

Effect of Temperature and Aeration on Fluid-Elastomer Compatibility

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ABSTRACT

To investigate the effect of aeration on fluid-elastomer compatibility, 4 types of elastomers were aged in three gear lubes. The four types of elastomers include a production fluorinated rubber (FKM) and production hydrogenated nitrile rubber (HNBR) mixed by the part fabricator, a standard low temperature flexible fluorinated rubber (FKM, ES-4) and a standard ethylene-acrylic copolymer (AEM, ES-7) mixed by SAE J2643 approved rubber mixer. The three gear lubes are Fluid a, Fluid b and Fluid c, where Fluid b is a modified Fluid a with additional friction modifier, and Fluid c is friction modified chemistry from a different additive supplier.

The aeration effect tests were performed at 125°C for 504 hours. The aerated fluid aging test was performed by introducing air into fluid aging tubes as described in GM Materials Specification GMW16445, Appendix B, side-by-side with a standard ASTM D471 test. Shore A hardness, tensile strength, elongation, modulus at 50% & 100% elongations and volume swell were measured before and after the designated fluid aging period (504 hours).

The effect of aeration on fluid-elastomer compatibility showed a strong dependence on the types of fluids and types of elastomers. Aeration provides positive influence to fluorinated elastomers (FKM), but became detrimental to hydrogenated nitrile rubber (HNBR) and ethylene-acrylic copolymer (AEM). Among the three fluids, Fluid c appeared to be more aggressive towards HNBR and AEM regardless of whether the fluid was aerated or not. Both FKM materials showed good resistance in all three fluids.

Aged fluid usually has a tendency toward oxidation, which in turn produces acidic by-products evidenced with an increase of Total Acid Number (TAN). Aeration, a process of introducing air to fluid during aging process, is expected to accelerate oxidation reaction, in turn generate more acidic by-products. However, testing results from this study actually showed a decrease of TAN of aerated fluids, even though aeration did cause catastrophic deterioration of the material properties for HNBR and AEM.

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INTRODUCTION

It is well known that fluid resistance depends on both, type of fluids and type of elastomers. Fluorinated elastomers (FKM) are considered to have the best fluid resistance and are popularly used in a broad range of applications, including harsh (acidic) environments and high temperatures. Some FKMs (typically bisphenol cured dipolymers or terpolymers) showed surface crack, significant decrease of tensile strength and elongation in fluids with high levels of organic bases, such as amines¹. These types of fluid additives seem to be friendly towards acrylic types of elastomers, such as polyacrylates (ACM) and ethylene-acrylic-copolymers (AEM).

Elastomer fluid resistance is typically tested per ASTM D471 without aeration. For transmission applications, a certain level of aeration is expected. Benefits of aeration in the fluid resistance of FKM elastomers have been published in several papers ^{2, 3, 4, 5, 6}. It was believed that aeration might increase the Total Acid Number (TAN) helping to neutralize the base nature of the fluids. This would be beneficial to FKM. Some publications ^{3, 4, 5, 6} suggest that aeration would be detrimental to silicone rubber, nitrile rubber (NBR) and hydrogenated nitrile rubber (HNBR) for the same reason it benefits FKM.

Other types of fluid additives, such as friction modifiers, anti-oxidants and esters are needed for desired fluid performance. These chemicals can be harmful to elastomers. Besides amine additives, esters could cause increased volume

swell for elastomers, especially in AEM. Increased volume swell makes network structures of the elastomers more accessible to attack by the chemicals in the fluids.

In this study, four compounds representing three material families were tested in three gear lube fluids, with and without introduced aeration, to investigate the effect of aeration on elastomer fluid resistance. This study also evaluated the interaction of elastomer and fluid in various combinations, and the temperature effect on elastomer fluid resistance.

EXPERIMENT

Material - Elastomers

Four elastomers were tested covering four types of elastomers: a production fluorinated rubber (Compound A - FKM) and production hydrogenated nitrile rubber (Compound C - HNBR, 96% saturation) that were mixed by the part fabricator, a standard low temperature flexible fluorinated rubber (Compound B - FKM Standard ES-4, Tg at -30°C) and a standard ethylene-acrylic copolymer (Compound D - AEM Standard ES-7, VAMAC G) mixed by an SAE J2643 approved rubber mixer.

Material - Fluids

Three gear lubes were used for this study, which are labeled: Fluid a, Fluid b and Fluid c. Additives for Fluid a and Fluid b came from the same company; Fluid b is a modified Fluid a with additional friction modifier. Fluid c is a different chemistry from a second supplier.

Aerated Fluid Aging Test

The aerated test was performed per GMW16445, Appendix B, also described in US Patent US 8,087,285 B2. Eight specimens were placed in a tube with air inlet, condenser and elastomer hanger insert, as shown in Figure 1. Apparatus dimensions and set-up were as specified in ASTM D6594-08 section 6. Stainless steel washers were used to separate specimens. All specimens were completely suspended and surrounded by testing fluid (300 ml) and care was taken to ensure the coupons did not touch each other or the tube walls. The specimens were aged for 504 hours at $125 \pm 1^{\circ}\text{C}$ with air continuously blowing into the fluid at a rate of 5 liters per hour from the air tube extending through the bottom of the support hanger (32, Figure 2). Ultra-High Purity (UHP) bottled air is recommended. If dry house air is to be used, the air should go through a desiccant to remove moisture before being introduced into the aerated fluid test unit. Air bubble size was not controlled or monitored.

At the end of the designated fluid aging period, 504 hours, the specimens were removed from test tubes and immediately placed on a clean absorbent pad or laboratory grade paper towels and were covered with the same material. The specimens were cooled to room temperature for at least 30 minutes before working with the specimens. The method

requires physical tests and measurements be performed within 2 hours upon the completion of the fluid aging.

Non-Aerated Fluid Aging Test

The non-aerated fluid aging test was performed according to ASTM D471, tested at the same temperature.

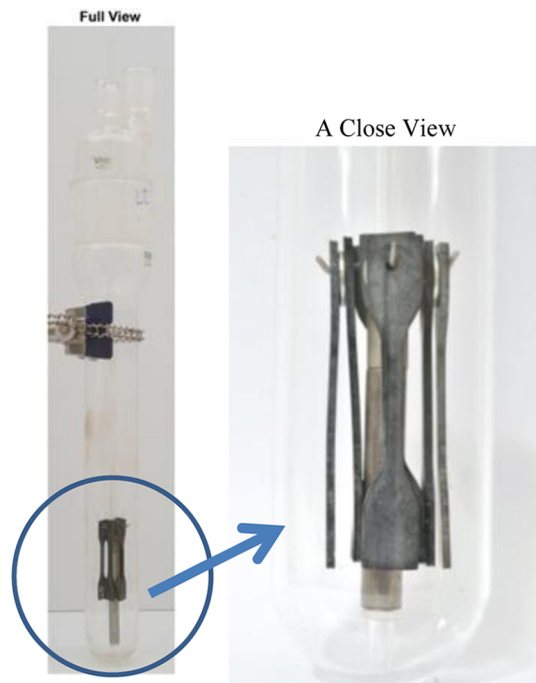


Figure 1. Aerated Seal Test Set-up per GMW16445 Appendix B

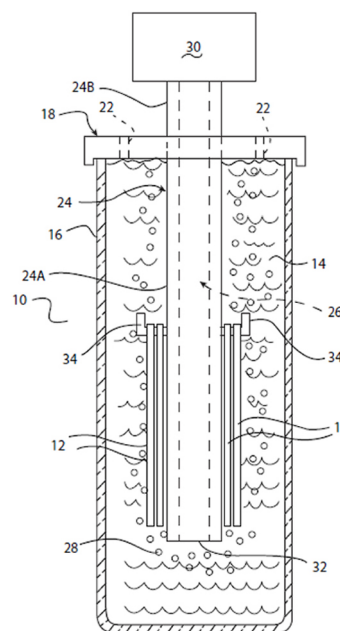


Figure 2. Aerated Seal Test Set-up per United States Patent US8087285 B2

Physical Property Measurements

The following physical properties were measured before and after the designated fluid aging periods at defined conditions: Shore A hardness per ASTM D2240, tensile strength, elongation, modulus at 50% & 100% elongations per ASTM D412, volume swell per ASTM D471, glass transition temperature (T_g) using Differential Scanning Calorimeter (DSC), decomposition temperature & composition using Thermogravimetric Analysis (TGA). The DSC test was performed in nitrogen atmosphere from -60°C to 150°C at $10^\circ\text{C}/\text{min}$ heating rate. TGA test was carried out at $15^\circ\text{C}/\text{min}$ heating rate from room temperature to 600°C in nitrogen, switch to oxygen, then ramped to 800°C at the same heating rate.

Total Acid Number of Petroleum Products

The TAN (Total Acid Number) was performed per ASTM D664 using KOH (potassium hydroxide) titration of acidic organic components.

RESULTS AND DISCUSSIONS

Tendency of Gear Lube Carbonization at High Temperature

Based on transmission design requirement, fluid-elastomer compatibility tests are usually accelerated by running the transmission fluid aging tests at 150°C . However, when similar tests were performed on gear lube, the fluid showed a high tendency of carbonization with significant amount of hard carbon particles (coke) depositing on the surfaces of elastomer specimens, which are very difficult to remove. Fluid carbonation demonstrated strong dependence on types of elastomers and fluids. Table 1 shows photos of samples after 168 hours fluid age at 150°C . The samples were wiped with paper towel soaked with methyl-ethyl-ketone (MEK) solvent to remove any loose coke particles.

The tendency of carbonization showed a strong dependence on fluid chemistry and types of elastomers.

When tested in the same fluid, Compound D (AEM) formed the most coke deposit, where Compound C (HNBR) the least. Not much coke particles were observed on the surface of HNBR specimens, if any, they can be easily removed with MEK solvent. Among the two FKM samples, the elastomer with T_g of -30°C (Compound B) generated much less coke compared to the production FKM product (Compound A).

When comparing the same elastomer in different fluids, the trend is not as consistent as different types of elastomers in the same fluid. Compound A (production FKM) and Compound D (AEM) showed a very high tendency of fluid carbonization in both Fluid a and Fluid b. These two fluids have the same chemistry except additional friction modifiers were added to Fluid b. Compound B (FKM with T_g of -30°C) generated more coke particles in Fluid c. Compound

C hardly had any coke particles in Fluid b and Fluid c, and had very small amount in Fluid a that can be easily removed.

Overall, Fluid c showed significant improved resistance of carbonization regardless types of elastomers tested.

Typical gear box application temperature is about 100°C , and the expected maximum temperature is about 125°C . To avoid measurement variation caused by fluid carbonization, the fluid aging tests, both aerated and non-aerated were performed at 125°C .

Effect of Aeration on Elastomers and Fluid

Compounds A to D were aged in Fluid a, Fluid b and Fluid c at 125°C for 504 hours under aerated (GMW16445, Appendix B) and non-aerated (ASTM D471) conditions, and test results are summarized in Table 2.

In Fluid a, aeration provided slight benefit of improving fluid resistance for Compounds A (Production FKM), Compound B (FKM with -30°C T_g), and Compound D (AEM). Aeration however caused more elongation deterioration for Compound C (HNBR). It also resulted in a significant increase of modulus, which is an indication of elastomer hardening. The elastomers behaved similarly in Fluid b as they did in Fluid a due to the very similar chemistry of the two fluids (Fluid b has more friction modifier). Compound D (AEM) performed the same in Fluid b whether the test was aerated or non-aerated. Elastomers in Fluid c behaved significantly different. Aeration still had some advantage towards the two FKM compounds. Its effect on Compound D (AEM) turned negative: aerated fluid aging in Fluid c resulted in a tensile strength change of -61% (vs -21% for non-aerated fluid aging), elongation change of -74% (vs -44% for non-aerated fluid aging). The same detrimental effect was also observed for Compound C: aerated fluid aging caused a tensile strength change of -62% (vs -28% for non-aerated fluid aging), elongation change of -97% (vs -53% for non-aerated fluid aging). A combination of high sulfur content of fluid c and aeration would have negative impact on HNBR with 96% saturation. Significant drop of elongation would cause an elastomer to lose its flexibility, in turn reducing its sealing life.

Aerated fluid aging promoted more volume swell regardless of elastomer type. Compound A (Production FKM), Compound B (FKM) and Compound C (HNBR) in aerated fluids swelled as much as twice compared to the non-aerated fluids, except Compound C in Fluid c. Aeration did not cause any noticeable difference towards the volume swell of Compound D (AEM) in any fluid.

Table 1. Pictures of EOT samples, ASTM D471, 150C for 168 hours cleaned with solvent

Fluids	Fluid a	Fluid b	Fluid c
Compound A Production FKM			
Compound B FKM Standard ES-4 T _g at -30°C			
Compound C Production HNBR			
Compound D AEM Standard ES-7 VAMAC G			