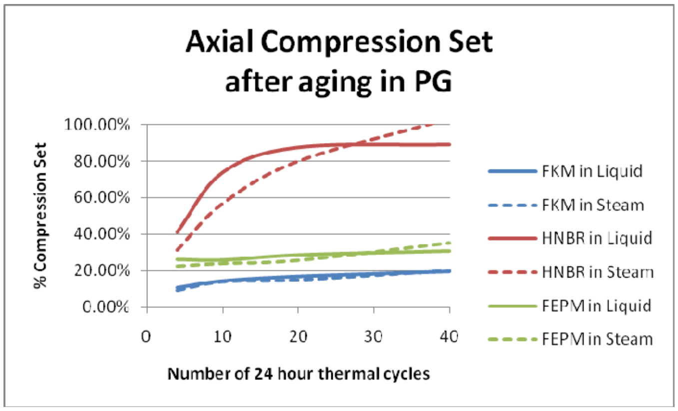

Fig 27 – Axial Compression Set in PG

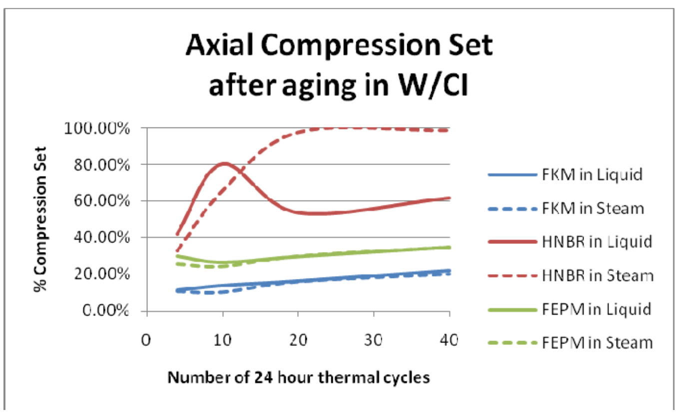

Fig 28 – Axial Compression Set in W/CI

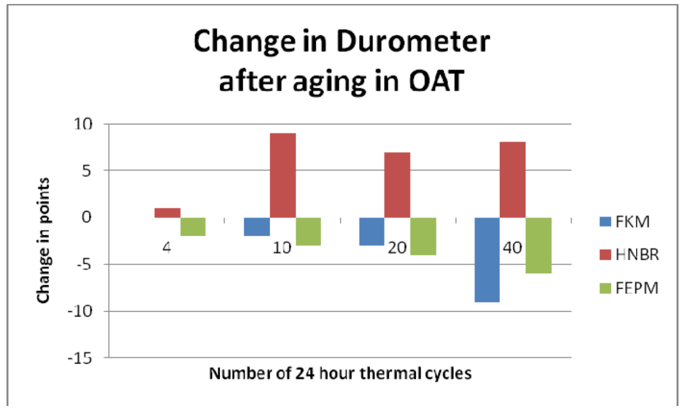

Fig 29 – Change in Hardness after aging in OAT

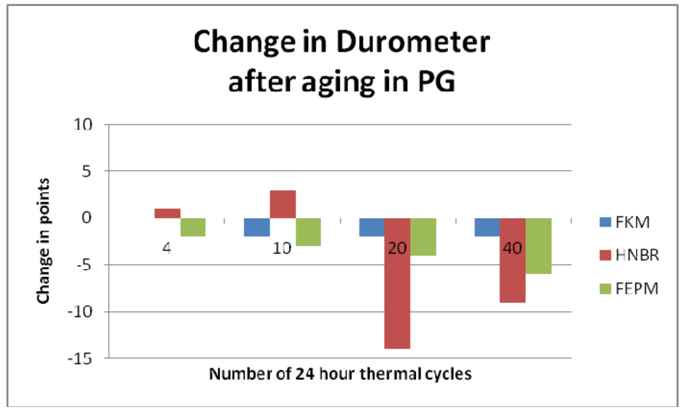

Fig 30 – Change in Hardness after aging in PG

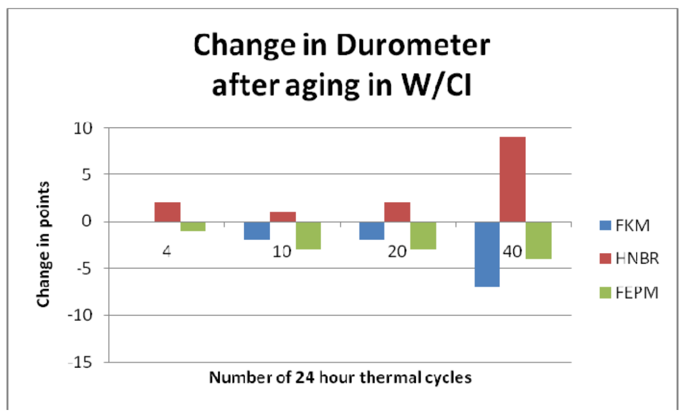

Fig 31 – Change in Hardness after aging in PG

HNBR exhibited excessive compression set characteristics relative to FKM and FEPM.

Hardness (Type M)

The change in hardness relative to baseline after aging in OAT, PG, and W/CI coolants are measured from D412 dumbbells and plotted in figures 29 – 31 respectively.

Remarkable changes in the durometer of HNBR were noted after aging in OAT and PG.

Compressive Stress Relaxation

The median value of percent retained contact stress (as tested in SK1303) is reported.

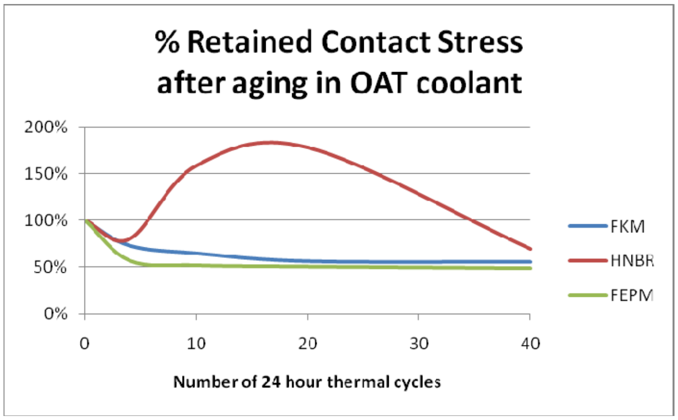

Figure 32 – Retained Contact Stress in OAT

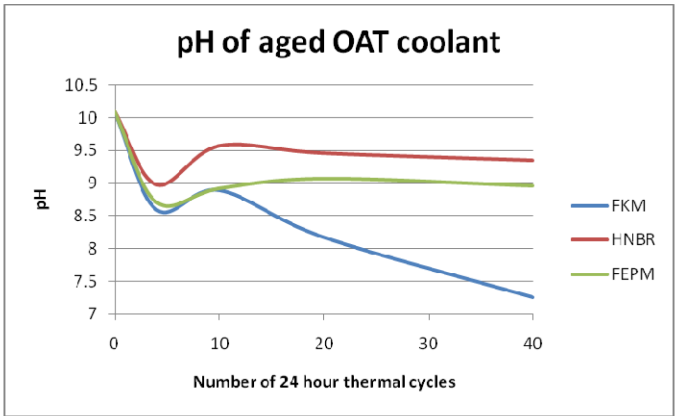

Figure 33 – pH of Aged OAT Coolant

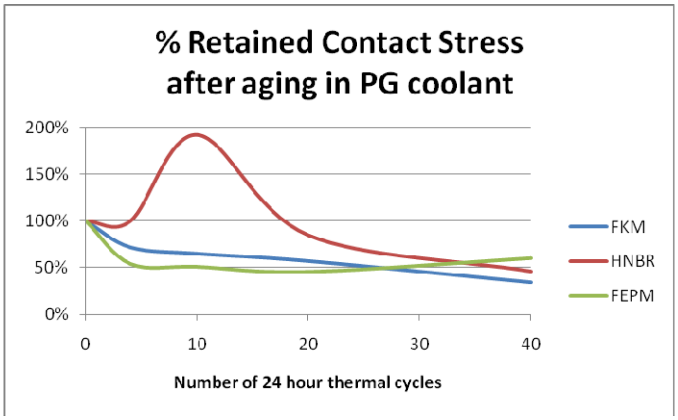

Figure 33 – Retained Contact Stress in PG

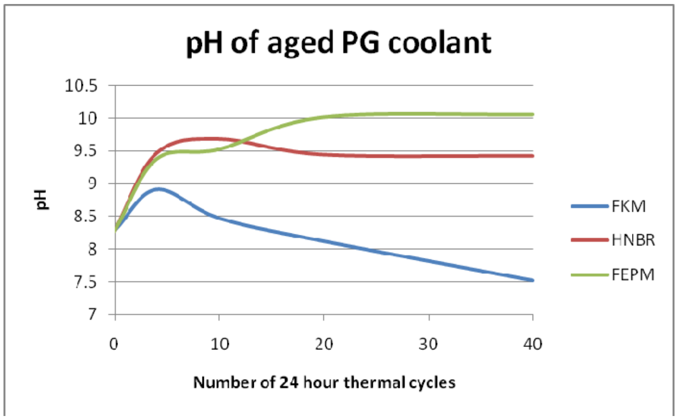

Figure 34 – pH of Aged PG Coolant

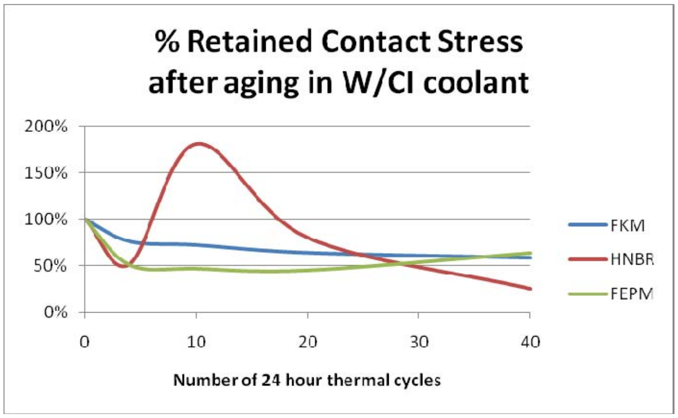

Figure 32 – Retained Contact Stress in W/CI

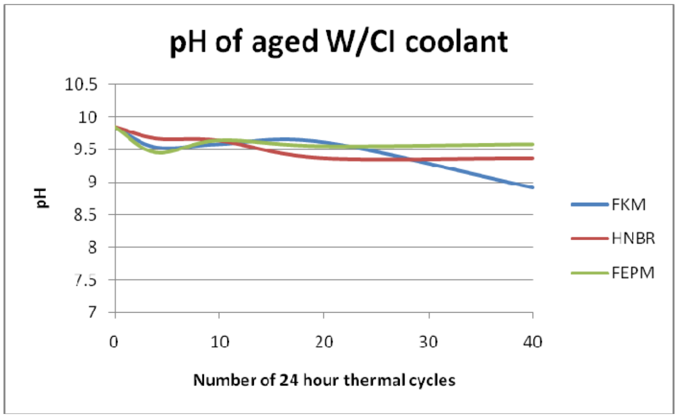

Figure 35 – pH of Aged W/CI Coolant

Remarkable increases in retained contact stress of HNBR are observed indicative of a material instability.

Remarkable drops in pH of the coolants in contact with FKM (see figures 33 – 35) indicate chemical interaction between the polymer and coolant.

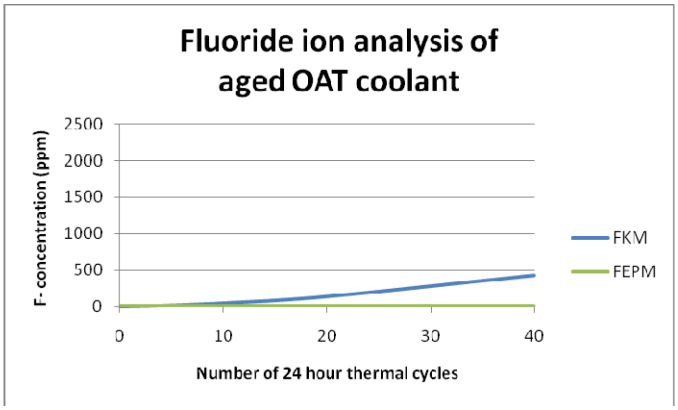

Figure 36 – Fluoride Ion of OAT Coolant

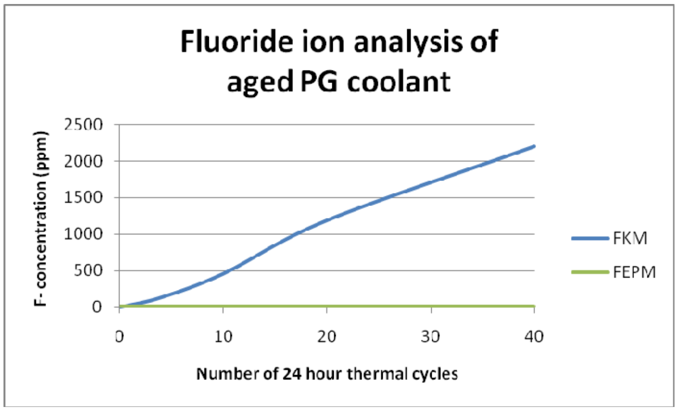

Figure 37 – Fluoride Ion of PG Coolant

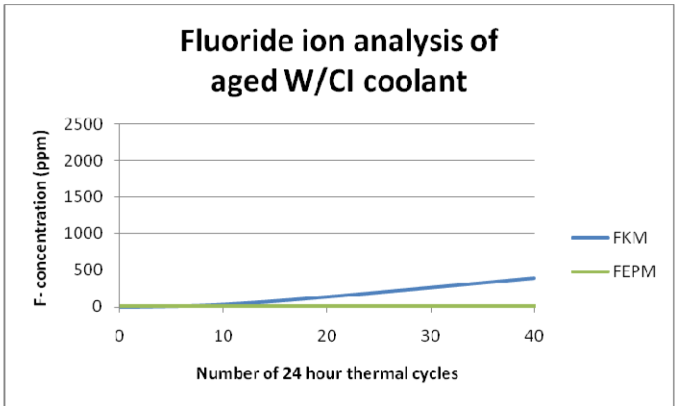

Figure 38 – Fluoride Ion of W/CI Coolant

The increase in measured fluoride ion associated with FKM in each coolant coincides with the measured reduction in pH. This observation corroborates the premise of chemical interaction between FKM and hot alkaline coolants.

CONCLUSIONS

The test results indicate that HNBR is not a suitable elastomer for high temperature service (~150˚C) in the three coolants examined.

Absent data to the contrary, data based on 40 cycles (1,000 hours) of testing indicates FEPM and FKM are suitable materials in the coolants studied. However, the increasing trend in fluoride ion, and associated reduction in pH, indicates longer term testing and validation of FKM in hot coolant is warranted.

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