
Elastomers in Automotive Fuels, Oils & Fluids at High Temperatures

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ABSTRACT

Elastomers in fuels, oils and other fluids are increasingly being tested (and subjected to) 3000 hour life tests. These tests are not only realistic but also overdue if we are building world-class automobiles. As engineers we must not only consider the best candidate elastomers but also be aware of the potential of various elastomer degradation mechanisms. This paper will detail briefly these mechanisms and their cause/effect relationships, specifically in the engine compartment applications.

oils and fluids on different elastomers when subjected to the various operating environments ie: fuels, engine lubricants, automatic transmission fluids, power steering fluids, engine coolants and refrigerants.

GASOLINE/OXYGENATED SOLVENT BLENDS

Much has been written on these blends and one should remember that these are essentially a "mixed-solvent" system (1) since they consist of the non-polar gasoline blended with (2) a polar alcohol (methanol, ethanol) and or ether (MBTE or ETBE). The polar components have a strong physical attraction to the acrylonitrile-butadiene (NBR or nitrile) elastomers as well as the hydrogenated equivalents (HNBR). The source of attraction is the acrylonitrile group-specifically the triple bonded nitrogen via it's unshared electron pair. The mechanism is similar to the forces that make water a liquid rather than a gas.

Essentially this is a "likes attracts likes" situation. The polarity imparted by the acrylonitrile group is what creates the hydrocarbon (non-polar) resistance in NBR and HNBR elastomers. In the case of fluoroelastomers (FKM) the vinylidene fluoride (VF₂) molecule is also strongly polar. Gasoline/methanol combinations allow very strong bonding of alcohols (2). Swelling of fluoroelastomers is decreased by increasing the tetrafluoroethylene (TFE) monomer (a component of terpolymer class of fluoroelastomers) which is non-polar. Increasing TFE levels not only increases the weight percent of fluorine (3) with an increase in cost but also decreases the low-temperature performance of FKM elastomers.

ALCOHOL COMPLICATIONS WITH NBR AND HNBR –

Ordinary engine startups plus low temperatures (causing phase separation) will cause a certain amount of unburned alcohols to end up in the crankcase. These

INTRODUCTION

One of the failures of a typical mechanical engineering education is the continued emphasis on treating courses such as chemistry, physics, thermodynamics, etc. as "stand alone" events. In reality they should be taught in a "materials science" concept and design engineers should be comfortable with facing up to these various disciplines.

Consider polymers in the simplistic sense: their physical state might be glassy, crystalline or amorphous (rubbery) but the long chain molecule is common to each. The molecules of construction are often 2 and 4 carbon gases polymerized to a high molecular weight ie: chemistry. Their physical properties are dictated to a great extent by physics. Their time-temperature relationships are governed by thermodynamics and elastomers might be categorized as super-condensed gases. The polymer viscosity is sufficiently high so that they can be defined using mechanics. This is a little more complicated since they have a nonlinear viscoelastic response.

Having briefly defined the engineering material of discussion we will now consider the effects of fuels,

alcohols normally acting as a base, can also act as an acid by losing a hydrogen ion, forming the alkoxide ion, RO⁻ (4). We now have the strong potential a Thorpe reaction (5) whereby two adjacent nitrile molecules can crosslink through each other. This reaction can increase the hardness of either an NBR or HNBR seal or gasket to an unacceptable level.

ENGINE LUBRICANTS

Typical engine oils must operate routinely at 110-120°C, heavy-duty service (trailer towing etc) and higher operating ambients can raise this temperature to 150°C. There is nothing simple about today's modern lubricants with additives ranging from 5 to 25% of their content (6). Typical additives are low-molecular polymers serving as viscosity index improvers - relatively benign. Detergents, ie: succinimides (dominant), as well as calcium and magnesium sulfonates are also added. There is a strong possibility that the magnesium ion, a very reactive metal could also serve to drive metal-catalyzed reactions.

The prime source of attack on elastomers are the various antioxidants added, typically a primary-secondary combination of zinc dithiopropanate (ZnDTP) and nonylated diphenylamine (base). The amine component not only can crosslink a standard NBR (but not HNBR) but also dehydrofluorinate any VF₂ containing fluoropolymer (7). The rate of attack on these polymers at 150°C can range from rapid to slow but the reaction is inevitable.

The only truly base resistant elastomers for this service must contain fully-saturated monomers (TFE- as opposed to partially saturated ie: VF₂) or hydrocarbon monomers. Candidate elastomers not subject to dehydrofluorinations are AFLAS® (FEPM) from the 3M Company or VT-R-6279 from the Dupont Company. A test routinely utilized by one of the oil-tool suppliers is fluoride-ion analysis (8) and is a very repeatable test procedure. The amine antioxidants by their nature are sacrificial and are readily consumed neutralizing the air typically entrained in the oil due to engine-operation. Remember that many motorists duly replace their engine oil every 3000 miles (approximately 75 hours of service at 40 mph). This means the few seals in the crankcase are subjected to 4 litres of new oil many times during the life of the seal. CAUTION: Much laboratory testing is done using an infinite amount of elastomer with a finite amount of test fluid thus the elastomer serves as a titrant rapidly bringing down the pH (created by the amines) to a low level. Subsequent testing is now at a level where by the aggressive component (amine) is no longer available at the concentration necessary to drive

the inevitable reaction. Always consider that in the real world, the seal - a finite amount of elastomer, is subjected to an infinite amount of fluid (numerous oil changes).

AUTOMATIC TRANSMISSION FLUIDS

Typical automatic transmission fluids must operate routinely at 110°C average. Again heavy-duty service (trailer towing etc., higher operating ambients as well as mountainous terrains will raise this limit to 160°. Automatic transmission fluids are even more complex than lubricating oils since they incorporate "friction modifiers" (9), typically polar oil-soluble materials such as fatty acids, amides or salts. These might be amine salts of fatty acids or fatty acid amides with attendant natural or synthetic esters of the fatty acids. Such materials are good plasticizers for NBR and HNBR seals.

The higher operating temperatures dictate higher levels of antioxidants - typically amine-types so the attack mechanism on VF₂ type fluoroelastomers is even more aggressive than the lubricating oils. The elastomer considerations should be similar to those recommended for lubricating oil service.

POWER STEERING FLUIDS

Typical power steering fluids routinely operate at 110-115°C and under peak conditions the temperatures will rise to 160°C. This peak can create many problems, both with metals and non-metals so at least one manufacturer is considering an oil-cooler to minimize upper temperatures to 125°C. This limit will allow the use of HNBR seals except in areas subject to seal oxidative attack. The latest trend is to improve the viscosity-temperature function (VT) relationship specifically at low temperature.

This is achieved by utilizing branched paraffinic oils whereby the side groups (branches) prevent main-chain crystallization. Unfortunately some of the newest oils work so well that units are suffering low-temperature leakage. This occurs because formerly the hydraulic fluid increased in viscosity as did the seal at low temperature. Now only the seal increases in stiffness with a concurrent decrease in elastic recovery rate. If the seals (specifically metal-cased shaft seals) have an elastic recovery rate slower than the disturbing frequency the unit is subjected to, leakage will be inevitable. Seal elastomers should always be tested using dynamic mechanical rheological tests (DMRT) by scanning the various operational frequencies the unit is subjected to in service versus temperature (10).

ENGINE COOLANTS

Typical engine coolants are maintained at about 88°C. The antifreeze consists of polyalkylene glycols and various inhibitors that not only maintain a basic pH (as high as 10.8) to prevent engine block corrosion but also minimize attack of the aluminum radiator cores (aqueous base initiated). The high pH affects different elastomers although the reactions are much slower due to the lower temperatures. Various elastomers and potential reaction mechanisms of water/glycol mixtures are listed:

NBR/HNBR - PEROXIDE CURED - As long as there is no zinc oxide or magnesium oxide present (normally not present but sometimes used to enhance heat resistance-serves as antioxidant). There will be a gradual increase in hardness due to acrylonitrile groups being converted to carboxylic acid groups.

FKM ELASTOMERS - There is a very strong potential above 125°C to dehydrofluorinate if the seal is in a "hot-spot". Non-VF₂ fluoropolymers ie: AFLAS[®], VT-R-6387[®] have no problem at any temperature.

AIR CONDITIONING REFRIGERANTS & LUBRICANTS

Typical first generation refrigerants (R12 etc.) operated at an average temperature of 120 to 127°C while the newer "ozone friendly" types (R134A) operate at 132 to 138°C. The increase in both operating temperature and pressure of the R134A has created problems with the elastomers in both thermal stability and "explosive decompression" in elastomeric seal boots, o-rings and hose liners. Halogenated refrigerants are very similar chemically to the various degreasing agents and as such have the ability to extract not only the antidegradents (antioxidants, antiozonants) but also plasticizers, process aids and low molecular weight uncrosslinked elastomers.

The extraction process is exaggerated at the higher temperatures since the refrigerants are often operating in the supercritical region of the gas phase diagram. Lubricating oils (serving both as a pump lubricant and enhancing pumping efficiency) have to be soluble in the refrigerant. The nitrile and neoprene elastomers typically utilized would be moderately swollen by these first generation hydrocarbon-based lubricants which in turn offset volume changes due to the material extraction previously noted.

COMPRESSOR LUBRICANTS -The newer generation of compressor lubricants range from polyalkylene glycols (PAG) to polyalpha-olefins (PAO) to

alkylbenzenes. The swelling effects range from very moderate to possibly 25%. These are values measured at room temperature after testing so the system values at operating temperature can be substantially higher. The alkylbenzenes like the PAG & PAO are available in several viscosities (molecular weights) - their swelling effect is directly related to molecular weight - the higher the value the lower the swelling effect.

ELASTOMER SELECTION - As with any material selection process, one chooses the elastomer that performs the best. The higher operating temperatures coupled with the normal low-temperature requirements create a difficult elastomer selection process. The hydrogenated nitriles (HNBR) seem to be the leading candidate however they are operating marginally at both high and low temperature.

Typical compounding ingredients utilized to enhance aging and low-temperature improvement are vulnerable to the refrigerant extraction effect previously noted. A major air-conditioning manufacturer's elastomer specification incorporates an acetone extraction test per ASTM D297. Maximum shrinkage allowed after dry-out is -7%. This test requirement can only be met using what is basically described in the rubber industry as an unplasticized formulation. Such compounds are not very popular with the seal factory managers.

EXPLOSIVE DECOMPRESSION FAILURE (XDF) - in the oil and gas industry. It was originally solved by using high hardness (90 Shore A+) NBR seals. As the energy industry increasingly exploited the "sour" oil and gas fields (methane plus carbon dioxide and hydrogen sulfide) XDF again became a problem.

In thermodynamic terms the combination of hydrogen sulfide (dipole), carbon dioxide (quadrupole) and methane (octopole) is a "mixed-solvent" system. The pressures were sufficiently high which in turn created high gas densities with good solvent power. The end result in a planned or unplanned "blow down" was extensive seal damage. An up to date outline of the XDF phenomenon (12) and the effects of polymer/filler interactions (13) will adequately explain the mechanics of this problem.

ELASTOMERIC COMPOUND MECHANICS XDF- phenomena is related to at least two (2) critical considerations:

a. System pressure versus the Young's modulus-E of the formulation. It is as simple as the consideration of a pressure vessel and it's critical strength. Early on (14) it was assumed the gas critical

pressure leading to XDF was $\cong 5/6$ of Young's modulus-E of the elastomer. The Young's modulus-E values are not typically a part of a compound specification but can be supplied with a minimum of effort (15).

b. Effect of polymer-filler interactions (13) is readily apparent by noting "energy/unit volume at 20% drain" or "work" (15). A simple recent carbon black-elastomer study using N990, N770, N550, N330 and N220 showed tensile stress at 100% extension (M-100) at a maximum with N550. The "work" values at 20% extension continued to show an increase with N330 and a maximum with N220. Subsequent explosive decompression testing demonstrated the N220-elastomer combination to have the best XDF performance. Again, these are formulations that antagonize the factory manager so we have the classic situation; satisfy the application (customer) or keep the factory manager happy (production).

COMMENTS

The chemical and physical responses of the basic elastomers and the elastomer compounds are not only logical but also predictable. Better test methods utilizing ion analysis, infra-red spectroscopy, physical testing and dynamic mechanical rheological testing (DMRT) should be considered. With the exception of DMRT most rubber laboratories can perform these tests as well as developing Young's and shear modules (E & G). The Rubber Division - ACS "Advanced Rubber Technology" correspondence course is particularly valuable to the serious rubber chemist. The Division's newest publication, "Engineering with Rubber" edited by Alan N. Gent is a major contribution to any engineering library. The book has relevant chapters on every aspect of elastomers, covering materials and compounds, elasticity, dynamic mechanical properties, strength, fatigue, durability, design, FEA and tests and specifications.

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