

**ATTACHMENT A**

**Compatibility and Permeability of Oxygenated Fuels to  
Materials in Underground Storage and Dispensing Equipment**

A Technical Assessment of the Literature circa 1975-1997<sup>1</sup>

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## Table of Contents

	<u>Page Number</u>
1.0 Executive Summary	7
2.0 Scope	8
3.0 Technical Summary	8
3.1 Materials Compatibility with Oxygenated Gasoline	8
3.2 Permeability of Polymeric Materials to Oxygenated Gasoline	9
3.3 Technologies to Reduce Permeation of Oxygenated Hydrocarbons	10
4.0 Definitions	10
4.1 Chemical Compatibility	10
4.2 Chemical Permeation	10
4.3 Thermal-Chemical Environment	11
<i>(Gasoline -- Aromatic, Aliphatic, Olefinic Hydrocarbons</i>	
<i>Ethers - MTBE, ETBE, TAME, DIPE, etc.</i>	
<i>Alcohols - MeOH, EtOH, TBOH, AmOH, etc.</i>	
<i>Temperature -- Ambient (0 -- 120 °F)), Pressure 0-60 psi</i>	
4.4 Basic Data	11
5.0 Theoretical Overview	12
5.1 Chemistry of Oxygenated Hydrocarbons	12
5.1.1 Oxidation of Ethers	12
5.1.2 Alcohols as Bases	13
5.1.3 Hydrogen-Bonding of Ethers and Alcohols	13
5.2 Solution Thermodynamics	14
5.2.1 Ideal Solutions --	15
<i>(Hydrocarbon Blends including Ethers</i>	
<i>Chemical Potential, Activity and Vapor Pressure)</i>	
5.2.2 Non-ideal Solutions	17
<i>(Hydrocarbon Blends with Alcohols</i>	
<i>Chemical Potential, Activity and Vapor Pressure</i>	
<i>Phase separation, Effects of water)</i>	
6.0 Corrosion Mechanisms	19
6.1 Non-metals --	19
6.1.1 Equilibrium Swelling of Nonmetallic Materials by Solvents	20
<i>(Lattice model)</i>	
6.1.2 Unsteady Mass Flow of Solvents through Nonmetallic Membranes	22
Linear Permeation Theory -- Fick's Law	23
Example 1: Absorption into an Immersed Slab (swelling)	24
Example 2: Mass Flow through a Membrane (permeation)	25

6.1.3	<i>Plasticization and Extraction</i>	27
	<i>Underground Storage Tank Membranes</i>	27
	<i>Extraction of Plasticizers</i>	29
6.1.4	<i>Environmental Stress Cracking (ESC)</i>	29
	<i>Thermal Effects</i>	30
	<i>Effect of Temperature on Swelling Behavior</i>	30
	<i>Effect of Temperature on Permeation</i>	
30		
	<i>Effect of Temperature on Elastomeric Seals</i>	31
	<i>Pressure Effects</i>	31
	<i>Effect of Time</i>	32
6.1.5	<i>Testing Standards for Nonmetallic Materials</i>	32
	<i>Fuel Stability</i>	32
	<i>Compatibility Testing</i>	32
	<i>Permeability Testing</i>	34
6.2	Metals	35
6.2.1	<i>Dry Corrosion</i>	36
6.2.2	<i>Galvanic Corrosion</i>	37
6.2.3	<i>Electrolytic Corrosion</i>	37
6.2.4	<i>Wet Corrosion</i>	37
6.2.5	<i>Multiphase Corrosion</i>	38
6.2.6	<i>Wear</i>	38
6.2.7	<i>Erosion-Corrosion</i>	39
6.2.8	<i>Effect of Contaminants in Solution</i>	39
6.2.9	<i>Effect of Alloying Elements</i>	39
6.2.10	<i>Environmental Stress Cracking</i>	39
6.2.11	<i>Thermal Effects</i>	40
6.2.12	<i>Effect of Time, Corrosion Inhibitor</i>	40
6.2.13	<i>Testing Standards for Metallic Materials</i>	40
7.0	Results and Discussion	41
7.1	Non-metals	41
7.1.1	<i>General observations on the Effects of Model Fuel Blends on Polymeric Materials</i>	41
7.1.2	<i>Swelling of Polymeric Materials in Model Fuel Blends and Neat OxygenatedHydrocarbons</i>	43
7.1.3	<i>Permeation of Polymeric Materials by Model Fuels Containing no Oxygenates</i>	45
7.1.4	<i>Permeation of Polymeric Materials by Ether Blended Model Fuels</i>	46
7.1.5	<i>Permeation of Polymeric Materials by Alcohol Blended Model Fuels</i>	48
7.1.6	<i>Thermosetting Materials -- Underground Storage Tanks</i>	50
7.1.7	<i>Thermosetting Materials -- Rigid Fiberglass Piping</i>	52
7.1.8	<i>Thermoplastic Materials -- Flexible Plastic Piping</i>	52
7.1.9	<i>US EPA Evaporative Emission Regulations</i>	53
7.2	Metals	53

Compatibility and Permeability of Oxygenated Fuels to Materials  
4 in Underground Storage and Dispensing Equipment

7.2.1	<i>Corrosion by Ethers</i>	53
7.2.2	<i>Corrosion by Alcohols</i>	54
7.3	Other Materials	55
7.3.1	<i>Ceramics</i>	55
7.3.2	<i>Pipe Dope</i>	55
7.3.3	<i>Coatings</i>	55
	<i>Organic Coatings</i>	55
	<i>Inorganic Coatings</i>	56
8.0	Review Articles	56
9.0	American Petroleum Institute Documentation	57
10.0	Conclusions	61
9.1	Compatibility	61
9.2	Permeability	61
11.0	Recommendations	62
Appendices		
APPENDIX A	-- Swelling Data	63
APPENDIX B	-- Permeability Data	66
APPENDIX C	-- Chemical and Physical Description of Common Fuel Resistant Elastomers	70
References		75

## List of Tables

### Table

- 1 Properties of hydrocarbons commonly used in compatibility and permeability studies.
- 2 Approximate compositions of vapor liquid equilibrium for a 15 percent by volume blend of MTBE in ASTM Fuel C.
- 3 Approximate compositions of vapor liquid equilibrium for a 10 percent by volume blend of MeOH in ASTM Fuel C.
- 4 Performance ranking system for elastomeric hoses based upon permeability to fuels (from SAE J2260).
- 5 Volume swelling ranges of polymeric materials exposed to model fuels with and without oxygenates.
- 6 Volume swelling of polymeric materials exposed to neat oxygenated hydrocarbons.
- 7 Component geometry for permeation mass flow considerations.
- 8 Permeability, solubility and mass flow properties for various materials exposed to gasoline blends containing no oxygenates.
- 9 Permeability, solubility and mass flow properties for various materials exposed to gasoline blends containing 15 percent v/v MTBE.
- 10 Permeability and solubility of modified ASTM Fuel C, containing 15 to 20 percent by volume MeOH, in polymeric materials.
- 11 Permeability and solubility of modified ASTM Fuel C, containing 10 to 15 percent by volume EtOH, in polymeric materials.
- 12 Corrosion rates for selected metals immersed in methanol fuels at 40 °C for 2000 to 8000 hours (Lash et al.).
- 13 Corrosion rates of selected metals in 10 percent methanol blends.
- 14 Unsuitable elastomers for neat alcohol and diethyl ether.
- 15 Compatibility of commonly used materials with ethanol and ethanol blends.
- 16 Compatibility of commonly used materials with gasoline-methanol/cosolvent blends.

## List of Figures

### Figure

- 1** Activity of MTBE, toluene and isooctane as a function of ether concentration in Fuel C.
- 2** Activity of EtOH, toluene and isooctane as a function of alcohol concentration in Fuel C.
- 3** Schematic representation of unsteady mass flow by Case 1 diffusion of a permeant through a membrane.

## 1.0 Executive Summary

No material incompatibility concerns associated with storage and dispensing of methyl tertiary butyl ether (MTBE) blended gasoline at retail facilities have been documented. Gasoline containing up to 15 percent by volume of MTBE will not induce or enhance new or existing failure mechanisms in metallic or nonmetallic components. Additionally, the performance properties of the fuel itself, in contact with the construction materials, are not altered in ways which lead to impairment of vehicle performance. These observations are in contrast to the well documented aggressive character of alcohol blended fuels toward certain metals and polymers alike as well as certain vehicle driveability concerns.

Gasoline, oxygenated or not, does not absorb into or permeate through metals. The phenomenon of permeation is thus limited to certain nonmetals and will typically vary greatly depending upon the type of material in question. Permeation of gasoline through composite materials typical of fiberglass tanks, rigid piping and sumps *has not been observed* despite two reported attempts to measure it. As such, permeation of fuel components through fiberglass directly into the ground is expected to be very low, perhaps below detectable limits. Permeation of reformulated gasoline through thermoplastic and elastomeric materials typical of flexible hoses and piping has been observed. Most of this fugitive hydrocarbon emission is produced directly into the air.

There is not enough data to estimate the total fugitive emission of hydrocarbons and, especially, the individual contribution due to oxygenates permeating through all polymeric membranes at a retail facility. Where data is available, the component contribution of the oxygenated hydrocarbon to the total hydrocarbon permeation is not reported. In the case of elastomer hose construction, theoretical considerations may allow one to estimate the mass flow due to MTBE component permeation. This contribution is expected to be less than ten grams per day per station.

Absorption and permeation of alcohol blended fuels in and through polymeric materials are observed to be of considerably greater magnitude than that observed for ether blended fuels. As with MTBE, component contribution due to alcohol permeation alone is unknown. However, theoretical and practical considerations prevent the estimation of the component contribution of alcohol permeation, even in elastomers.

Direct observation of the permeation rate of MTBE and other oxygenated hydrocarbons in composite, plastic and elastomeric materials of construction is recommended for further study.

## **2.0 Scope**

This review discusses metallic and nonmetallic materials compatibility to gasoline containing various concentrations of oxygenated hydrocarbons. Permeability of oxygenated gasoline through nonmetallic materials is also discussed. Documentation published during the 1975 through 1997 time frame is used as the primary source material.

Although the current interest is focused primarily on the effects of methyl tertiary-butyl ether on materials of construction in retail facilities, this review discusses the effects of other common oxygenated additives such as alcohols and other ethers. Both above-ground and buried components are considered. A broad scope is offered for two reasons. First, a study of the effects of both alcohols and ethers will increase awareness of the various chemical phenomena that are manifest when materials are brought into contact with various oxygenated fuel blends. Second, should alternate oxygenated hydrocarbons be considered for addition to automotive fuels, it is hoped that this document may serve as a beginning reference for materials considerations.

Installation and operational procedures and practices are not considered in this review.

## **3.0 Technical Summary**

### **3.1 Materials Compatibility with Oxygenated Gasoline**

There is general agreement among observers that, if a material is resistant to alcohol blended fuels, it will be resistant to ether blended fuels as well. Although there is some merit to this assertion, it has led to considerably more documentation of materials issues involving alcohol blended gasoline.

Even so, there are no documented materials incompatibility issues associated with storage and dispensing of MTBE blended gasoline. From a metals corrosion viewpoint, gasoline is a rather benign liquid and MTBE does not increase the corrosiveness of the hydrocarbon blend.

From a polymer compatibility viewpoint, neat MTBE is an aggressive swelling agent for some, but not all, polymers. The mitigating factor for polymer compatibility in a reformulated gasoline environment is that the swelling power of MTBE is diluted in approximate proportion to its volume fraction in solution. At 15 percent concentration in gasoline, the effects of MTBE do not compromise equipment integrity.

Conversely, the corrosive nature of alcohol blended fuels with regard to metals and polymers alike is well documented. Even dilute alcohol blends are more aggressive to materials than any of the pure components. Methanol is more aggressive than higher molecular weight alcohols.

Key to the nature of metal corrosion by gasohol containing gasolines is the role of trace components in the fuel, such as water, chloride ion, sulfur compounds, pH, etc., and also alloying

elements such as copper. Lead, zinc, aluminum, magnesium, and other metals are actively corroded under certain conditions.

Swelling of polymers is enhanced by alcohols through the various associations possible among solvent-solvent and polymer-solvent interactions. Even in relatively dilute alcohol blends, considerable loss of stiffness and strength are caused by plasticization and are well documented for many polymeric materials.

Introduction of trace concentrations of water (ca. 1000 parts per million) into alcohol blended fuels often passivates corrosion of some metals and reduces absorption into some polymers. However, hydrated gasohol may introduce new degradation mechanisms for materials. Close to the water content required for passivation of corrosion, aqueous phase separation occurs. The electrical conductivity of hydrated fuel is increased to the point where galvanic and electrolytic corrosion may be enabled. Considerable loss of lubricity, leading to increased wear of wetted parts, is also observed near the point of phase separation. Corrosion and/or wear products may become entrained in the fuel and cause subsequent drive ability issues for customers vehicles.

### **3.2 Permeability of Polymeric Materials to Oxygenated Gasoline**

Likewise, permeability data for MTBE blended gasoline are sparse compared to alcohol blends. There are not enough data to estimate the total hydrocarbon fugitive emission due to permeation from retail gasoline stations. No data for fiberglass composites common to tanks and piping are found. Some data for elastomers and thermoplastics common to hoses and flexible piping are available.

Generally, the presence of oxygenates accelerates permeation of hydrocarbon fuels in elastomers and thermoplastics. Alcohols, particularly methanol, produce more excess permeation than does MTBE. Among ethers, MTBE may be more permeable than TAME.

Since observers report total mass flow due to permeation, without consideration of component contributions, estimating the contribution of MTBE to the total mass flow through a membrane requires theoretical techniques which may be questioned. For alcohols, deconvolution of the data are not possible due to substantial excess permeation. Therefore the mass flow of oxygenates (when dissolved in gasoline) through materials of interest, should be measured using techniques and instrumentation capable of resolving and quantifying individual chemical species.

From the available data, an attempt to estimate the component contribution of MTBE permeation through hoses is made in this paper. Many assumptions are involved. Depending on the total surface area of hoses and other considerations, calculations suggest that up to 10 grams total MTBE emission may be observed from permeation of nitrile rubber (NBR) based hoses per station, per day. Permeation through hoses contributes to direct evaporative emission to the air and not the soil.

### **3.3 Technologies to Reduce Permeation of Oxygenated Hydrocarbons**

Incorporation of a thermoplastic liner in flexible hose constructions, similar to liners found in some flexible underground piping, may reduce the total permeation of hydrocarbons including MTBE.

The solubility characteristic of ETBE indicates that it may be substantially less permeable in fluorocarbon elastomers than either MTBE or TAME. Lower permeability of ETBE is likely to be observed in polar polymers and is related more to stereo-chemical effects than to molecular size.

## **4.0 Definitions**

Definitions of chemical compatibility, permeability and the chemical environments of interest in this document are defined below.

### **4.1 Chemical Compatibility**

Chemical compatibility refers to changes in the physical, chemical or mechanical properties of a material resulting from thermal-chemical exposure. Any property change should not alter the performance of a part in ways which induce or enhance new or existing failure mechanisms.

For metals, chemical compatibility often implies corrosion resistance. While the term corrosion is not generally used to describe nonmetallic performance, a change in properties due to chemical exposure is often considered a form of corrosion.

For the gasoline, chemical compatibility must also mean that degradation products, if any, must not contaminate the fuel and impair automotive performance.<sup>1</sup>

### **4.2 Chemical Permeation**

Permeation is mass transport, or flux, through a material that is driven by an activity gradient. Activity is a thermodynamic term which is related to the change in the chemical potential with chemical composition. Mass flux is proportional to the permeability coefficient of the solvent-material pair and also the surface area to thickness ratio of a membrane.

### **4.3 Thermal-Chemical Environment**

Gasoline is a blend of aliphatic, olefinic and aromatic hydrocarbons and also, more recently, oxygenated hydrocarbons. Other organic additives such as corrosion inhibitors and detergents are also common. However, it has been shown that there are no measurable effects of these additives on elastomer performance factors.<sup>2</sup> Thus, for compatibility and permeability testing, model gasolines generally contain iso-octane and toluene in various proportions. An oxygenated hydrocarbon, or oxygenate, has at least one covalently bonded oxygen atom in the molecule. Generally, oxygenated additives for gasoline contain alcohol or ether functional moieties.

Over the past 25 years, oxygenates have been added to increase the octane number of gasoline and, more recently, to comply with Federal and State automotive emissions standards. These standards require addition of an oxygenated hydrocarbon to gasoline such that it will contain a specified weight percentage of bound oxygen. Depending on the molecular weight of the additive, up to 15 percent by volume of added oxygenate may be required to meet regulatory requirements.

Reformulated gasoline may be composed of hydrocarbons blended with ethers such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE) tertiaryamyl methyl ether (TAME), and perhaps others.

Gasohol may be composed of hydrocarbons blended with alcohols such as methanol (MeOH), ethanol (EtOH), tertiarybutyl alcohol (TBOH), amyl alcohol (AmOH), and perhaps others. The term Gasohol is usually confined to blends containing ethanol up to 10 percent by volume. Higher volume alcohol blends, such as 85 percent MeOH are also known.

Ambient temperatures are expected to range between zero and 120 °F. Although underground equipment may not experience such wide temperature fluctuations, the product dropped into the tank may be delivered at various ambient temperatures.

Operating pressures are expected to range between atmospheric and 60 pounds per square inch gauge (psig).

#### 4.4 Basic Data

**Table 1** summarizes some chemical and thermodynamic data for constituents commonly used to study chemical compatibility with oxygenated fuels. ASTM Reference Fuel C is composed of a 50 percent by volume blend of iso-octane and toluene. Oxygenated hydrocarbons are added to this mixture to obtain a blend of interest.

**Table 1** - Properties of hydrocarbons commonly used in compatibility and permeability studies.

Chemical	Formula	Mole Weight	Vapor Pressure	Density g/cc	Boiling Point	$\Delta H_{vap}$ BTU/lb
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			@ 100°F	@20 °C	°F	
Isooctane	C <sub>8</sub> H <sub>18</sub>	114.2	1.70	0.6919	210.6	116.7
Toluene	C <sub>7</sub> H <sub>8</sub>	92.1	1.00	0.8660	231.1	156.2
MeOH	CH <sub>4</sub> O	32.0	4.60	0.7915	148.1	502.0
EtOH	C <sub>2</sub> H <sub>6</sub> O	46.0	2.30	0.7890	173.0	396.0
TBOH	C <sub>4</sub> H <sub>10</sub> O	74.1		0.7857	180.3	
AmOH	C <sub>5</sub> H <sub>12</sub> O	88.2		0.8083	216.5	
MTBE	C <sub>5</sub> H <sub>12</sub> O	88.2	4.73	0.7404	131.4	138.0
ETBE	C <sub>6</sub> H <sub>14</sub> O	102.2				
TAME	C <sub>6</sub> H <sub>14</sub> O	102.2				
DIPE	C <sub>6</sub> H <sub>14</sub> O	102.2		0.7258	155.0	

## 5.0 Theoretical Overview

### 5.1 Chemistry of Oxygenated Hydrocarbons

It is important to briefly consider the chemistry of oxygenated hydrocarbons in order to establish their stability and propensity to form other compounds in gasoline. The chemical behavior of oxygenated hydrocarbons in solution governs the behavior of materials in contact with them.

#### 5.1.1 Oxidation of Ethers

During prolonged storage in the presence of air, some aliphatic ethers are known to slowly oxidize to form peroxides in low concentrations.<sup>3</sup> Peroxides can be unstable and hazardous in the presence of hydrocarbons and other materials. Moreover, they serve to reduce octane number by a disproportionate amount. Ethers with alpha hydrogen atoms attached to the carbon adjacent to the ether linkage, such as diisopropyl ether, DIPE, are most susceptible to this type of oxidation reaction as illustrated below.



MTBE and TAME, with no labile methylene hydrogen atoms will be least prone to undergo this type of oxidation under normal ambient storage conditions.

Peroxide formation in gasoline reformulated with ETBE and without normal antioxidant levels was tested for six months at room temperature with periodic exposure to air. Tests show a minor amount of peroxide formation.<sup>4</sup> The peroxide level was deemed negligible with respect to hazard or octane detriment. Therefore peroxide formation in MTBE, TAME, and ETBE reformulated gasolines should not be an issue especially since antioxidants are added to prevent oxidation of olefins also present in the fuel. Furthermore, air exposure to gasoline in transportation and storage equipment is limited.

Another author considered peroxide formation in automotive fuel return lines.<sup>5</sup> This concern is primarily due to the increased temperature of the fuel and is not considered an issue for the retail environment.

### 5.1.2. Alcohols as Bases

Alcohols may act as a base in the presence of active metals.<sup>6</sup> The reaction products include an alkoxide anion and the metal cation as shown below:



The smaller the alkyl group, the more acidic the alkoxide acts. Methanol forms the strongest anion and tertiary alcohols the weakest. This reaction explains the rapid corrosion phenomenon observed for active metals such as magnesium and aluminum in dry alcohol solutions, particularly methanol.

Citing this reaction, Hertz<sup>7</sup> indicated that an alkoxide ion would subsequently be reactive to elastomers and other nonmetallic materials. However, because an hydroxide ion is a weaker base, the alkoxide is very short-lived in the presence of even trace amounts of water. Water reacts with the alkoxide ion to produce the alcohol back again and the metal hydroxide. Since water is common in gasoline distribution and storage systems, degradation of materials by alkoxide ions is not considered to be an important mechanism.

Unlike some ethers, alcohols are not known to oxidize under normal ambient storage conditions.

### 5.1.3. Hydrogen-bonding of Ethers and Alcohols

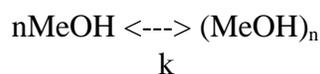
Unlike non-oxygenated hydrocarbons found in gasoline, alcohols and ethers are electrostatically dipolar molecules. That is, certain moieties in the molecule carry a partial positive charge and others in the same molecule carry a partial negative charge. This charge polarization creates attractive forces among complementary charged moieties of other similar or dissimilar molecules.

Due to the electronegativity of oxygen atoms relative to carbon and hydrogen, the oxygen atoms of both an ether or an alcohol (hydroxyl) group carry a partial negative charge. The two pair of unshared electrons in the oxygen atom of both groups make those moieties proton acceptors or "Lewis bases." Both carbon atoms adjacent to the ether oxygen carry smaller partial positive charges. In contrast, the hydroxyl group contains a partially positive hydrogen atom. This positive charge on a hydrogen atom makes it weakly acidic. Thus, the hydroxyl group is said to be a proton donor, or a "Lewis acid", as well as a Lewis base.

Lewis acids and Lewis bases are attracted to one another through a process called hydrogen-bonding. Water is perhaps the most familiar of hydrogen-bonding substances. Strong hydrogen bonding is responsible for some of water's interesting properties such as high melting and boiling temperatures. In hydrogen-bonding, one acidic proton is shared between two basic sites by mutual coulombic attraction of the proton. A review of the theoretical concepts associated with hydrogen bonding phenomenon is beyond the scope of this paper but an excellent review may be found elsewhere.<sup>8</sup>

As a result of hydrogen bonding, alcohols are attracted both to each other and to other molecules with Lewis base sites. In contrast, because ethers have no acidic hydrogen atoms, they show very little affinity for each other but will be attracted to Lewis acids, if present in solution. Further, both ether and alcohol based solvents will hydrogen-bond with Lewis acid sites that may be present in polymeric materials. This phenomenon leads to excess swelling and these concepts will be discussed further in the section on Corrosion Mechanisms.

Favored by an exothermic interaction energy, associated species of Lewis acids and bases are present in solution along with their parent species. For example, it has been shown that neat methanol may exist as a hydrogen-bonded cyclic tetramer.<sup>9</sup> Both the neat alcohol monomer and an associated species exist in equilibrium. The concentration of each species will depend on an equilibrium constant,  $k$ , which, in turn, depends on the association energy of the hydrogen-bonded species relative to the absolute temperature. An equilibrium reaction may be written to describe this type of solvent-solvent self-association as follows:



Hydrogen-bonded oligomeric species have unique chemical properties just as covalently-bonded monomeric species do. As such they are able to interact with materials in a similar manner as their disassociated parent species.<sup>10</sup> Insofar as chemical interaction with materials is concerned, some self-associating solvents like alcohols must be considered as multicomponent solvent blends of polar and non polar solvents even when they are pure. Methanol, existing as the monomeric species, is quite polar; whereas methanol existing as a tetramer, is considerably less polar. For this reason, self-associating solvents like dry methanol and chloroform are often powerful swelling agents for both polar and, surprisingly, nonpolar polymers alike. Small quantities of added water tends to break-up the tetramer methanol species and lower swelling has been observed for FKM-66 copolymer elastomers (myers and abu-isa) in hydrated methanol.

## 5.2 Solution Thermodynamics

Electrostatic interaction of chemical species in solution creates other interesting behavior in gasoline blended with ethers and alcohols. One must also consider the change in chemical potential of a solution as new species are introduced. The resulting activity of a solvent in solution has been shown to play an important role in determining equilibrium absorption of solvent by a material.

### 5.2.1. Ideal solutions

An “ideal solution” is defined as one in which the enthalpy of mixing the components is zero. In an ideal solution, the activity of each species is equal to its mole fraction in solution. The activity coefficients, defined as the activity of each component divided by its mole fraction, are therefore

equal to unity. In ideal solutions, most linear blending rules used for solution property correlations, such as Raoult's law for vapor pressure, are obeyed.

In general, gasoline which contains a blend of aliphatic, olefinic and aromatic hydrocarbons is considered to be an ideal solution. Addition of oxygenated hydrocarbons in the form of ethers does not appreciably change the ideal behavior of gasoline. Because an ether is a Lewis base, some minor interaction among the pi electrons of aromatic species and the ether is known. However, there is not enough chemical interaction in an ether blended gasoline to invalidate the ideal solution assumption for most applications. The activity coefficients of all components in reformulated gasoline are approximately equal to one.

**Figure 1** illustrates this ideal behavior. The activities of MTBE, toluene and iso-octane in model fuels containing various concentrations of MTBE are approximately equal to their mole fraction in solution.

The vapor phase composition may be easily computed from equations governing vapor-liquid equilibrium. The mole fraction  $x_i$ , the activity coefficient  $\gamma_i$ , and the vapor pressure  $P_i$  of each component in the liquid phase must be known. Assuming the vapor is an ideal gas, the equilibrium vapor composition  $y_i$  may be computed as follows:<sup>11</sup>

$$y_i = \frac{g_i x_i P_i}{\sum g_i x_i P_i}$$

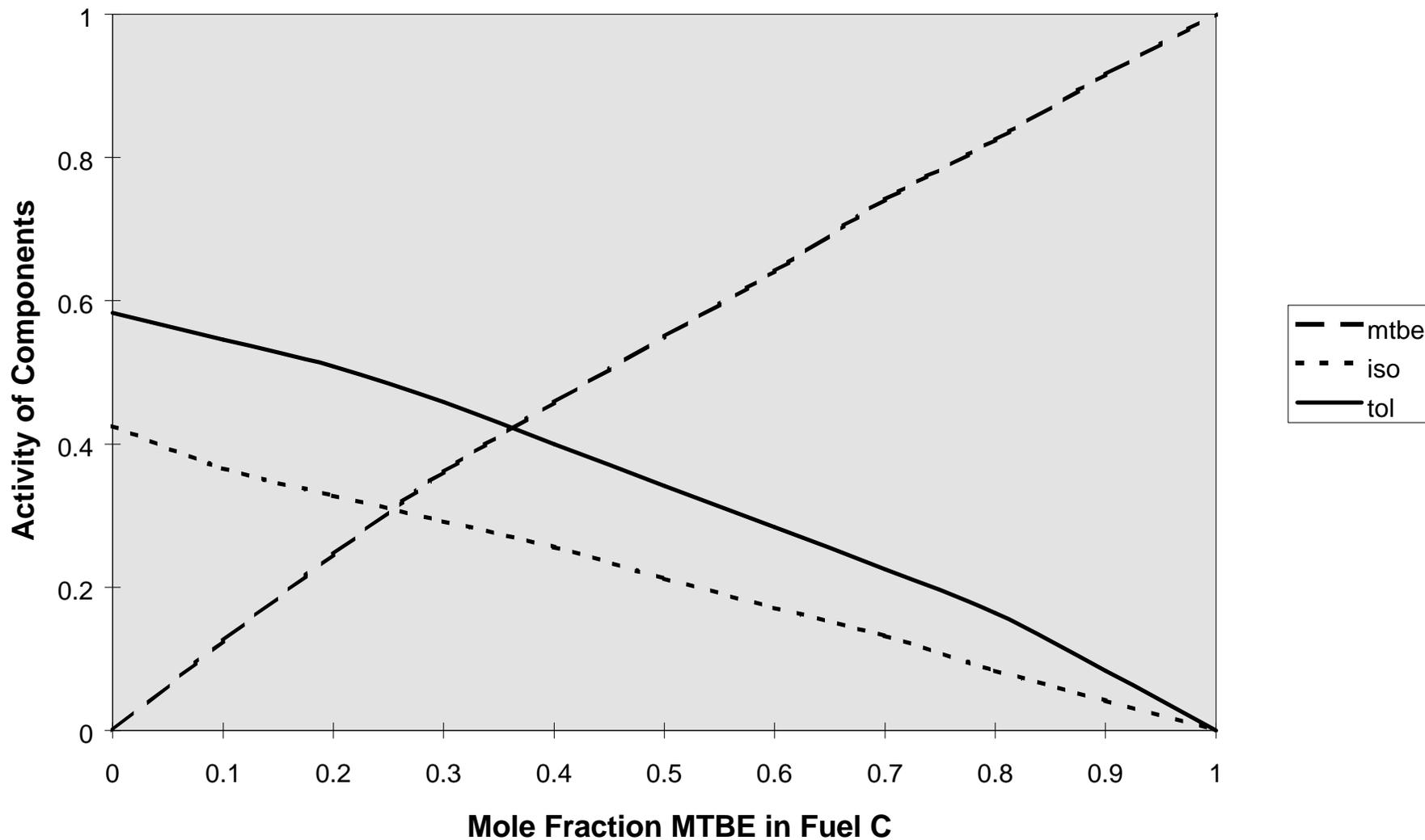
For ideal solutions, the activity coefficients are equal to one and the vapor phase composition scales linearly with the mole fraction of components in the liquid. Further, the molar volumes are approximately equal; thus, volume fractions are approximately equal to the mole fractions. This simple calculation is conducted for 15 percent by volume MTBE blend in ASTM Fuel C.

**Table 2** - Approximate compositions of vapor liquid equilibrium for a 15 percent by volume blend of MTBE in ASTM Fuel C.

Component	$x_i$	$a_i$	$P_i$	$a_i P_i$	$y_i$
Isooctane	0.425	0.425	1.7	0.723	0.390
Toluene	0.425	0.425	1.0	0.425	0.229
MTBE	0.150	0.150	4.7	0.705	0.380
<b>total</b>	1.000			1.853	0.999

It is observed in **Table 2** that the mole fraction of MTBE in the vapor phase,  $y_i$ , is about 2.5 times greater than its mole fraction in the liquid,  $x_i$ . This concentrating effect of the oxygenated

**Figure 1 Activity of MTBE, Toluene and Isooctane as a function of ether concentration in Fuel C**



component in the vapor phase is due to the elevated vapor pressure of MTBE relative to the other hydrocarbon constituents.

### 5.2.2. Non-ideal solutions

Both positive and negative deviations from ideal solution behavior are possible whenever polar interaction among species in solution occurs. Alcohol blended fuels exhibit positive deviations where the activity coefficients are much greater than one. This deviation is a direct result of the interaction that alcohol molecules have for each other. Driven by the entropy of dilution with non-polar gasoline, the heat of mixing is endothermic because the self-associating alcohol species are being dissociated.

**Figure 2** illustrates this non-ideal solution behavior. The activities of EtOH, toluene, and iso-octane are all considerably greater than their mole fraction in solution. Since the total pressure is the sum of component vapor pressures multiplied by the component activities, the vapor pressure of a blend of alcohol and gasoline is greater than the vapor pressure of the neat components.

Another practical implication of the high activity of alcohol in gasoline blends containing more than 10 percent alcohol is the tendency for phase separation. By definition, if the activity of any blend component equals one, then phase separation occurs. It is well known that, depending on the temperature and the aromatic content of the gasoline, addition of 0.5 percent by volume water to gasoline blends containing 10 percent EtOH or more will cause aqueous phase separation. Methanol blends are even more sensitive to water. Here, an alcohol molecule prefers to separate into an aqueous phase where it has an exothermic hydrogen-bonding interaction with water rather than remain in the hydrocarbon fuel where its heat of mixing is endothermic.

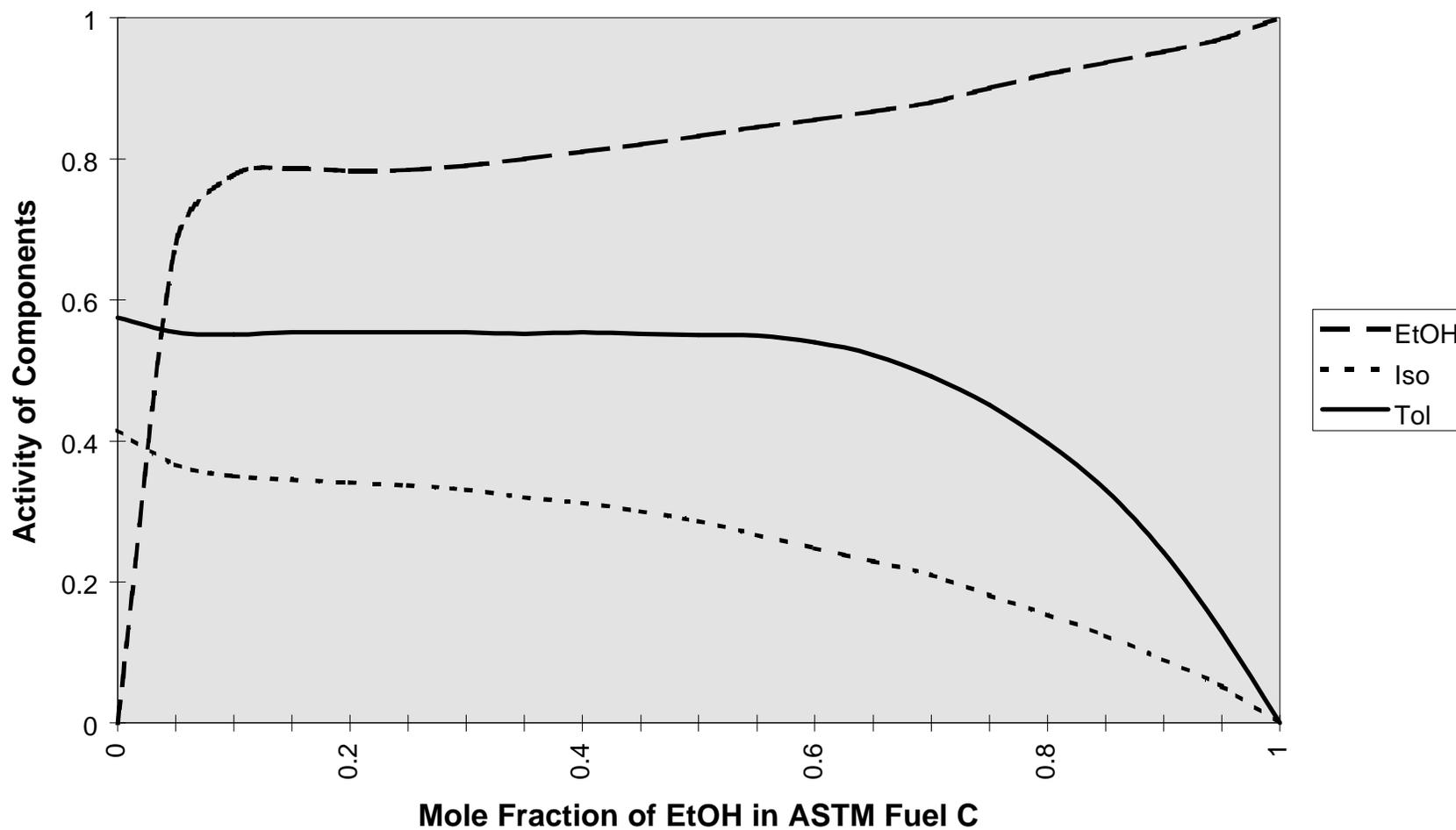
Now consider the vapor liquid equilibrium for MeOH blended fuels. For non ideal solutions, the activity coefficients are not equal to one and the vapor phase composition scales linearly with the activity of the components in the liquid. A further accounting is required for the difference in molar volumes among the species. Assuming again that the vapor phase is an ideal gas, the calculation is repeated for a 10 percent by volume MeOH blend in ASTM Fuel C.

**Table 3** - Approximate compositions of vapor liquid equilibrium for a 10 percent by volume blend of MeOH in ASTM Fuel C.

Component	$x_i$	$a_i$	$P_i$	$a_i P_i$	$y_i$
Isooctane	0.375	0.45	1.7	0.765	0.149
Toluene	0.375	0.45	1.0	0.450	0.088
MeOH	0.250	0.85	4.6	3.910	0.763
<b>total</b>	<b>1.000</b>			<b>5.125</b>	<b>1.000</b>

It is observed in **Table 3** that the mole fraction of MeOH in the vapor phase is about five times greater than its mole fraction in the liquid. This is due to its relatively high vapor pressure as well as its non ideal behavior in the hydrocarbon liquid. Furthermore, the vapor pressure of the

**Figure 2** Activity of EtOH, Toluene and Isooctane as a function of Alcohol Composition in Fuel C



blend is much greater than any of the neat constituents.<sup>12 13 14</sup> Similar non-ideal behavior is also observed for ethanol blends.

These phenomena, higher vapor pressure of the blend and also phase separation sensitivity, observed in gasolines blended with alcohol are indications that a greater driving force exists for alcohols to leave dilute solutions with gasoline than there is for ethers to leave reformulated gasoline. The relative magnitude of this driving force has further implications regarding compatibility and permeability issues for nonmetallic materials. These issues will be more fully discussed in the following sections.

## 6.0 Corrosion Mechanisms

### 6.1 Non-Metals

Non-metallic materials do not corrode by electrochemical processes as metals do. This is because nonmetals are dielectric materials which cannot conduct corrosion currents and most do not form stable ionic species. However, dimensional changes and mechanical property changes observed in nonmetallic materials are directly attributable to absorption of hydrocarbons and the resultant swelling and plasticization. These concepts will be discussed below.

Nonmetallic materials commonly found in a retail gasoline station may be classified into three categories: elastomers, thermoplastics, and thermosets.

An elastomer may be defined as a material which can be stretched beyond its yield point and yet its strain is largely recoverable upon relaxing the applied stress. This strain recovery property is usually obtained by mild cross-linking (three mole percent or less) or vulcanization of a rubbery gum. Elastomers are commonly used in flexible hose constructions, seals, gaskets and packing.

A thermoplastic is usually either a semi-crystalline or glassy amorphous material which, upon heating, will reversibly melt into a processable liquid. Thermoplastics are commonly used in flexible underground piping, sumps, vapor recovery tubing, etc.

A thermoset is usually a glassy material which is cured into a highly cross-linked network. Once vitrified, a thermoset cannot be melted and reprocessed like thermoplastics. Thermosets are commonly used in reinforced composites and are found as matrix materials for rigid piping and underground storage tanks (UST).

A brief theoretical description of swelling and permeation phenomena which occur in these classes of polymeric materials is presented in the following sections.

### 6.1.1. Equilibrium Swelling of Nonmetallic Materials by Solvents:

A critical performance factor for nonmetallic materials exposed to a mixed chemical environment is the degree of solvent absorption by the material at equilibrium. Swelling not only affects the physical dimensions of a part but the mechanical properties are affected as well.

Given an observation of elastomer swell in a pure solvent,  $v_{i,E}$ , Flory<sup>5</sup> suggested that the activity coefficient of a solvent absorbed in an elastomer,  $\Omega_{i,E}$ , may be estimated from a solvent-elastomer interaction parameter,  $\chi_{i,E}$ , and an elastic retraction constant,  $\epsilon$ , as follows:

$$\ln(\Omega_{i,E}) \cong v_{i,E} + \chi_{i,E} v_{i,E}^2 + \epsilon (v_{i,E}^{1/3} - v_{i,E}/2) \quad 2$$

The first term on the right hand side of **Equation 2** accounts for the dilution entropy of the solvent in the elastomer. The second term expresses the enthalpy of dilution. The last term expresses a contribution to chemical potential due to the elastic retraction energy in the material.

Although this theory was intended only for elastomers exposed to pure solvents, it provides a useful framework to qualitatively discuss the compatibility of many polymeric materials exposed to solvents. For example, the elastic retraction parameter is proportional to the number density of cross-links in the neat material. Since thermosets are cross-linked more than elastomers they typically swell less than elastomers in any given solvent.

More important is the role of the polymer-solvent interaction parameter,  $\chi_{i,E}$ . If this value is zero, then no interaction enthalpy exists and intermediate swelling is observed. This type of swelling is driven by entropy and opposed by elastic retraction energies. This case is typical of non-polar polymers exposed to conventional non-oxygenated gasoline.

If the polymer-solvent interaction parameter is positive, the resulting interaction is endothermic. Endothermic interaction implies that the polymer prefers interaction with itself rather than with the solvent molecules. The resulting solvent absorption will be very low because swelling is opposed by the heat of mixing as well as elastic retraction. This behavior is the basis for one strategy of obtaining fuel resistance: incorporate acid-base sites into the polymer backbone which, in turn, repel the non-polar solvent molecules in non-oxygenated gasoline. Most fluorocarbon elastomers, nitrile rubber and polychloroprene elastomers, for example, gain their resistance to gasoline in this way.

If the value of  $\chi_{i,E}$  is negative, then the enthalpy of mixing polymer and solvent is exothermic. Exothermic interaction implies that complementary attractive forces exist between Lewis acid and/or Lewis base sites on the polymer backbone and on the solvent molecule. In such cases, swelling will be relatively great because it is driven by the enthalpy and the entropy of mixing. This type of interaction may occur when polar polymers come into contact with polar oxygenated hydrocarbons.

The degree of solvent uptake in a material depends on both the activity of the solvent molecule in solution and the interaction parameter of the polymer-solvent pair. For the case of small

interaction parameters (i.e. aggressive solvents), a further simplification to Flory's model has been shown to be useful. The three component energy balance may be estimated by a series of partition coefficients. This simplification is valid provided that one partition coefficient is assigned for each species present in solution, associated or not. Therefore, the volume fraction of a mixed solvent absorbed in a material,  $C$ , is related to the product of the solvent activity in solution  $a_i$  and a partition coefficient. The partition coefficient, or solubility  $S$ , is the volume fraction of pure solvent absorbed at unit activity.

$$C_i = S_i a_i \quad 3$$

This expression for liquid partitioning into materials at equilibrium is analogous to Raoult's Law for vapor liquid equilibrium. The volume fraction of solvent in the elastomer, rather than the volume swell or weight gain, is a useful way to characterize the swelling power of ideal solutions. This utility for gasoline reformulated with MTBE has been shown on a theoretical as well as experimental basis. Thus, for substantial swelling to occur, both the solvent activity *and* the solubility must be greater than zero, and either one should be relatively large.

In a review article, Davidson<sup>15</sup> refers to the increased mole fraction of oxygenated hydrocarbons in the vapor phase relative to the liquid phase which was discussed in the previous section. He poses an interesting question regarding the potential for excess swelling and permeation in the vapor recovery system and in the head space of an UST as a result of this compositional difference.

The key to understanding this swelling problem is to recall that it is an activity gradient which drives swelling of polymeric materials by solvents, not necessarily concentration. From a theoretical standpoint, as long as the saturated vapor phase is in thermodynamic equilibrium with the liquid phase, the activities of each component in both phases are equal. Therefore the vapor cannot be a more aggressive swelling media than the liquid. However, under some conditions, the reverse may be true. If the components in the liquid phase are strongly self-associating, such as with alcohols, then the vapor phase may be a less aggressive swelling media. This is because the associated species does not partition into the vapor phase (being an ideal gas). If the associated species accounts for a significant contribution to the total swell, then the vapor phase may actually be a weaker swelling media.

If the enriched vapor phase is allowed to condense in some region away from the mother liquor, then there is a potential for increased swelling and permeation. Condensing a saturated vapor may occur by either increasing the pressure or decreasing the temperature. If temperature is decreased, then this may be a temporary condition. When reheated, the liquid will return to the vapor phase. If the pressure is increased, due to some processing step in the recovery system, then there is indeed increased potential for swelling and permeation of polymeric materials.

### **6.1.2. Unsteady Mass Flow of Solvents through Nonmetallic Membranes:**

The preceding discussion concerned equilibrium absorption of solvents by polymeric materials. The present section reviews the kinetics of mass transport into and through a polymer membrane. A study of the kinetics of absorption and permeation leads to an understanding of experimental parameters required to reach equilibrium absorption and steady state permeation. Later in this review, some literature permeation data will be interpreted using linear diffusion kinetics as summarized in the following discussion.

Most observers of gasoline permeation report total permeability and permeance (permeance is the permeability coefficient normalized by the thickness of the membrane) values for the fuel blend. However, desired information regarding the permeation rate of individual components, such as MTBE, are not reported. If applicable, mathematical analysis of permeation data from mixed solvents as a function of concentration may yield information regarding the individual contributions to the total mass flow. Therefore a discussion regarding the limitations of such an analysis is warranted. A more complete discussion of these issues may be found elsewhere.<sup>16</sup>

Linear diffusion kinetics are often referred to as Fick's Law or Case I diffusion. Case I diffusion in materials usually holds for vapors such as oxygen, helium, etc.; but, may not be valid for diffusion of solvent liquids. The key assumption in Case I diffusion is that the diffusion coefficient is independent of concentration of solvent in the material. Increasing diffusion coefficient with concentration is usually observed for strongly absorbing solvents. A convenient way to relax this constraint is to perform piecewise analysis whereby diffusion coefficients are valid over limited concentration ranges.

Case II diffusion is another useful theoretical construction where there is an abrupt transition between solvated material and unsolvated material. Here the diffusion coefficient is several orders of magnitude greater in the solvated material. The abrupt change in diffusion coefficient is often associated with a change in morphology in the host material such as glassy to rubbery phase transition. For example, Case II diffusion has been observed for strongly associating solvents, such as methanol, permeating glassy polymers, such as polymethylmethacrylate. Case II diffusion is the dominate mechanism for methanol permeation in fiberglass laminates.

As with swelling, activity gradients drive permeation as well. For permeation of vapors, the activity gradient is often expressed as a change in pressure on either side of a membrane. Henry's law is used to assign coefficients which describe the concentration of permeant in the membrane as a function of its partial pressure. However, pressure will have little if any effect on the activity of a liquid permeant. Therefore activity (not necessarily concentration) gradients are used to represent the driving force for mass transfer. **Equation 3** is used to describe the concentration, by volume fraction, of permeant as a function of its activity in solution. This is in contrast to those authors who choose to scale the driving force in terms of vapor pressure or concentration<sup>17</sup> expressed as mass per unit volume. The present approach utilizes different units in the diffusion equations but does not change the fundamental character of the analysis.

Using this scheme of scaling the permeation driving force in terms of activity, the permeation data of reformulated gasoline containing nearly ideal solutions of ethers is successfully modeled. Therefore an estimate of ether permeation rate from a blended fuel can be made. By contrast, a

large excess permeation is observed for non ideal fuel blends containing dilute alcohols. This excess permeation is related to the excess absorption observed for these systems. In this reviewer's opinion, current linear permeation theory is not able to account for this excess permeation and component contribution of alcohol permeation from gasohol cannot be estimated. If the mass flow of alcohol by permeation through materials is desired, then it must be measured directly and these measurements have not been reported.

Several very nice summaries are available which discuss the morphological parameters that affect permeation through materials.<sup>10-18</sup> Important considerations include: permeant concentration (activity), size and shape and flexibility of the permeant, temperature, permeant/polymer chemistry, thickness and crystallinity and void content in the membrane, polymer chain stiffness and interchain interaction. Plasticizer content, if any, is also very influential.<sup>19</sup>

### Linear Permeation Theory--Fick's Law

Whenever a flow pathway through a material is narrow relative to the mean free path of the solute, then molecular flow will govern. Molecular flow often occurs in vacuum systems and is the dominant mechanism of solvent permeation in polymers. It is a gradient in chemical activity,  $a_i$ , which drives diffusion into and permeation through a membrane. As discussed above, the activity of a liquid component  $a_i$  may or may not be equal to its volume fraction in solution. For ideal solutions, the concentration of a solvent is often substituted for activity.

The isothermal mass flow rate,  $Q_m$ , of a liquid solvent through a membrane is driven by the activity gradient according to the following equation:<sup>20</sup>

$$Q_m = \Gamma \left( \frac{RT}{M} \right)^{1/2} S_i \frac{(a_1 - a_2)}{L} \quad 4$$

where,  $\Gamma$  is a geometrical constant,  $R$  is the ideal gas constant, and  $T$  is the absolute temperature. The mass flow rate of liquid  $Q_m$  is inversely proportional to the molecular mass  $M$  of the solvent and the thickness  $L$  of the membrane. Since the solvent molecules do not contact one another, there is no viscous dissipation in molecular flow.

**Equation 4** is commonly simplified via dimensional analysis by introducing a lumped constant known as the permeability coefficient,  $P$ . Assume that the solvent activity is constant on one side and zero on the other side of a membrane. The steady state value of mass transport now becomes:

$$Q_i = P S_i a_i \frac{A}{L} \quad 5$$

where  $A$  is the cross sectional area of a membrane.  $S_i a_i$  is the concentration of solvent in the material at fractional activity. If a pure solvent is considered,  $a_i$  is unity.  $P$  will have unique values for any given polymer-solvent system and will vary with temperature. Once  $P$  is known,

the steady state mass flow of a diffusing solvent may be computed for a given solvent activity drop and membrane geometry.

Multiplying both sides of the above equation by thickness, **L**, utilizing **Equation 3**, and differentiating concentration with respect to distance through the membrane, the familiar form of Fick's first law for steady state permeation emerges:

$$P = -D * \frac{dC}{dx} \quad 6$$

Another material constant, diffusivity **D** is expressed as the square of the membrane thickness divided by a characteristic time. To examine the unsteady diffusion behavior, allow **C<sub>i</sub>** to represent the concentration of solvent as a function of time **t** and position **x** through the membrane thickness. Differentiating **Equation 6** with respect to time, the one-dimensional unsteady differential form of Fick's second law is expressed as follows:<sup>9</sup>

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad 7$$

To analyze unsteady diffusion behavior, Fick's second law may be solved for various cases of solvent diffusion in materials.

### Example 1: Absorption into an Immersed Slab (swelling):<sup>21</sup>

In the study of absorption kinetics, one requires an expression for the amount of solvent which has been absorbed into a material after a given time. Choose an infinite area slab geometry with a solvent free initial condition. Further choose boundary conditions for solvent concentration at both surfaces a constant value of **C<sub>1</sub>**. This condition implies that the slab is immersed in solvent. We wish to measure the amount of solvent absorbed as a function of time. Integration of **Equation 7** gives the concentration profile across the sample thickness as a function of time. This function is an infinite series as shown below.

$$C(x,t) = \left(\frac{4 C_0}{P}\right) \sum_{m=1}^{\infty} \frac{1}{(2m+1)} \sin \left[ (2m+1) \frac{\Pi x}{L} \right] \exp \left[ -D (2m+1)^2 \frac{\Pi^2 t}{L^2} \right] \quad 8$$

Integration of **Equation 8** with respect to position yields the total volume fraction absorbed, **V**, in a slab as a function of time. This function is also an infinite series where approximately five terms are required for an adequate estimate.

$$\frac{(V(t) - V_0)}{V_{\infty}} = 1 - \frac{8}{\Pi^2} \sum_{m=1}^{\infty} \frac{1}{(2m+1)} \exp \left[ - (2m+1)^2 \left(\frac{\Pi}{L}\right)^2 D t \right] \quad 9$$

Concentration values can be converted to mass or volume changes by using appropriate conversion factors. The unsteady absorption behavior of **Equation 9** is plotted schematically in **Figure 3**. This figure teaches that, for a slab of unit thickness, time  $t$  of magnitude  $0.28/D$  is required to achieve 95 percent of the equilibrium absorption. Diffusivity is known to range over several orders of magnitude among materials: elastomers generally exhibit the highest values while thermoset materials typically exhibit the lowest values. Therefore, experimental requirements for measuring absorption of solvents in different materials is expected to vary considerably. This means that a period of years may be necessary to achieve and measure steady state permeation in composite material. One way to accelerate the permeation measurement is to use thinner materials in experiment.

A useful simplification of **Equation 9** may be used for materials which exhibit a low diffusivity. At short immersion time, it may be simplified to the following approximation:

$$\frac{V(t)}{V_{\infty}} = 4 D^{1/2} \frac{t^{1/2}}{\pi^{1/2} L} \quad 10$$

Therefore a plot of  $V(t) / V_{\infty}$  versus  $t^{1/2} / L$  will yield a straight line in the initial absorption region. The slope of this line is proportional to  $D$ .

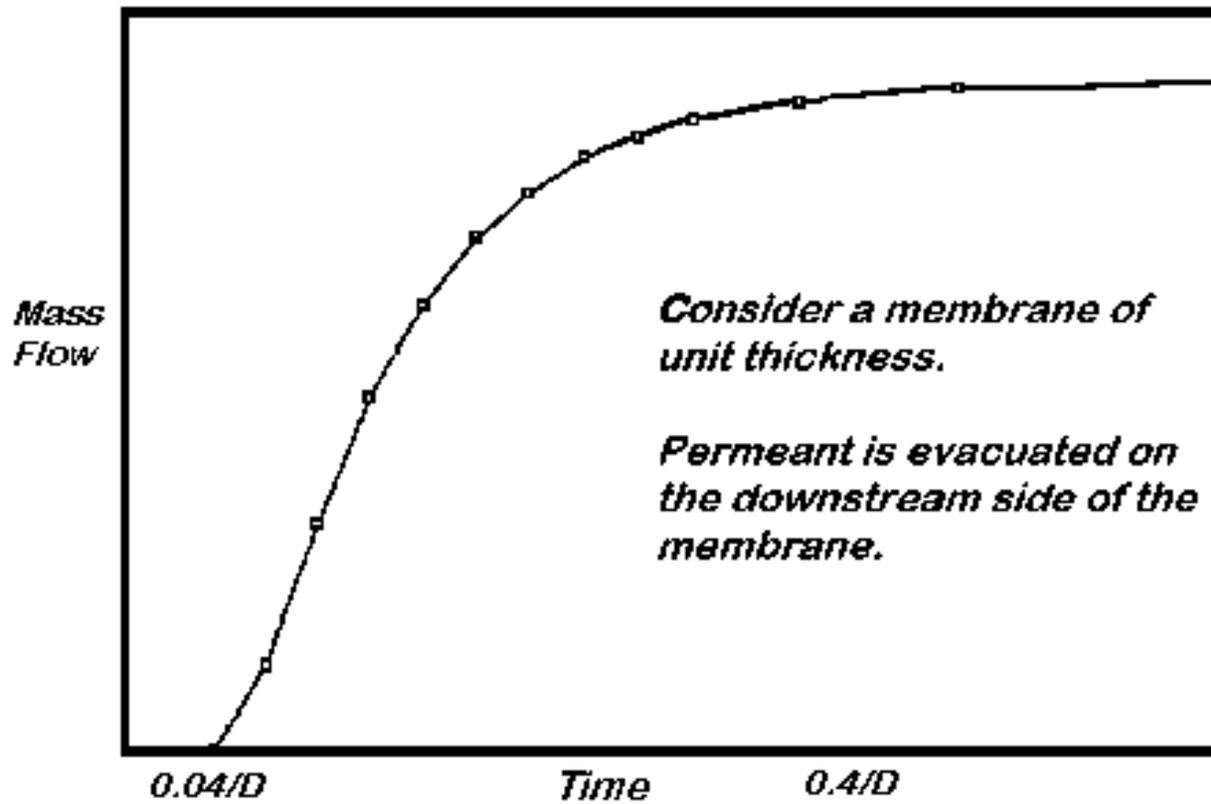
### **Example 2: Mass Flow through a Membrane (permeation):<sup>22</sup>**

If one is measuring the rate of flow of a solvent through a membrane, or permeation, there will be an interval of time from the moment the solvent comes into contact with the membrane until it emerges on the other side. Further time will be required to achieve steady state mass flux. For ease of analysis, choose an infinite slab geometry with a solvent free initial condition. Further choose boundary conditions for solvent concentration at the inside surface as a constant value of  $C_1$  and the concentration of solvent at the outside surface as a constant value of zero. The latter boundary condition implies that mass transport is diffusion limited or, equivalently, the solvent permeates the external environment much faster than the membrane. As such, accumulation of permeant in a boundary volume located on the outside surface of the membrane is negligible.

As measured at the outside surface, the total mass flow through the membrane increases with time to a steady state value. The solution of **Equation 5** under these conditions is also an infinite series where approximately five terms are required for an adequate estimate.

$$Q_m = D S a_i \frac{A}{L} \left[ 1 + 2 \sum_{n=0}^{\infty} \cos(n\pi) \cdot \exp\left(-\left(\frac{n\pi}{L}\right)^2 D t\right) \right] \quad 11$$

**Figure 3** Schematic representation of unsteady mass flow by Case 1  
diffusion of a permeant through a membrane



As the concentration gradient reaches a steady state value, the mass flow rate through a membrane is constant and **Equation 11** reduces to **Equation 5**. The interested reader may also note that **Equation 11** is actually the derivative of a more common expression used to describe permeation through a membrane where the permeant concentration is allowed to build-up on the downstream surface. **Equation 11** is valid for the present case where the permeant is continually removed from the outer surface.

**Figure 3** teaches that, for a membrane of unit thickness, an onset time of approximately  $(0.04/D)$  is required to measure the first one percent of the steady state mass flow of molecules which permeate through a membrane. About an order of magnitude more than the onset time is required to measure steady-state mass flux. Diffusivity is known to range over several orders of magnitude among polymers: elastomers generally exhibit the highest values while thermoset materials typically exhibit the lowest values. Therefore, experimental requirements for measuring permeability in these different materials is expected to vary considerably.

In summary, mass flow by permeation is proportional to the product of diffusivity, solubility and the activity of a solvent molecule. The diffusivity depends upon the inverse square root of the molecular mass of the diffusing solvent whereas the solubility depends upon a binary interaction parameter that is related to the enthalpy of mixing of polymer and solvent. Therefore a high permeability may be observed with either small, volatile solvents or with solvents that strongly associate with the matrix material or both.

### 6.1.3 Plasticization and Extraction

Diffusion of solvents in and through polymers is generally accompanied by a change in properties of the material. In addition to the change in physical dimensions associated with swelling, mechanical properties such as strength and stiffness are usually affected. As little as 20 percent volume swell can reduce physical properties such as hardness, strength, and tear resistance of an elastomer by 60 percent.<sup>23</sup> Twenty percent by volume swelling is generally considered a conservative upper limit for solvent absorption by an elastomer in a sealing application.<sup>24</sup> Solvent absorption is also of critical importance to thermoplastic and thermoset materials. Although these materials typically absorb much less solvent, substantial changes in mechanical properties and a reduction of upper-use temperature are also observed.

#### Underground Storage Tank Membranes:

Perhaps the most critical application where plasticization of a material by solvent ingress is important to consider is the underground storage tank (UST). Since an UST is buried, it will be subjected to combined compressive loads from the soil, the water table and the live loading. To resist global buckling, composite UST's are equipped with circumferential stiffening rings.<sup>25</sup> As such, UST design incorporates large factors of safety against global buckling. The limiting design criteria for UST's is local elastic buckling of the membrane between the ribs.

Buckling formulas for cylinders under external loading show the importance of the stiffness of the membrane, E. If an *unsupported* thin-walled tube containing stiffening rings is subjected to external pressure, then the formula for critical buckling load, P<sub>c</sub>, is proportional to the stiffness of the membrane according to the following form.<sup>26 27</sup>

$$P_c = 2Et \sqrt{D(n^2-1)(1+k)} + 8EI \left[ \frac{n^2 - 1 + 2n^2 - 1 - nh_1}{(1+k)D^3(1-nh_1nh)} \right]$$

## 12

where “t” and “D” are the thickness of the membrane and the diameter of the tube, “L” is the distance between stiffening rings, “ν” is Poisson’s ratio of the material and “k” is a dimensional constant equal to 2nL/πD. Notice that the only material property of consequence (other than ν) is the stiffness of the material “E.” Strength of the material is unimportant to buckling analysis. Thus any drop in membrane stiffness will result in the same percentage drop in the local buckling resistance of the shell according to this equation.

If the cylinder is buried, additional support may be afforded by the soil. A modified Luscher formula has been proposed<sup>28</sup> to describe the local buckling resistance of a ribbed cylinder under uniform soil support. This empirical function is written as follows:

$$FS * P_c = (32R_w B' E' E / D^3)^{1/2} \tag{13}$$

Where “E” is the soil modulus, “B” is Luscher’s coefficient of elastic support and “R<sub>w</sub>” is an empirical constant. “FS” is a safety factor. In **Equation 13**, the soil is assumed to contribute significantly to the local buckling resistance of the tank. Because of uniform soil support, any decrease in laminate stiffness has a square root effect on the critical buckling load of the laminate.

It is for this reason, that fiberglass UST vendors emphasize the importance of good installation practices.<sup>29</sup> Well compacted back-fill is required to provide maximum soil stiffness and uniform soil support of the membrane. This is especially important because deformations associated with localized buckling are much smaller than those associated with global buckling. If uniform, compacted soil is not provided, either by installation or service considerations, then the behavior of the critical buckling load with laminate stiffness may actually lie somewhere in between the functions described empirically by **Equations 12 and 13**.

Thus, for sound design, a safety factor in **Equation 13** is utilized. The safety factor is proposed to be 2.5 and it incorporates at least five elements including, creep, environmental effects, as well as other uncertainties such as soil support variations. The allowance for reduction of stiffness due to plasticization by environmental exposure is about 12 percent. This is presumably based upon Owens Corning’s experience with plasticization of isophthalic polyester laminates by gasoline and water environments. After more than ten years exposure, the laminate has been shown to retain more than 80 percent of its original stiffness.<sup>30</sup> Since (1/0.8)<sup>1/2</sup> is about 1.12, an allowance of 12 percent modulus drop in the composite is allowed in this formulation.

### Extraction of Plasticizers:

The inverse phenomenon of plasticization by solvent ingress is the migration of plasticizers and other additives out of polymers. Additives such as antioxidants, heat stabilizers, processing aids and plasticizers, etc. are commonly added to polymeric materials in order to achieve a certain property set. These additives are generally not covalently bonded to the polymer and are able to migrate. If a material containing additives comes in contact with a solvent, the additives may be extracted by the solvent.<sup>31 32 33 34</sup> If the solvent is not refreshed, the degree of extraction will depend on a partition coefficient for the solvent-polymer pair. If the solvent is refreshed, plasticizer extraction can be complete.

Extractable plasticizers are generally low molecular weight phthalate esters and are most commonly used in elastomers such as NBR and flexible thermoplastics such as PVC and PA.<sup>35</sup> They are, however, much higher molecular weight than the constituents in oxygenated gasoline. Interestingly, no firm relationship has been established linking the molecular weight of the plasticizer to its rate of permeation.

Often, plasticizer extraction is also accompanied by solvent swelling and the magnitude of these phenomena will mask each other. Often the material will swell through a maximum value then begin to shrink as the plasticizer leaves the host material. This has been described as a solvent exchange process. Therefore the effects of plasticizer extraction may not be observed until the polymer is removed from the solvent allowed dry-out for several hours or days.

Extraction of plasticizers will lead to significant change in properties such as: shrinkage, increasing the brittle-ductile transition temperature of materials. Shrinkage of seal materials can compromise their sealing behavior. MTBE is thought to be capable of extracting solid fillers, such as titanium dioxide as well.<sup>36</sup>

### **6.1.4 Environmental Stress Cracking (ESC)**

Environmental Stress Cracking (ESC) is a term commonly used to describe the combined influence of the thermal-chemical environment and the applied load on crack initiation and propagation mechanisms.

Increasing crystallinity and molecular orientation and decreasing molecular weight of polymers has a tendency to promote ESC.<sup>37</sup> Thus, in some polymer formulations, plasticizers are often added to improve their flexibility and toughness especially at low temperatures. Extraction of these plasticizers by solvent exposure can lead to embrittlement especially at lower temperatures. Rupture of embrittled materials is a form of ESC.

On the other hand, unsteady migration of solvents into polymers will lead to swelling of the surface layers more than the inner layer. In this case, the surface layers are put into compression which is balanced by tensile loads in the non swelled inner layers. If the applied stresses, from differential swelling, external loading or residual stress, is greater than the breaking stress, ESC will occur. This effect may be more pronounced in glassy thermoplastics and thermosets where diffusion into the polymer substrate is more likely to be described by Case II.

Another form of ESC, called explosive decompression, occurs when vapors are condensed inside polymers at high pressure. Rapid release of pressure causes expansion of these vapors. If the vapor pressure is greater than the strength of the material, blistering will occur. Although this type of failure mechanism is common for elastomers, operating pressures at retail gasoline stations and distribution terminals are not high enough to cause this type of failure.

It should be mentioned that ESC is not discussed in the literature as an important failure mechanism for materials exposed to oxygenated fuel environments. Therefore ESC will not be discussed further.

## **Thermal Effects**

### **Effect of Temperature on Swelling Behavior**

As indicated above, equilibrium swelling of materials by mixed solvents is determined by the product of a partition coefficient and the activity of the swelling species. Therefore, the swelling behavior will depend on the nature of solvent interaction with other solvent species and with the polymer.

It has been suggested (imbazano) that increasing temperature increases permeability because both the diffusivity and solubility increase with temperature. If there are no interactions among polymer and solvent molecules, this is expected to be true.

If there are exothermic interactions among polymer and/or solvent molecules, then increasing temperature will tend to shift the equilibrium away from formation associated species in favor of the non-associated species. The resulting swelling behavior with temperature will depend on the relative magnitude of the partition coefficients. For example, if high swelling observed at ambient temperature is a result of strong partitioning of associated species, then increasing temperature will tend to dissociate these species and the observed swell will decrease. This phenomenon has been observed for the swelling of fluoroelastomers in MeOH. On the other hand, if low swelling observed at ambient temperature is a result of strong interaction of the polymer with itself, then increasing temperature will tend to break these associations and swelling of the observed swell will increase as indicated above.

### **Effect of Temperature on Permeation**

Permeation of solvents through polymers has been shown to be a thermally activated process.<sup>38</sup> Therefore an Arrhenius form may be adopted to correlate the observed mass flow increase with temperature as suggested below:

$$\frac{Q_T}{Q_{T_0}} = \exp\left\{ E/R \left( \frac{1}{T} - \frac{1}{T_0} \right) \right\} \quad 14$$

where  $E$  is a lumped constant. In essence,  $E$  is the sum of an activation energy for viscous flow and a binary interaction parameter associated with solvent absorption as discussed above. Therefore, effect of temperature on permeation rate will depend on the relative changes in these two energies. However it is common to observe permeability increase with temperature, especially when no interaction exists among polymer and solvent species.

For example, consider methane permeating through PTFE near ambient temperature.<sup>39</sup> The value of  $E/R$  is observed to be approximately 3300 °K. This value implies that permeation rate approximately doubles over a 17 °C increase in temperature.

A similar result was observed for the permeation of oxygenated fuels in elastomers. The permeation rates doubled every 10 to 15 °C.<sup>40</sup>

### **Effect of Temperature on Elastomeric Seals**

At low temperature, elastomers undergo a physical transition called the glass transition temperature. Below its glass transition temperature, an elastomer behaves more like a rigid plastic. An elastomer begins to lose its ability to form a seal at temperatures slightly above its glass transition temperature. This low temperature limit for sealing is often reported in a standard test as TR-10 temperature. TR-10 is the temperature below which an elastomer exhibits less than ten percent retraction.

Most elastomers are formulated to have TR-10 values below -30 °C. However, more recent compounds have been formulated for increased fluid resistance. For example, elastomers have high fluorine content, in the case of fluoroelastomers, or high acrylonitrile content, in the case of NBRs. Increased fluid resistance often compromises low temperature sealing characteristics.<sup>41</sup> Sometimes plasticizers are added to highly fluid resistant elastomers to retain the low temperature sealing properties.

### **Pressure Effects**

As mentioned above, the operating pressures are very low. Also, all solvents are condensed liquids over the applicable range of operating temperatures and pressures. As such, the total pressure will not have any appreciable influence on activity coefficients of the solvents. Thus, pressure is not expected to exhibit an observable effect on the absorption and mass flow of solvents in and through polymers.

### **Effect of Time**

As mentioned above, the diffusion coefficient is observed to vary over several orders of magnitude. Therefore the time required to reach equilibrium absorption or steady state permeation is also expected to depend strongly on the type of material in question and the

thickness of the part. For example, fluorocarbon based elastomers<sup>42 43</sup> and thermoplastics are known to require much more time to reach equilibrium absorption than hydrocarbon based polymers require. One study reported 12 months were required for the swelling and extraction phenomenon to stabilize in some elastomers.<sup>44</sup> As a result, the diffusivity and permeability of fluorocarbon based materials to solvents is correspondingly lower.

### **6.1.5 Testing Standards for Nonmetallic Materials**

#### **Fuel Stability**

Two ASTM procedures test gasoline for gums and oxidative stability.<sup>45 46</sup> The purpose of these tests are to determine the quantity of oxidation products formed in a sample and or the propensity of a fuel to oxidize and form these gums. The results of these tests can be used to indicate the storage stability, due to oxidation, of the fuels.

#### **Compatibility Testing**

ASTM<sup>47</sup> defines non-oxygenated standard reference fuels for compatibility testing. Although gasoline is a complex blend of aliphatic, olefinic and aromatic hydrocarbons, test fuels are bicomponent mixtures of isooctane and toluene. Fuels A, B, C, D, and E contain a 0, 30, 50, 60 and 100 percent by volume toluene, respectively in isooctane. Since modern unleaded gasoline usually contains between 30 and 50 percent by volume aromatics, most observers use Fuel C in their testing. Aromatic hydrocarbons are known to be more aggressive than aliphatic or olefinic hydrocarbons, so the use of Fuel C is thought to be a representative but conservative choice.

Standard methanol fuels are defined by SAE.<sup>48</sup> Reference Fuel C is the base fuel to which various concentrations of reagent grade methanol is added. For elastomers the abbreviations CM0, CM15, CM30, CM50, CM85 refer to zero to 85 percent methanol in the reference fuel. For plastics and metals, aggressive methanol is defined according to the following recipe: add 0.005g NaCl, 0.05ml formic acid, and 0.1% H<sub>2</sub>O (metals only) per liter of methanol. This aggressive methanol mixture is added to Fuel C in the above proportions. For auto-oxidized test fuel: 6.8ml of 70% t-butyl hydroperoxide per liter of fuel C is added along with 0.01mg cuprous sulfate per liter. The standard recommends performing tests in all fuels to determine the worst case. Then do additional testing in the worst case fuel. Similar procedures can be established for other oxygenates such as ethers and other alcohols.

ASTM provides applicable standards for testing the resistance of rubber<sup>49</sup> and plastic<sup>50</sup> to chemical reagents. Little guidance is given on establishing equilibrium conditions, however an interesting discussion is given in the latter standard on the combined action of stress and chemical exposure.

ASTM C 581 is a general standard for chemical resistance testing of composite materials.<sup>51</sup> Immerse samples for 30, 60, 90, 180 and 365 days in a media at a specified temperature. Note color, weight, thickness. Measure change in these properties and also changes in flexural strength and stiffness. Often the rate of change of properties with time is more significant than the absolute value of the property. It is desirable to obtain constant value stiffness, strength,

dimensions and weight after a period of time. This establishes that equilibrium conditions have been established. Appearance: absence of cracks, crazes, loss of gloss, blistering etching, pitting, softening. Discoloration of immersion media or accumulation of sediment. The sample should appear absent of cracks, crazes, loss of gloss, blistering etching, pitting, softening. Discoloration of immersion media or accumulation of sediment is also undesirable.

ASTM D 4021 is a standard which specifically addresses glass-fiber reinforced polyester USTs.<sup>52</sup> It suggests chemical resistance testing which is representative of the fluids to be contained inside the tank, which include: ASTM Reference Fuel C, commercial unleaded premium gasoline, unleaded gasoline, ethyl alcohol 90 percent to 10 percent by volume blended gasohol, and No. 2 fuel oil. Recognizing that water could be inside the tank, testing with distilled water, sodium carbonate-sodium bicarbonate solution at pH=10, potassium biphthalate buffer at pH=4 are also recommended. Further testing with the actual liquid to be contained in the tank, if different than any of the above, is recommended. Interestingly, other than the prior requirement, there is no specific requirement for MTBE compatibility testing as there is for alcohols. Testing conditions: ambient temperature, immersion times of 1, 3, 6, 12 months are recommended. Accelerated testing at 100 °F is suggested, immersion times of 1, 3, and 6 months or longer are required at this temperature if the data are inconclusive. Evaluation of the materials after exposure by conducting mechanical property testing consisting of flexural strength and stiffness, hardness, as well as a visual inspection of the sample and media. Plot property retention versus time on a log-log plot and extrapolate to 100,000 hours (11.4 years). No guidance is given regarding minimum property retention.

UL-1316 is a similar standard for fiberglass USTs which is more often cited than the above ASTM standard.<sup>53</sup> Like the ASTM standard, coupons are immersed in liquids for 30, 90, and 180 days at 100 °F. They are then subjected to flex strength and stiffness testing as well as izod impact toughness testing. There are two types of fluids to be tested. Type A fluids include: leaded and unleaded gasoline, reference Fuel C, No. 2 and No. 6 fuel oils, saturated sodium chloride, and sulfuric acid. Additional liquids for alcohol products include Reference Fuel C with 10, 15, 30, 50, 70, and 100 percent by volume ethanol, and 15, 50, and 100 percent by volume methanol. Greater than 50 percent property retention is required for coupons exposed to these media. Type B fluids include: toluene, deionized water, five percent hydrochloric acid, five percent nitric acid, sodium carbonate-bicarbonate buffer at pH=10, sodium hydroxide at pH=12. Greater than 30 percent property retention is required for coupons exposed to these media. As with the above ASTM standard, there is no specific requirement of MTBE compatibility testing. UL-971 discusses requirements for nonmetallic underground piping.<sup>54</sup> This standard requires compatibility testing similar to the tank standards as well as permeability testing. With regard to chemical compatibility, immersion testing of coupons for 30, 90, 180, and 270 days at 100 °F is required. Measure retention of crush strength, tensile strength, and adhesive shear strength. Here, four types of fluids are specified for testing: Type A and Type B, and internal and external fluids. Greater than 50 percent retention of properties is required for type A fluids and greater than 30 percent retention of properties is required for type B fluids. This is required for both primary and secondary piping. Type A internal fluids include: leaded and unleaded gasoline, reference Fuel C, No. 2 and No. 6 fuel oils. Additional liquids for alcohol products include Fuel C with 10, 15, 30, 50 percent by volume ethanol, as well as 15 and 50 percent by volume methanol. Type A external

fluids include: sulfuric acid at pH=3, and saturated sodium chloride. The type B internal fluid is toluene. Type B external fluids include: deionized water, one percent hydrochloric acid, one percent nitric acid, sodium carbonate-bicarbonate buffer at pH=10, and sodium hydroxide at pH=12.

UL-567 discusses requirements for construction and performance of piping connectors.<sup>55</sup> Leakage tests are to be conducted at 1.5 times the rated pressure and at the minimum bending radius of the connector. It also specifies swelling and extractable limits for rubber parts (seals) in contact with the media. After 70 hours at ambient temperature, the volume swell shall not exceed 25 percent (or 40 percent in reference Fuel C and its blends). Extractables are to be limited to ten percent by weight and not more than a one percent shrinkage of the material. If these dimensional stability limits are exceeded, additional proof testing is required. To preclude galvanic action, this standard prohibits direct metal-to-metal contact between copper, or a copper alloy, and aluminum.

### **Permeability Testing**

Several testing standards have been established for testing nonmetallic materials permeability and compatibility in oxygenated fuel blends.

In addition to the above chemical compatibility testing, permeability tests are required for underground piping in UL-971. This test is performed by taking 18 inches of the smallest diameter pipe, filling with liquid and then sealing it. Samples are weighed every month for 180 days. Permeance is computed every month and the maximum weight loss rate allowed is 4 g/m<sup>2</sup>/day (0.013 oz/ft<sup>2</sup>/day) for the primary conductor and 24 g/m<sup>2</sup>/day on the secondary pipe. Area basis is the inside area of the pipe. This permeation requirement is a standard based upon safety, not an environmental standard. Permeation test liquids are: unleaded premium gasoline, unleaded regular gasoline, Reference Fuel C and No. 2 fuel oil and toluene. For alcohol fuels, 100 percent methanol and ethanol as well as blends containing 10, 30, and 50 percent by volume blends of the same with Fuel C. Additionally, 10 and 30 percent by volume blends are required for ethanol. Again no specific requirement for permeability testing in MTBE solutions is mentioned.

ASTM standards for permeation of plastics are intended for the food packaging industry and, as such, focus on oxygen<sup>56</sup> and other gas<sup>57</sup> transport rather than hydrocarbons. However these standards do stress the requirement to achieve steady state permeation.

A procedure for determining permeation resistance of elastomeric tubing is SAE J1737.<sup>58</sup> This procedure specifies a reservoir to supply gasoline to the hose. In this way, speciation caused by rapid permeation of dilute components present in the fuel is thought to be minimized. The units of mass flow are expressed in terms of gm/m<sup>2</sup>/day. This number is called Permeance. Permeance multiplied by the thickness of the membrane is called the permeability coefficient (example: gm\*mm/m<sup>2</sup>/day).

SAE J2260 sets minimum requirements for multilayer tubing for gasoline and alcohol blends. Permeability performance is measured at 60 °C.<sup>59</sup> **Table 4** summarizes the performance criteria as specified in the standard:

**Table 4** - Performance ranking system for elastomeric hoses based upon permeability to fuels (from SAE J2260).

Performance Category Number	Permeation Range (gm/m <sup>2</sup> /day)	Suggested Time for Testing (hr)
1	0-25	over 1000
2	25-50	1000
3	50-100	800
4	100-200	600
5	200-400	500
6	over 400	400

SAE J30<sup>60</sup> specifies wall thickness standards for flexible hoses as follows: wall thickness for hoses is as follows: up to 1/4 nominal, 0.76mm (0.030"); greater than 1/4 to 7/8 nominal, 1.02 mm (0.04"); greater than 7/8, 1.27 mm (0.050"). For a permeation test, it specifies the reservoir method where the length of the hose is 300 mm. The reservoir size equals 460 to 490 ml but only filled to 300 ml. The assembly is weighed every day for an unspecified period. Agitate the fuel daily. Calculate gm/m<sup>2</sup>/24hr on a daily basis. Also a cold flexibility test is given as follows: Samples are conditioned at -40°C for five hours. Flex the hose through 180 degrees bend at a radius equal to ten times the hose diameter. Flexing cycles are to occur within four seconds and the hose must not show any signs of cracking. A proof pressure of 99 psi may be applied. Also, the composition of hoses are described as follows: R7 is as NBR/PVC blend liner with a CSPE cover, R8 is a CO liner with a CO cover and R9 is an FKM lined hose with an NBR/PVC blend outer cover.

## 6.2 Metals

Many general texts can be consulted regarding the phenomenon of metal corrosion by aggressive media.<sup>61 62</sup> A concise set of terminology relating to corrosion and corrosion testing is found in the ASTM standards literature<sup>63</sup> along with a recommended practice for statistical analysis of corrosion data.<sup>64</sup>

It is not the intent of the following discussion to teach corrosion concepts; however, a review of some fundamental aspects of the problem, as is associated with oxygenated fuels, is desired. In general, corrosion can manifest as general corrosion or pitting. General corrosion is a uniform attack of the surface and corrosion rate is expressed in terms of loss of thickness or weight per unit of time. Lifetime estimates may be made based upon a corrosion allowance. Pitting corrosion is localized attack appearing as a series of holes in the surface. Under certain conditions, pitting corrosion can bore holes completely through a metal part and cause pinhole leaks. Both types of corrosion can occur simultaneously and the processes which govern pitting corrosion versus general corrosion are very complex.

### 6.2.2 Dry Corrosion

The corrosive behavior of alcohols has been divided into two major types: dry corrosion and wet corrosion.<sup>65</sup> Dry corrosion refers to the corrosion of metals in the presence of very dry fuel blends. Dry alcohols can react with lead, magnesium and certain aluminum alloys with the formation of alkoxide or alcoholate corrosion products. The alkoxide reaction in the absence of oxygen was described above. The cathodic reduction of ethanol (and presumably methanol) in the presence of oxygen and a metal has also been proposed as follows:<sup>66</sup>



The two electrons would presumably be supplied by the anodic dissolution of a metal. Aluminum alkoxides have been proposed to decompose to Aluminum oxides and water by the following mechanism:



If this mechanism is correct, it implies that ethanol blended gasoline cannot remain dry when in contact with aluminum and other active metals. Water is a corrosion product and therefore hydrated alcohol will result.

Hydrated alcohol contains water levels in the parts per million range. For example, as little as 0.1 to 0.2 percent water can effectively passivate aluminum and ferritic stainless steels and inhibit dry corrosion of materials in neat alcohols. A threshold minimum concentration of water of about 0.25 percent by weight of methanol is required to suppress the corrosion of magnesium by methanol blends.<sup>67</sup>

In addition to chemical reaction, water can get into gasoline from other sources such as absorption from humid air,<sup>68</sup> condensation, etc. Whenever water is present in gasohol, the electrical conductivity of the gasohol solution increases to the extent that new corrosion mechanisms are enabled. For example, mechanisms such as electrolytic and galvanic corrosion have been observed. Galvanic and electrolytic corrosion processes described below are not observed in gasoline which does not contain alcohol. This is because addition of ethers to gasoline does not increase the solubility of water and therefore the conductivity of the hydrocarbon phase.

### 6.2.2 Galvanic Corrosion

Galvanic corrosion occurs when two dissimilar metals are in electrical contact. When an electrolyte solution wets this junction, an electrical circuit is completed. Whenever the conductivity of the fuel exceeds 40 (Naegeli) to 70<sup>69</sup> microseimens per meter, the electrolyte is of sufficient strength to support galvanic attack as well as electrolytic attack (described below). In a sense, a battery is formed where the more active material is corroded at the cathode. In turn, the

less active metal acts as an anode and is protected from corrosion. Galvanic corrosion may occur in the absence of other corrodants such as oxygen.

Galvanic corrosion is of particular concern for existing underground metallic components and for components in the dispenser.<sup>1</sup> Many of these systems were designed only for low conductivity fluids and, as such, galvanic attack was not considered as a failure mechanism. Therefore, there may be many dissimilar metal junctions in existing facilities which may be subject to galvanic attack when storing and dispensing alcohol blended fuels. Of particular concern are bimetallic junctions between aluminum and brass, because there is a large electrochemical potential driving the corrosion of aluminum.<sup>70</sup>

### 6.2.3 Electrolytic Corrosion

Electrolytic corrosion is dissolution of metal by an impressed electrical current. If an electric potential of greater than approximately one volt exists, stray electric currents can cause corrosion of metal at a very rapid rate. This process will be limited only by the conductivity of the media. Stray electrical currents of up to 40 microamperes have been observed between the fuel pump and the fuel tank of automobiles.<sup>71</sup>

Conventional fuels are not conductive and therefore electrolytic corrosion may not have been a design consideration for some retail gasoline tanks and dispensing equipment. Electrolytic corrosion may be avoided by proper grounding of submerged components such as electric pumps and level gauges.

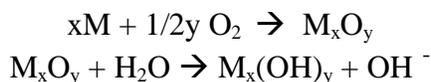
### 6.2.4 Wet Corrosion

Depending upon the aromatic content of the fuel, the temperature, the presence of alcohol, and perhaps other factors, water content above 0.1 (MeOH blends) to 0.5 (EtOH blends) percent in gasohol will cause phase separation of the fuel blend.<sup>72</sup> Water is essentially insoluble in gasoline which does not contain alcohol, and phase separation occurs at very low levels of water. Many UST's have an aqueous layer in the bottom of the tank. Wet corrosion occurs in this lower aqueous phase.

Due to a favorable exothermic interaction with water, the alcohol preferentially partitions into the aqueous phase and depletes the alcohol content in the gasoline. The aqueous phase becomes saturated with alcohol and ionic contaminants. The hydrocarbon phase in equilibrium with the aqueous phase is hydrated gasohol. In contrast, ethers are soluble in water only to approximately five percent at ambient temperature<sup>73</sup> and non-polar hydrocarbons are essentially insoluble in water.

In the lower, aqueous phase, reactions involving oxygen are more pronounced because the solubility of oxygen is greater in the aqueous phase than in the hydrocarbon phase. Familiar corrosion reactions may be written schematically in the following manner ("x" and "y" refer to unspecified molar quantities):





These corrosion reactions are possible in the upper, hydrated alcohol hydrocarbon phase because the presence of alcohols and water greatly increases the conductivity of the hydrocarbon phase.

The rate of these corrosion reactions is affected by the presence of ionic contaminants such as salts and other corrosion products. Ionic species increase the conductivity of the media thereby speeding the electrochemical processes at the anode and the cathode. They also may play a direct role in defining the corrosion mechanisms as is discussed below.

### **6.2.5 Multiphase Corrosion**

Multiphase corrosion refers to the fact that a material exposed to both wet and dry conditions are exposed to all of the above corrosion mechanisms.

### **6.2.6 Wear**

Wear is the deterioration of a surface due to material removal caused by relative motion of it and another part. In corrosive media, wear may be synergistically accelerated by the combined influence of these removal processes. This is related to the erosion corrosion process described above.

Much of the discussion of wear phenomena is associated with upper cylinder wear in internal combustion engines.<sup>74 75 76</sup> This type of wear is associated with the formation of performic acid, or other aggressive species, from the partial oxidation of alcohol in cold engines. This process is not expected to occur in underground storage and dispensing equipment.

However, alcohol and alcohol blends do tend to promote more metal-to-metal wear than gasoline. Ethanol blends tend to provide less lubricity than methanol.<sup>77</sup> Temperature, sliding speed, and water content were found to be important parameters influencing wear rate.<sup>78 79</sup> The largest increase in the wear rate of steel is found just below the water content at which phase separation occurs in alcohol blended gasoline. This phenomenon was attributed to the formation of microdomains of an aqueous phase which has not coalesced

Additives have been found to improve the lubricity of alcohol blended gasoline. However, many of these additives such as corrosion and wear inhibitors have been found to have negative effects on engine performance due to the formation of deposits in and around the combustion chamber.

### **6.2.7 Erosion-Corrosion**

Erosion-corrosion occurs under dynamic fluid flow conditions and under conditions of wear. Under these conditions shear stress at the wall can remove protective corrosion product films from metal surfaces. Corrosion rates are increased due to this process of building protective

oxide/hydroxide layers and subsequent wear or washing away. Erosion-corrosion can be enhanced if the flow media is multiphase.

### **6.2.8 Effect of Contaminates in Solution**

In addition to containing small amounts of water, technical and industrial grades of alcohols also contain traces of organic acids, aldehydes, peroxides, ketones and esters and other materials.<sup>80</sup> Trace levels of contamination, such as the sulfate impurities from fermentation processes<sup>81</sup> or chloride ion from salts or pH variation can have a large influence on the observed corrosion mechanisms and therefore the observed corrosion rate. This has been shown systematically in electrochemical corrosion studies of aluminum<sup>82</sup> and iron alloys.<sup>83</sup> Synergistic effects are seen with the chloride ion and it is often thought to be the most aggressive counter ion.<sup>84</sup>

### **6.2.9 Effect of Alloying Elements**

Just as the level and type of contaminants in solution greatly affect corrosion rate, the type and level of alloying elements in metals can affect the rate at which corrosion is observed. This phenomenon is associated with the stability of the oxide layer of the metal surface. For example chromium is added to steel to promote its corrosion resistance. Conversely, pure aluminum forms a stable oxide film and alloying elements can disrupt the stability of this protective barrier. For example, addition of copper to aluminum<sup>85</sup> or steel<sup>86</sup> promotes corrosive attack by alcohols.

### **6.2.10 Environmental Stress Cracking**

Environmental stress cracking (ESC) most often occurs in stainless steels which are in the presence of ionic contaminants such as chloride or sulfide. ESC, however, generally occurs at temperatures above 140 °F and is not mentioned as an important failure mechanism in this literature. Therefore it will not be considered further.

### **6.2.11 Thermal Effects**

Temperature has very complex influence on the corrosion process. On one hand, all the aforementioned reactions are accelerated with temperature. On the other, the solubility of certain corrodants like oxygen decrease with temperature.

For example the corrosion rate of steel in hydrated alcohols is observed to increase exponentially with temperature in the range of 20 to 80 °C, from 0.04 to 0.14 g/m<sup>2</sup>/h. The corrosion rate of aluminum also increases with temperature. In contrast, the corrosion rate of copper goes through a maximum with temperature at approximately 50 °C. In the range of 20 to 80 °C, the corrosion rate is less than 0.01 at the extreme temperatures and 0.023 g/m<sup>2</sup>/h at 50 °C.<sup>87</sup>

### **6.2.12 Effect of Time, Corrosion Inhibitor**

The corrosion rate of metals may decrease with time if a stable, passive oxide film is formed. However, for steel immersed in ethanol blended fuels, electrochemical measurements have shown that the corrosion rate may either increase or decrease with time, depending upon the choice of corrosion inhibitor.<sup>88</sup> Inhibitors investigated include mono-, di- and tri-ethanolamines, with the smaller molecular weight inhibitors performing best. Another study found amine-based corrosion inhibitors are also effective for steel.<sup>89</sup>

### **6.2.13 Testing Standards for Metallic Materials**

There are many standards for evaluation of metal corrosion and/or wear phenomena. In addition to the nomenclature and statistical analysis standards mentioned above, there are several additional standards for evaluating corrosion. A few of the ASTM Standards will be briefly summarized in this section.

ASTM G-1 is a standard practice for preparing, cleaning, and evaluating corrosion test specimens<sup>90</sup>. It covers suggested procedures for preparing bare, solid metal specimens for tests, for removing corrosion products after the test has been completed, and for evaluating the corrosion damage that has occurred. Emphasis is placed on procedures related to the evaluation of corrosion by mass loss and pitting measurements.

ASTM G-31 - 95 is a standard for conducting laboratory immersion corrosion tests.<sup>91</sup> This practice describes accepted procedures for and factors that influence laboratory immersion corrosion tests, particularly general mass loss tests. These factors include specimen preparation, apparatus, test conditions, methods of cleaning specimens, evaluation of results, and calculation and reporting of corrosion rates. This practice also provides a checklist for reporting of test data.

ASTM G-46 - 94 is a standard for examination and evaluation of pitting corrosion.<sup>92</sup> It is intended to assist in the selection of procedures that can be used in the identification and examination of pits and in the evaluation of pitting corrosion to determine the extent of its effect. ASTM G-71 - 81 is a guide for conducting and evaluating galvanic corrosion tests<sup>93</sup> to characterize the behavior of two dissimilar metals in electrical contact in an electrolyte under low flow conditions. It can be adapted to wrought or cast metals and alloys. The guide covers the selection of materials, specimen preparation, method of exposure, and method for evaluating results to characterize the behavior of a galvanic couple.

ASTM G-119 - 93 is a guide for determining the synergism between wear and corrosion.<sup>94</sup> It provides a guide for computing the increased wear loss rate attributed to synergism or interaction that may occur in a system when both wear and corrosion processes coexist. The guide applies to systems in liquid solutions or slurries and does not include processes in a gas/solid system. The guide applies to metallic materials and can be used in a generic sense with a number of wear/corrosion tests. It is not restricted for use with approved ASTM test methods.

ASTM G-133 - 95 is a standard test for evaluating wear using a linearly reciprocating ball-on-flat sliding test.<sup>95</sup> It describes laboratory procedures for determining the sliding wear of ceramics,

metals, and other candidate wear resistant materials. The direction of the relative motion between sliding surfaces reverses in a periodic fashion such that the sliding occurs back and forth and in a straight line. The principal quantities of interest are the wear volumes of the contacting ball and flat specimen materials; however, the coefficient of kinetic friction may also be measured using the method described. This method encompasses both unlubricated and lubricated testing procedures. The scope of the method does not include testing in corrosive or chemically aggressive environments.

## 7.0 Results and Discussion

### 7.1 Non-Metals

As literature data are used to evaluate swelling and permeability of materials, be aware of certain complications associated with precise reporting of this behavior. When an aggressive solvent is present in dilute quantities, selective absorption into materials may deplete its concentration in solution. Also, some materials contain extractable materials and last, equilibrium swelling and permeation should always be verified. All of these effects can create an apparent absorption and permeation in materials which is less than the actual value. Absorption error tends to be more pronounced for lower swelling systems and permeability error tends to be more pronounced for higher permeating materials.

#### 7.1.1 General Observations on the Effects of Model Fuel Blends on Polymeric Materials:

**Tables A1** through **A6** in **Appendix A** summarize swelling data from the literature while **Tables B1** through **B6** in **Appendix B** summarize permeability data. These data are categorized by solution and by specific material. Standardized nomenclature is used to refer to generic elastomer<sup>96</sup> and thermoplastic<sup>97</sup> materials. A description of some common fuel-handling elastomers is offered in **Appendix C**.<sup>98</sup>

Data for composites, which compose rigid piping and USTs, and to a lesser extent thermoplastic materials, which compose flexible piping and sumps, are noticeably sparse. This lack of data is a primary result of the automotive industry reporting most of the data on materials compatibility and permeability. Composite materials are not used in automotive fuel systems.

Aside from the apparent variability of experimental observations in the data that do exist, some trends are widely observed. For example, increasing the ether content in reformulated gasoline generally increases the swelling response of elastomers monotonically.<sup>99 100 101</sup> This swelling behavior has been shown to scale linearly with the activity of the aggressive swelling agent in solution. By contrast, increasing alcohol content in gasohol generally produces a maximum swelling response in polymers.<sup>102 103 104 105</sup> This maximum is located at approximately 15 percent EtOH by volume and somewhat higher for MeOH. Generally, an alcohol fuel blend is more aggressive toward polymers than any of the neat constituents in the fuel. This result is related to the nonideal solution thermodynamics of gasohol solutions as discussed above.

Another general observation is that increasing the fluorine content in fluoroelastomers generally improves its resistance to swelling and permeation by oxygenated hydrocarbons.<sup>106</sup> The reason

for this can be found by studying the molecular structure of the FKM elastomer. FKM-66 is a copolymer of vinylidene fluoride and hexafluoropropylene. Hertz<sup>107</sup> explains that the vinylidene fluoride monomer preferentially polymerized in a head-to-tail fashion. As such there are alternating  $-CF_2-CH_2-$  moieties on the elastomer backbone. The electron withdrawing character of the fluorine atom causes the hydrogen atoms to become acidic. Thus, exothermic interaction occurs among the polymer chains and excellent resistance to hydrocarbons, including aromatic hydrocarbons is observed. However, when hydrocarbons with Lewis base sites, like many ethers and alcohols, are introduced to FKM, these intra-molecular forces are broken by enthalpy favored interaction with the solvent. Considerable elastomer swelling results. FKM elastomers with higher fluorine content achieve this composition by replacing some of the vinylidene fluoride monomer with tetrafluoroethylene monomer. The resulting terpolymer has fewer acid-base sites and therefore is swelled to a lesser extent by alcohols and ethers.

The swelling response of FKM elastomers, as a function of MTBE concentration in gasoline, as well as temperature and fluorine content, were correlated using a statistical model.<sup>108 109</sup> It was found that a linear correlation was sufficient to fit the data, no variable interactions were found to be significant. The resulting fit has the following form.

$$Y = m + b_1X_1 + b_2X_2 + b_3X_3 + e \quad 15$$

where  $m$  and  $b_n$  are fitting constants for the variables  $X_n$  and  $e$  is the estimated error. These equations are very useful for predicting changes in mechanical properties and hardness, etc. with changing fuel composition or temperature. The study found that temperature had the greatest effect on swelling with increased swell observed at higher temperatures. A reduction of properties was also coincidentally observed.

Fluorocarbon plastics offer better resistance to swelling and permeation than other plastics and elastomers.<sup>110</sup> For example, approximately hundreds of times less permeation to Fuel C than PA-11 was observed. The permeation values of fluoroplastics change very little with the addition of either alcohols or ethers to gasoline whereas permeation usually increases for most other thermoplastics.

Increasing acrylonitrile content in NBR improves its resistance to aromatic hydrocarbons<sup>111</sup> as well as its permeability to gasoline.<sup>112</sup> Higher acrylonitrile content in NBR has a lesser beneficial effect on the resistance to ethers and actually reduces the resistance of the elastomer to concentrated ethanol<sup>113</sup> and methanol<sup>114</sup> fuels. Unfortunately, increased acrylonitrile content also generally decreases low temperature flexibility.

Even though swelling and permeability behavior vary markedly among materials of the same class, materials are lumped together in classes such that a range of behavior in each material class is given. This is done for two reasons: The variability among observations from different observers of similar materials is in some cases nearly as significant as the range itself. Second it allows broad categorization by end-use.

### 7.1.2 Swelling of Polymeric Materials in Model Fuel Blends and Neat Oxygenated Hydrocarbons:

**Table 5** summarizes by class the swelling ranges of elastomers and other materials in model ASTM Fuel C blends with and without added oxygenated hydrocarbons. It is observed that, addition of 15 percent MTBE does not significantly change the performance of FKM and NBR elastomers commonly used for seals and hoses, respectively. That is, the swelling of FKM seals remains below 20 percent by volume and the swelling of NBR-based hose materials may actually decrease somewhat. However, addition of 10 to 15 percent by volume of MeOH may compromise the integrity of some components by increased swelling of common elastomers beyond acceptable limits set for certain seal and/or hose applications.

**Table 5** - Volume swelling ranges of polymeric materials exposed to model fuels with and without oxygenates.

<i>Materials</i>	<i>Primary Application</i>	<i>Percent Swell by Volume</i>			
		<i>ASTM Fuel C</i>	<i>Fuel C + 15 % MTBE</i>	<i>Fuel C + 10 to 15 % MeOH</i>	<i>Fuel C + 10 to 15 % EtOH</i>
NBR/Blends	Hose	23 to 56, 28*	19 to 38	49* to 106	22 to 70, 34*
FKM	Seal	1 to 14, 10*	6 to 18*	7 to 46*	6 to 24
FSi	Seal	18 to 21	24	30	19 to 20
CO, ECO		35 to 40		77 to 80	50 to 65
U	Seal	21	24	58	51
CSPE		61		66	81
CIIR		96		81	
CPE				87	
PS	Sealant	27		28	
PA	Pipe Liner	-0.5 to 0.5	-0.5 to 0.2		
Acetal	Molded Parts	1	0		
HDPE	Flexible Pipe	10.7	10.9		
Fiberglass	Rigid Pipe	-0.43	-1.3 to 2.3		
Fiberglass	Tank	-0.02	-0.51	10	

\* Behavior of the most common material used in the class.

**Table 6** summarizes by class swelling data for common elastomers exposed to neat oxygenated hydrocarbons. It is observed that neat MTBE and neat MeOH are both aggressive swelling agents for FKM whereas they are less aggressive toward NBR-based elastomers. In comparing **Tables 5 and 6**, it is interesting to note that the swelling power of ethers are reduced as they are diluted into the nonpolar gasoline whereas the swelling power of alcohols are not reduced.

**Table 6** Volume swelling of polymeric materials exposed to neat oxygenated hydrocarbons.

<i>Materials</i>	<i>Primary Application</i>	<i>Percent Swell by Volume</i>				
		<i>MTBE</i>	<i>ETBE</i>	<i>TAME</i>	<i>MeOH</i>	<i>EtOH</i>
NBR/Blends	Hose	36			14	11
FKM	Seal	59 to 180*	3 to 10, 5*	19 to 84, 70*	16 to 135*	2*
FSi	Seal				5	6
CO, ECO					31	2
U	Seal		8		18	19
CSPE					1	1
CIIR					-4	
CPE					-2	
PS	Sealant				3	

\* behavior of the most common material used in the class.

As per **Equation 5**, the absorption characteristics of neat oxygenated hydrocarbons are important indicators for the tendency of solvents to permeate polymer membranes. For example, it is shown that ETBE swells FKM and urethane elastomers far less than MTBE or even TAME. Since TAME is an isomer of ETBE, the stereochemistry of the oxygenated hydrocarbon is shown to play an important role in the swelling and permeation characteristic in FKM. Apparently, having both carbon chains longer than a single atom renders the ether moiety more inert towards interaction with polymeric materials. The ethyl group imparts enough steric hindrance that the Lewis base site is partially shielded from interaction with other Lewis acid sites in FKM elastomers. If this phenomenon is shown to be more generally true in thermoplastics and composite materials, it is an important observation because it suggests a method to reduce permeability by changing the structure of the oxygenate additive. Since no permeability data for ETBE was found, this hypothesis should be verified.

### 7.1.3 Permeation of Polymeric Materials by Model Fuels Containing No Oxygenates.

Generally elastomers have higher values of permeability coefficients while thermoplastics and thermosets exhibit lower values. To estimate the total mass flow, knowledge of the membrane area and thickness are also required. **Table 7** summarizes typical ranges for geometrical constants assumed for a gasoline retail station.

**Table 7** Component geometry for permeation mass flow considerations.

<i>Component</i>	<i>A (m<sup>2</sup>)</i>	<i>L(mm)</i>	<i>A/L (m<sup>2</sup>/mm)</i>
Hose	2.5 to 5	5.0	0.5 to 1.0
Piping	34 to 50		
Sumps			

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Tanks	157 to 234	6.4	24.5 to 36.6
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**Table 8** summarizes permeability ranges reported for many of the material classes exposed to ASTM Reference Fuel C. Expected mass flux values per station,  $Q$ , can be computed for some elastomers and plastics and all seem relatively low except for the NBR hose materials. Here it must be reiterated that the NBR/PVC material most commonly used in that application is better represented by the low end of this range.<sup>115</sup>

**Table 8** Permeability, solubility and mass flow properties for various materials exposed to gasoline blends containing no oxygenates.

ASTM FUEL C								
<i>Material</i>	<i>Primary Applicatio n</i>	<i>Permeability (g*mm/m<sup>2</sup>/d)</i>	<i>Solubility (g/mm*m<sup>2</sup>)</i>	<i>Diffusivity (mm<sup>2</sup>/day)</i>	<i>activity</i>	<i>A/L (m<sup>2</sup>/mm)</i>	<i>Q (g/d)</i>	<i>t = 1/D (d/mm<sup>2</sup>)</i>
<b>Elastomers</b>								
FKM	Hose liner	1 to 7	8 to 110	0.06 to 0.13	1	1 to 2	1 to 14	8 to 30
NBR/blends	Seals Hose	192* to 1200	230 to 760	0.9 to 1.6	1	0.5 to 1	100* to 1200	0.5 to 1
<b>Thermoplastics</b>								
ETFE	Hose liner	0.01 to 0.18			1	6 to 12	0.06 to 2	
PE	Flexible pipe	36	107	0.1	1	8	12	
PA	Sump Flexible pipe liner	5 to 26	-5 to 5		1			
<b>Thermosets</b>								
Epoxy	Rigid Pipe		-4					
Polyester	Tank		-0.2					

\* Base fuel 72 octane.

Laminating a hose with FKM elastomer, such as with SAE J30R9 hoses, is anticipated to greatly reduce the total fugitive emission of hydrocarbons. This type of hose is used in the automotive industry to help meet fugitive emission guidelines for fuel systems in cars. It can be speculated that the majority of the total emission of Fuel C from NBR-based hoses is aromatic hydrocarbons since these are known to swell NBR whereas isooctane does not.<sup>116</sup> Thus NBR selectively absorbs and permeates aromatic hydrocarbons. When lined with FKM elastomer the permeation is reduced because FKM is much more resistant to swelling and permeation of aromatics.

#### 7.1.4 Permeation of Polymeric Materials by Ether Blended Model Fuels:

**Table 9** summarizes the available permeation data for reformulated gasoline containing 15 percent by volume MTBE. Comparing **Tables 8 and 9**, notice that FKM elastomers show a marked increase in permeability to reformulated fuel. Evidently FKM elastomer selectively absorbs and permeates MTBE relative to the aromatic and aliphatic hydrocarbons even though MTBE is the minor constituent in reformulated gasoline. Conversely NBR elastomer shows a slight decrease in permeability which is indicative of it being a better barrier to MTBE relative to aromatic hydrocarbons.

**Table 9** - Permeability, solubility and mass flow properties for various materials exposed to gasoline blends containing 15 percent v/v MTBE.

ASTM FUEL C + 15 percent volume MTBE								
Material	Primary Applicatio n	Permeability (g*mm/m <sup>2</sup> /d)	Solubility (g/mm*m <sup>2</sup> )	Diffusivity (mm <sup>2</sup> /day)	activity	A/L (m <sup>2</sup> /mm)	Q (g/d)	t = 1/D (d/mm <sup>2</sup> )
<b>Elastomers</b>								
FKM	Hose liner Seals	15 to 38	60 to 180	0.21 to 0.25	1	1 to 2	15 to 76	4 to 5
NBR/blends	Hose	176*	190 to 380	0.5 to 1	1	0.5 to 1	88 to 176	1 to 2
<b>Thermoplastics</b>								
ETFE	Hose liner	0.1**			1	6 to 12	0.6 to 1.2	
PE	Flexible pipe Sump		109					
PA	Flexible pipe liner		-5 to 2					
<b>Thermosets</b>								
Epoxy	Rigid Pipe		-13 to 23					
Polyester	Tank		-5					

\* Base fuel 72 octane.

\*\* ETBE value = 0.05

An attempt is made to estimate the fraction of the total mass flow in NBR and FKM elastomers which is associated with oxygenate permeation alone. These estimates are made by using the observed permeability with and without MTBE and assuming a linear component contribution to the total hydrocarbon permeability according to the following relationship:

$$P_t = \sum a_i P_i \quad 16$$

Where  $P_t$  is the total permeability,  $P_i$  is the permeability of each constituent and  $a_i$  is the activity of each constituent in the fuel. This computation is theoretical and therefore subject to question. However as a first approximation, the approach seems appropriate because all the hydrocarbons in the model fuel exhibit nearly ideal mixing. It has been previously established that the solubility contributes to the permeability scale according to the activity coefficients.

Following this line of reasoning, the intrinsic permeability of MTBE in a gasoline environment is estimated by this technique to be approximately 85 (g\*mm/m<sup>2</sup>/day) for NBR and 206 (g\*mm/m<sup>2</sup>/day) for FKM-66 copolymer, respectively. To calculate the estimated component fugitive emission of MTBE from dispenser hoses we apply **Equation 16** assuming an activity of MTBE of 0.15 and a surface area of 2.5 to 5.0 m<sup>2</sup> and a thickness of 5 millimeters for an NBR hose. Therefore the total fugitive emission of MTBE is estimated to be 6 to 13 g/d/station. Here, mass flow of MTBE in NBR based hoses is low compared to the permeation of total hydrocarbon. Apparently MTBE is a less aggressive swelling and permeation agent for NBR than are aromatic hydrocarbons.

An interesting exercise is to determine the effect of adding an FKM-66 copolymer liner to the inside of the dispenser hose, similar to the SAE 30R9 specification for automobile fuel lines. Permeation of solvents in multilayered structures are additive as conductances,<sup>18</sup> thus:

$$P_t = \frac{P_1 P_2}{(P_1 + P_2)} \quad 17$$

If a five millimeter thick NBR hose is laminated with an FKM liner in the inside half, the total permeability of all the hoses in a typical station can be shown to increase to about 18 g/d MTBE.

Therefore it is expected that laminating a dispenser hose with FKM elastomer will lead to increased MTBE permeation even though the total hydrocarbon permeation will be reduced. This increase is due to the selective absorption and permeation of MTBE by FKM copolymer elastomers. It is interesting to note that FKM-lined SAE30R9 hoses are common in the automotive industry. A thermoplastic liner would be required to reduce the total permeation of MTBE in hoses. Such lined hoses have been developed for automotive flex fuel lines and are common styles for air conditioner hoses and natural gas fuel lines.

To summarize the effects of ethers on polymers, pure MTBE is aggressive to many polymeric materials. However, the effects of MTBE on polymers is not expected to cause performance problems when it is diluted into gasoline at the 15 percent level. The permeability of MTBE through elastomers and thermoplastics is also proportional to its concentration in the gasoline. ETBE is apparently less aggressive than MTBE or TAME in some elastomers.

Before leaving the subject of the effects of ethers, it should be mentioned that one author has expressed concern over the effects of MTBE on materials even at the five percent level.<sup>117 118</sup> These papers describe the effects of MTBE on floating roof tank seal materials. Many of these materials are foams in which considerable weight gain can be obtained as the pore volume becomes saturated with condensate. Due to the expectation of wear in this application, only minor changes in dimensions and material properties can be tolerated. In fact, the author considers greater than ten percent weight gain to be “significant deterioration” for this application and selected PTFE fabrics as the only compatible material. However, these results should not be of concern for the retail gasoline environment. USTs are not sealed in this manner.

### 7.1.5 Permeation of Polymeric Materials by Alcohol Blended Model Fuels:

**Table 10** summarizes permeability and solubility results for gasoline blends with MeOH while **Table 11** presents similar data for gasoline blends with EtOH. Notice that the volume swell of the lower grades of FKM in MeOH blended fuels exceed the limits for reliable seal operation. Even the best grades of NBR swell too much for reliable hose applications in MeOH fuels. The higher molecular weight EtOH is somewhat less aggressive swelling and permeation agent than MeOH.

**Table 10** - Permeability and solubility of modified ASTM Fuel C, containing 15 to 20 percent by volume MeOH, in polymeric materials.

<b>ASTM FUEL C + 15 to 20 % volume MeOH</b>								
<i>Material</i>	<i>Primary Application</i>	<i>Permeability (g*mm/m<sup>2</sup>/d)</i>	<i>Solubility (g/mm*m<sup>2</sup>)</i>	<i>Diffusivity (mm<sup>2</sup>/day)</i>	<i>activity</i>	<i>A/L (m<sup>2</sup>/mm)</i>	<i>Q (g/d)</i>	<i>t = 1/D (d/mm<sup>2</sup>)</i>
<b>Elastomers</b>								
FKM	Hose liner Seals	6 to 50	52 to 340	0.11 to 0.15	1	1 to 2	6 to 100	
NBR/blends	Hose	1300 to 2700	370 to 780	2.7 to 3.2	1	0.5 to 1	600 to 2700	
<b>Thermoplastics</b>								
ETFE	Hose liner	0.05 to 0.43			1	6 to 12	0.3 to 5	
PE	Flexible pipe Sump	46			1	8	196	
PA	Flexible pipe liner	27 to 100			1			
<b>Thermosets</b>								
Epoxy	Rigid Pipe							
Polyester	Tank	1	100	0.011				

**Table 11** - Permeability and solubility of modified ASTM Fuel C, containing 10 to 15 percent by volume EtOH, in polymeric materials.

<b>ASTM FUEL C + 10 to 15 % volume EtOH</b>								
<i>Material</i>	<i>Primary Application</i>	<i>Permeability (g*mm/m<sup>2</sup>/d)</i>	<i>Solubility (g/mm*m<sup>2</sup>)</i>	<i>Diffusivity (mm<sup>2</sup>/day)</i>	<i>activity</i>	<i>A/L (m<sup>2</sup>/mm)</i>	<i>Q (g/d)</i>	<i>t = 1/D (d/mm<sup>2</sup>)</i>
<b>Elastomers</b>								
FKM	Hose liner Seals	2 to 100	52 to 270	0.03 to 0.37	1	1 to 2	6 to 100	
NBR/blends	Hose	1000 to 2000	170 to 560	3.5 to 5.8	1	0.5 to 1	600 to 2700	
<b>Thermoplastics</b>								
ETFE	Hose liner	0.03 to 0.15			1	6 to 12	0.3 to 5	
PE	Flexible pipe Sump							
PA	Flexible pipe liner	33						
<b>Thermosets</b>								
Epoxy	Rigid Pipe							
Polyester	Tank							

Permeability values represent the sum of all hydrocarbon contributions. Notice that the total mass flow due to permeation is very high even in comparison to MTBE permeation. Fluoroelastomers and fluoroplastics exhibit the lowest levels of permeation in alcohol blends while fluorosilicones and nitrile elastomers exhibit the highest level. Permeation rate drops with increasing acrylonitrile content in NBRs and also drops with increasing fluorine content in FKM<sup>s</sup>.<sup>119 120</sup>

The permeation values reported for alcohol fuels are “peak” values. Many authors observed the permeation rate to go through a maximum value several days after the test began. This phenomenon has been attributed to speciation.<sup>121 122</sup> Speciation occurs when the membrane selectively absorbs and permeates one of the components in the solution. In this case, the alcohol

permeates very quickly and depletes its concentration in the reservoir. The changing activity of permeant in the reservoir causes the apparent permeation rate to decrease with time.

Several authors reported attempts to improve the measurement technique by increasing the size of the reservoir and other techniques.<sup>123</sup> Therefore reported permeation values will be greatly dependent on the experimental technique employed. In an attempt to introduce some consistency, the permeation values summarized in this review are all “peak” values.

Since there have been no successful attempts to model the swelling behavior of materials exposed to alcohol blended fuels over the entire composition, no attempt is made to estimate the component contribution of alcohol permeation. Because there is substantial excess swelling of elastomers in the alcohol blends, the best swelling models are applicable only over a limited composition range.<sup>124 125 126</sup> For this reason, the linear combination rule of **Equation 14** will not apply for scaling component contributions.

The limited data available for swelling and permeation of oxygenated fuels in composite materials, which is shown in the preceding tables, will be discussed below. Epoxy matrix composites are found in rigid nonmetallic piping while polyester matrix composites are found in nonmetallic underground storage tanks.

#### **7.1.6 Thermosetting Materials -- Underground Storage Tanks.**

Very limited information is available regarding the sorption and plasticization of isophthalic polyester laminates by reformulated fuels containing 15 percent MTBE. It is generally assumed that MTBE and other ethers will not be as aggressive to FRP as alcohols. Therefore observers have concentrated testing efforts on the effects of alcohol containing fuels. Kamody et al. state, “Test results indicate this is true,” but no data with regard to the effects of MTBE were offered.<sup>127</sup><sup>128</sup> It was indicated that MeOH is very aggressive to FRP, especially those made from less premium resins. Introducing MeOH into older tanks tended to dissolve gums and other polar residues which accumulated throughout the years and wound-up fouling automotive equipment such as fuel lines. Ethanol does this as well but it seems that MeOH is more notorious.

It has been reported,<sup>129</sup> from a seven month immersion study, that reformulated gasoline produced less weight change (actually lost weight) than nonoxygenated gasoline. Loss of weight may be due to extraction of residual unreacted monomers in an unpostcured material. However no data on modulus retention are offered.

Reports of an eight-year immersion study of polyester fiberglass laminates by Fluid Containment indicate that hardness and strength did not vary by more than two percent. Fluid Containment quoted “the MTBE fuel blend acted no differently than the straight gasoline and had essentially no effect on the tank sample after eight years.” But, no data on modulus retention are reported. Certainly there are no data to indicate MTBE is more or less detrimental or permeable to UST materials than is gasoline. There is no theoretical reason to expect strong selective absorption of MTBE by isophthalic polyesters. This is because no strong Lewis acid sites are present in these

polymer materials which would drive MTBE absorption by exothermic interaction. The chemical structure of the polyester contains only Lewis base sites (ester linkages and aromatic pi electrons).

However, selective absorption of alcohol by isophthalic polyesters may be anticipated due to a potential exothermic interaction among ester moieties in the polymer and the hydroxyl group of alcohol. Indeed, selective absorption of alcohols is observed. After one, six and 12 months of immersion, 2.2, 3.8 and 4.7 percent weight gain, respectively, were observed for isophthalic polyester immersed in 10 percent MeOH, 10 Percent TBOH balance gasoline blend.<sup>130</sup> Coincident with the observed absorption, a seventy percent retention of flexural stiffness was also observed. Post-curing the laminate significantly improves the resistance of the material to methanol blends.

These results are corroborated by Kamody who observed a 30 percent retention of isophthalic polyester resin laminates after nine month immersion in 30 percent methanol/gasoline blends. Although premium resins show better resistance to methanol, the loss of stiffness of isophthalic polyester laminates in methanol fuels exceeds the levels allowed by UL and ASTM standards.

Broutman and Associates<sup>131</sup> performed immersion testing of tank laminates in alcohol blended gasoline and measured property retention as a function of time, up to 15,000 hours. The property retention data were extrapolated to thirty years. Weight gains were observed to be in the range of two to ten percent, depending on the laminate studied and the oxygenated hydrocarbon immersion media. Interestingly, the laminate exposed to blends of alcohol-gasoline always absorb more weight than they do in either of the neat constituents. They point-out that older tanks, installed before 1979 are more prone to absorption of alcohols than newer tanks designed for 10 percent EtOH service. In older tanks, flexural stiffness retention was estimated to be 70 percent after 30 years exposure to 10 percent EtOH blends while methanol blends retained only 25 percent stiffness. Newer tanks, listed for ethanol service retain properties considerably better. They concluded that gasohol storage may lead to an increased frequency of buckling failures in tanks that were not designed to store these oxygenated fuels.

Graduate work performed at the University of Minnesota<sup>132</sup> generally confirms the observations of Broutman and Associates that swelling of isophthalic polyesters in methanol containing fuels is greatest for the fuel blends rather than the neat constituents. Up to ten percent swell may be expected. A coincidental loss of stiffness of up to 40 percent may be observed after 30,000 hours.

No successful attempts to measure permeation of ethers or alcohols in pipe or tank composites have been reported. Smith Fiberglass apparently attempted to measure permeation of EtOH in fiberglass piping after 31 days exposure and they were unable to find any. It is generally held that since MTBE is a large molecule relative to alcohols, it is not likely to swell fiberglass or permeate through it.

Theory maintains, however, that any hydrocarbon which can be dissolved into a membrane will permeate through it at some rate. For example, the diffusion coefficient of methanol in an isophthalic polyester laminate can be estimated by applying **Equation 13** to some unsteady absorption data reported above. The absorption of methanol into a 6 mm laminate was measured after one month to be 2.2 percent. The total equilibrium absorption was estimated by Craggie et

al.<sup>133</sup> to be ten percent. The diffusion coefficient for methanol in fiberglass is now theoretically estimated to be 0.011 mm<sup>2</sup>/d. The swelling behavior of MeOH in the isophthalic polyester laminates shows classical Case II permeation. Now the permeability and the total mass flow of MeOH can be estimated for a UST as summarized in **Table 10**. Although the permeability is low, substantial surface area exists for a UST and the total mass flow may not be negligible.

The inability to measure permeation of oxygenated hydrocarbons may be related more to experimental impatience than impermeability of the solvent. For a six millimeter thick laminate, the estimated time to reach steady state permeation of MeOH is estimated to be about 3.5 years. About four months would theoretically be required to observe the first indications of MeOH permeation. This may explain why attempts to measure permeation in fiberglass laminates have not produced results.

One final comment on UST compatibility. The Steel Tank Institute released a rather impassioned statement in an effort to convince its readers of the incompatibility of fiberglass tanks to alcohol blended fuels. Many statements in this publication may be considered controversial. However, it is interesting to note that with all the concern voiced over alcohol blended fuels, no mention is made regarding the effects of MTBE in reformulated fuels on fiberglass UST's. Also no mention is made of fiberglass piping with regard to either alcohols or ethers.

### **7.1.7 Thermosetting Materials -- Rigid Fiberglass Piping**

As with UST laminates, very little information is available regarding the absorption and permeability of oxygenated hydrocarbons in these composites. Generally the matrix material is amine cured epoxy and, as such, is theoretically expected to selectively absorb both alcohols and ethers. However, these components operate under a positive pressure so there is no risk of compressive buckling failure. In tensile loading, continuous fiberglass laminates are very strong and any drop in matrix stiffness is not expected to impact the performance of these materials.

### **7.1.8 Thermoplastic Materials -- Flexible Plastic Piping.**

Flexible piping, running from the tank to the dispenser, is a rather new innovation. HDPE is usually used for this application and it is lined with PA or PK for permeation and swelling resistance. If swelling or shrinking is extensive, the pipe may either sag or pull from its fixtures.<sup>134</sup> However there has been no evidence to show that this is a problem for this type of buried piping.

Permeation of MTBE from flexible piping can be estimated from the available data. Assuming 500 square feet of surface area in a typical gasoline station with secondary containment of underground piping, the fugitive emission is expected to be approximately 8 g/day of vapor into the soil column. This compares with the allowable standard set by UL of 40 g/day.

### **7.1.9 US EPA Evaporative Emission Regulations.**

The reader may have noticed that there is a considerable effort reported in the SAE technical papers regarding the permeability of oxygenated gasoline in elastomers and thermoplastics. This is a direct result of Evaporative emissions regulations enacted as part of the Clean Air Act of 1990. These regulations, in effect since 1994, state that the fugitive emission from an automobile fuel system must not be greater than 2 grams total hydrocarbon per car per day. This amounted to a decrease in the allowable permeation rate by a factor of ten.

Existing rubber fuel lines, NBR/PVC blends, and plastic gasoline tanks, HDPE, could not meet these standards, especially when flexible fuel vehicles were considered. Therefore newer materials<sup>135</sup> and laminated constructions were developed. Some automotive companies returned to steel tanks to reduce fugitive emission.<sup>136 137</sup> Others developed laminated plastic tanks.<sup>138</sup> FKM-lined hoses were made to comply with the regulation but they are quite expensive.<sup>139</sup>

## 7.2 Metals

### 7.2.1 Corrosion by Ethers

There is very little information regarding the corrosion of metals by ethers and, in particular, MTBE. This observation is significant in light of all the corrosion studies performed with alcohols. For estimation of corrosion rates of carbon steel piping in the finishing section of an MTBE plant, a regional corrosion specialist for Shell wrote, "... no corrosion is expected ..."<sup>140</sup> One may anticipate that in relatively benign chemical environments, extensive corrosion studies will not be performed.

One study on MTBE effects looked at the corrosion resistance of zinc, aluminum, and brass (these are active metals known to corrode in alcohol fuels) in neat MTBE and gasoline containing 20 percent MTBE at 20 °C.<sup>141</sup> These metals were not affected by either MTBE solution. However, brass was corroded with water present in the blend.

In another study involving flexible fuel vehicles, a seven percent by volume blend in gasoline was included in a fleet vehicle test.<sup>142</sup> No evidence of fuel system material or component damage was found due to the extended use of oxygenated fuels.

One study looked at the corrosive effects of ETBE.<sup>143</sup> Metals tested included: galvanized steel, cast iron, copper, magnesium, brass, aluminum, 1018 carbon steel, and terneplate. Samples of each of the metals were stored in the fuels to which had been added about 1 percent water. None of the experimental fuels shown were treated with the anti-corrosion additives normally used in finished gasoline. Samples were maintained at room temperature for 168 days. The data show ETBE containing blends to have corrosion rates not significantly different from the neat fuels. The terneplate showed 12.5 g/yr/12fts<sup>2</sup> loss of weight but it was not considered to be of great significance. No detrimental effects of the ETBE on metal parts common to gasoline delivery and fueling system were found.

Therefore it may be concluded that gasoline is a rather benign chemical environment from a metals corrosion perspective and addition of ethers does not increase the aggressiveness of the fuel.

### 7.2.2 Corrosion By Alcohols

Corrosion rates for methanol have been reported by Lash. **Table 12** summarizes some of the observations.

**Table 12** - Corrosion rates for selected metals immersed in methanol fuels at 40 °C for 2000 to 8000 hours (Lash et al.).

<u>Material</u>	<u>15 percent MeOH</u>		<u>85 percent MeOH</u>
	<u>Average</u> ( $\mu\text{m}/\text{year}$ )	<u>Lower, Aqueous Phase</u> ( $\mu\text{m}/\text{year}$ )	( $\mu\text{m}/\text{year}$ )
SS 304	0.0	0.0	0.0
SS 444	0.0	0.0	0.1
Tin	0.1	0.5	0.2
Brass	1.4	6.7	6.4
Zinc	2.1	10.0	13.9
Terneplate	2.7	12.9	86.9
Zinc-Iron	2.8	13.3	7.5
Zinc-Nickel	2.5	11.9	13.3
Zinc-Cobalt	1.9	9.0	18.1
Cadmium	7.5	35.7	22.9
Steel, CRS	10.0	7.6	1.8
Aluminum 356			24.0
Aluminum 319			55.0
Aluminum 380			63.0
Magnesium			146380.0

With 10 percent methanol blends and one percent total added water, corrosion rates were also reported as summarized in **Table 13**.<sup>144</sup> Weight increases are presumably associated with corrosion product which was not removed prior to weight measurement. Materials to avoid in methanol fuel systems include magnesium and terneplate especially. Also avoid bare aluminum, brass zinc, zinc alloys, and cadmium.

A more recent alcohol blend is called Oxinol. It is a blend 50 percent volume blend of MeOH and gasoline grade tertiary butyl alcohol (GTBA). This blend is added to gasoline to achieve the required bound oxygen content. From a materials point of view, this blend has several interesting aspects. First, the methanol activity is dropped because the volume fraction is lower and because the GTBA disrupts the normal hydrogen bonding characteristic of MeOH. Not much data is reported for this alcohol blend, but it is expected that its aggressiveness to metallic and nonmetallic materials will be reduced compared to straight methanol blends.

**Table 13** - Corrosion rates of selected metals in 10 percent methanol blends.

**10% MeOH**

<u>Material</u>	<u>mg/d/m<sup>2</sup></u>
Zinc	-10.7
Iron	-26.3
Copper	+8 to 11
Brass	+8 to 11
Aluminum	+1.4

## 7.3 Other Materials

### 7.3.1 Ceramics

There is no mention of any compatibility or permeability issues for ceramic materials to oxygenated fuel blends in the literature. Nor is there any reason to suspect these types of problems.

### 7.3.2 Pipe Dope:

There are several indications in the literature which state that freshly applied pipe dope is subject to washing-out by gasoline containing alcohol. Some pipe dope is alcohol-based and the solids may be redissolved if the pipe dope has not had ample time to dry. Washed-out pipe dope can lead to leaks in threaded connectors. PTFE-based tape may be considered as an alternative thread sealant.

### 7.3.3 Coatings:

Coatings may be found on the inside or outside of steel tanks to protect them from corrosion. Coatings may be organic or metallic.

#### **Organic Coatings:**

In the absence of cathodic protection, barrier organic coatings will protect metals if they can be applied and maintained pore free but, this is very difficult in practice. In a laboratory evaluation, it was found that gasohol tends to extract an epoxy coating from a gasoline storage tank.<sup>145</sup> A practice was established to store gasohol in unlined tanks and a recommendation made to study the suitability of various coatings for use in gasohol service.

Several authors indicated the superior performance of urethane based coatings for splash exposure to gasohol. These coatings are automotive finishes, however, and they may not be appropriate for liquid immersion service.

Ethylene acrylic acid copolymer is a polymer coating for steel substrates.<sup>146</sup> It is nonconductive and provides good adhesion to steel and good resistance to MeOH. After a two year immersion tests of coated steel samples in gasoline and M15, M85, and M100 with and without one percent water, there was no evidence of laminate deterioration or adhesion loss on any sample.

#### **Inorganic coatings:**

Sacrificial metal coatings such as terneplate, which cathodically protected steel and other structural metals, are inappropriate for systems in contact with alcohol blended gasoline. Terneplate coatings are the most widely used inorganic coating for automotive applications to protect steel gasoline tanks from corrosion. Terneplate is a coating consisting of lead and zinc and many authors report that it is unsatisfactory for use in alcohol services. There is also a danger that corrosion products may become entrained in the fuel and enter the automobile fuel system.<sup>147</sup>

Steel, nickel plate,<sup>148</sup> and also prepainted zinc-nickel has been suggested to work well in methanol, but prepainted terneplate is not acceptable.<sup>149 150</sup> For replacement of terneplate, tin coatings<sup>151 152</sup> are most often mentioned (wolyne) as giving excellent performance. Cadmium plate is also mentioned.

Electroless nickel plating can be used to protect aluminum in dry methanol environments but is not recommended in the phase separated wet environments (lash). Anodized alloys 319 and 356 are reported to work reasonably well.

## 8.0 Review Articles

A general reference book is available which summarizes compatibility data for elastomers.<sup>153</sup> This book contains some information on alcohols and diethyl ether but not the ethers that are commonly used in reformulated gasoline. A summary of unsuitable materials for these pure oxygenates is summarized in **Table 14**:

**Table 14** - Unsuitable elastomers for neat alcohol and diethyl ether.

<b>Diethyl Ether</b>	<b>Ethanol</b>	<b>Methanol</b>
ABR	ABR	ABR
	AU	AU
Butyl, IIR		
Hypalon		
EA		
	EU	
EPDM		
FKM	FKM	

In a review article, Davidson<sup>154</sup> mentions that fiberglass UST manufacturers claim tests in MTBE blends show no deleterious effects and therefore they warrant the tanks for thirty years in reformulated gasoline service. All studies indicate that USTs are compatible with MTBE blended gasoline.

Downstream Alternatives, Inc. surveyed major equipment manufacturers in 1997 regarding the compatibility of their products to MTBE and reformulated gasolines.<sup>155</sup> With regard to tanks, piping, seals, dispensing equipment, vapor recovery and related equipment, they concluded, “the data clearly indicates (sic) that gasoline containing MTBE is compatible with all these products. Claims and insinuations that gasoline containing MTBE are not compatible with equipment are not based on scientific evidence.”

Other review articles focused on the materials issues associated with alcohol fuels.<sup>156 157 158 159 160 161</sup>  
<sup>162</sup> (F. Black) In addition to materials compatibility issues, drive ability, and emissions were considered. Some interesting observations which these articles have in common are as follows: Materials that laboratory tests indicate as being susceptible in immersion tests do not always give problems in fleet vehicle testing. Therefore, it is sometimes difficult to say which materials are unsuitable based on laboratory testing alone. In general, a material which is resistant to methanol will be at least equally resistant to ethanol. Minimizing water in alcohol fuel systems is one way of reducing corrosion problems. However, magnesium and magnesium alloys corrode very rapidly in dry methanol. This review article, written in 1984, concludes “essentially all of the aforementioned problems can be eliminated or improved by appropriate choice of construction materials.”

Alcohols (MeOH and EtOH) have much wider explosive flammability limits than gasoline. Thus the saturated vapor of a storage tank is within the explosive range at normal ambient temperature. Precautions must be taken to shield this vapor from spark or flame. This danger does not exist with straight gasoline or reformulated gasoline.

Alcohol loosens rust and dirt from the walls of fuel tanks or fuel lines of an automobile. A fuel distribution system which has been used in former gasoline service should be completely cleaned out before use of alcohol blends.

None of the aforementioned review articles considered the phenomenon of permeation of fuels and their constituents through nonmetallic materials.

## 9.0 American Petroleum Institute Documentation

The American Petroleum Institute (API) has released three documents on materials compatibility with oxygenated fuels. These two Recommended Practices and one Publication do not consider permeability issues. The recommended practices consider alcohols only while the publication considers all oxygenated fuels and their neat constituents. **Tables 15 and 16** are copied directly from these Recommended Practice documents.

**Table 15** - Compatibility of commonly used materials with ethanol and ethanol blends.<sup>163</sup>

<i><b>Recommended</b></i>	<i><b>Metals</b></i>	<i><b>Not Recommended</b></i>
Aluminum		Zinc-galvanized (ethanol only)
Carbon Steel		
Stainless Steel		
Bronze		
	<i><b>Elastomers</b></i>	
NBR (Hoses and Gaskets)		NBR (seals only)

CIIR (hoses and gaskets)	CIIR(seals only)
FKM	U
FSI**	
Polysulfide	
Natural Rubber (neat ethanol only)	

**Polymers**

Acetal	Polyurethane**
PA	Alcohol-based Pipe Dope**
PE	
PP	
PTFE	
FRP**	

\*\*The manufacturer of the specific material should be consulted.

**Table 16 -** Compatibility of commonly used materials with gasoline-methanol/cosolvent blends.<sup>164</sup>

<b><i>Recommended</i></b>	<b><u>Metals</u></b>	<b><i>Not Recommended</i></b>
Aluminum		Galvanized metals
Carbon Steel		
Stainless Steel		
Bronze		
	<b><u>Elastomers</u></b>	
NBR (Hoses and Gaskets)		NBR (seals only)
CIIR (hoses and gaskets)		CIIR(seals only)
FKM		
FSI**		
Polysulfide		
	<b><u>Polymers</u></b>	
Acetal		Polyurethane**
PA		Alcohol-based Pipe Dope**
PE		
PP		
PTFE		
FRP**		

\*\*The manufacturer of the specific material should be consulted.

In 1994 the API published results of a 1992 survey of petroleum and other companies for their use of nonmetallic materials in oxygenated fuels.<sup>165</sup> The survey did not differentiate among oxygenate type or material type in a given class. Forty-four companies responded to the survey, following are some observations from that document.

Regarding the use of elastomers in static sealing, dynamic sealing, tank seals and high shear seals, it is clear that most companies increased their usage of FPM type materials and PTFE for handling oxygenates. Forty-four percent of the companies reported having some sealing problems while 42 percent reported making changes to elastomer seals. These changes are:

- A 12 percent decrease in the use of PU was documented. “Embrittlement of PU” was mentioned as one reason for this decrease.
- An eight percent decrease in the use of FKM was documented. “Swelling of FKM” was the predominant observation.
- A four percent increase in the use of NBR was reported.
- A 600 percent increase in the use of FPM was observed; however one respondent cautioned about the use of FPM below 32 degrees Fahrenheit.
- A 100 percent increase in the use of PTFE was reported , however one commentator cautioned, “valves equipped with PTFE seals are difficult to get good positive shut-off.”
- One commentator reported degradation of FRP tank liners by oxygenated fuels.

Most of the above problems were probably encountered while handling the pure oxygenates rather than the fuel blends. One respondent supports this position saying, “15 % MTBE no problems reported. Changed trim (seals) for neat MTBE only.”

In 1995, the API sponsored an “O&E Symposium on Materials/Fuels Compatibility.” A brief summary of information presented at this workshop is provided below.

- Electrochemical measurements of steel with various compositions of MeOH, Fuel C and water showed less than 0.1 mils per year corrosion rate.<sup>166</sup>
- Manufacturers have recommended the use of fiberglass USTs and piping up to the limits of 10 Percent EtOH, 5% MeOH and 15% MTBE. Gasohols have been used successfully since the late 1970’s. MTBE , TAME, ETBE have not been found to be a concern.<sup>167</sup>
- API Recommends consideration of the following dispensing system components when converting a retail station to handle gasoline-alcohol blends: Alcohol resistant materials, Hoses, seals, nozzles.<sup>88</sup>
- It is a common misconception that pure alcohols are more aggressive toward materials than the fuel blends. Flexible piping manufacturers use liners of PA-12, PA-11, PVDF, and PA doped PE to provide compatibility with the fuel blends.<sup>168</sup>
- Sumps are constructed of either FRP or PE. Cross-linked PE is preferred over HDPE as it is stiffer, more chemically resistant, and has better low temperature impact.<sup>89</sup>
- Some case histories regarding submersible pumps in USTs were also reported.
  - Owing to the conductivity of alcohol fuels, electrolysis from electric level gauge caused corrosion of 316 SS casing.

- Submersible Pump impellers are made from Acetal. Acetal exhibits 0.2 percent swelling in a mixture of MeOH and Gasoline. The swollen impellers locked against the pump stator causing the pump to malfunction. Five thousandths of an inch were trimmed from the radius of the blades.
- NBR lathe cut gasket seals used in submersible pump flow manifolds were involved in fuel leaks. Leaks occurred when oxygenated fuel was dropped. NBR seals were in use for many years in non-oxygenated fuel. Newer NBR gaskets do not seem to experience this problem.
- Regarding dispensers: Oxygen dissolved in a 93% EtOH, 7% H<sub>2</sub>O solution caused corrosion of cast iron rotors in pumps. Certain Aluminum alloys tubing can be corroded 30 mil/year by methanol with water. Treated leather piston cups in 6% of dispensers. NBR and Cork gaskets and o-rings.<sup>90</sup>
- Regarding hoses: Common hose constructions include:<sup>90</sup>

ECO	Inner layer of fuel containing hose.
CIIR	Outer layer of hoses.
NBR	Inner layer of fuel containing hose.
NBR/PVC	Outer layer of hoses.
PA & other	Hose components in contact with vapors.
Thermoplastics	

Heat Stabilizer for PA is soluble in MTBE, caused mesh screens to become clogged. NBR is the material of choice for dispenser manufacturers due to cost. Modern NBR's are much improved.
- Regarding nozzles and swivels, common seal materials include:<sup>90</sup>

NBR, FKM	Valve poppets and seals
PTFE	Swivel seals.
- For blends of ideal solvents, the volume fraction of aggressive solute in the swollen elastomer at equilibrium is proportional to the volume fraction of aggressive solute in the mixed solvent or gasoline. Thus the swelling behavior of many common fuel resistant elastomers in blends of gasoline and ethers may be adequately predicted by interpolating the component swelling behavior on a volume fraction basis.<sup>169</sup>
- In non-ideal hydrocarbon blends, the activity or partial pressure of ethanol as well as the non-polar hydrocarbons is nonlinear with its composition in gasoline. As a practical result, the swelling power of the blend is often better approximated by summing the component effects of the neat constituents rather than by interpolating the component effects based upon volume fraction.<sup>91</sup>

## 10.0 CONCLUSIONS

## 10.1 Compatibility

For any hardware designed for use in retail gas stations which has undergone testing, there are no documented material incompatibility issues for retail stations dispensing reformulated fuels containing ethers up to 15 percent v/v MTBE. In concentrations greater than about 20 percent by volume, MTBE and TAME cause swelling of some fluoroelastomers which may be excessive for some applications. Swelling of fluoroelastomers in neat ETBE is substantially lower than in other ethers.

UL and ASTM standards suggest chemical resistance performance criteria for nonmetallic piping and tanks. However, testing in MTBE containing fuels is not specifically required. Similar performance standards exist for plastic pipe, elastomeric hoses and seals, there is no evidence to suggest the hardware would not meet these performance standards in applied use.

In contrast, there are numerous material compatibility issues associated with the use of gasohol. API's Recommended Practices addresses materials recommended and not recommended for use with ethanol and ethanol blends and gasoline-methanol cosolvent blends. Generally, methanol blends are more aggressive than ethanol blends towards both metals and non-metals. MeOH blends with TBA are offered which mitigate some materials concerns. Metal corrosion issues include: general and localized corrosion of active metals, galvanic corrosion, electrolytic corrosion, wear, and aqueous phase separation. Issues for polymeric materials include: swelling and softening due to absorption of alcohol, extraction of plasticizers, and antioxidants. Generally, compatible material alternatives are available but they may not be currently in service.

## 10.2 Permeability

Any solvent which can absorb into a material will also permeate through it. The phenomenon of solvent permeation is therefore limited to polymeric materials. The permeation rate of oxygenated gasoline is greater than nonoxygenated gasoline in common hose materials. In general, alcohol blended fuels are more permeable than ether blends with MeOH being most aggressive. The permeation rate of ETBE is postulated to be considerably lower than other oxygenates.

Greater permeability is observed in elastomers (hoses, seals, gaskets, packing) relative to thermoplastics (flexible piping, sumps, vapor recovery, tubing) and composites (rigid piping). In general, fluorinated elastomers and thermoplastics offer better permeation resistance than nonfluorinated materials. Emissions from composite piping and tanks have not yet been observed. There are not enough data to estimate the total fugitive emission of hydrocarbons from retail stations.

There are no environmental standards that limit fugitive emissions for gasoline retail stations as there are for automobiles. UL-971, for safe operation of underground piping, suggests a permeability limit of 4 g/m<sup>2</sup>/day for the primary conductor and 24 g/m<sup>2</sup>/d for the secondary containment piping. No other permeation standards applicable to the retail gasoline environment were found.

Standards and procedures exist for measuring the total hydrocarbon permeability of gasoline in hoses, flexible piping, and some other non-metallic materials. No standards were found for measuring permeability in composite tanks or composite rigid piping. Existing standards do not cover mass flow contributions from individual hydrocarbon species. In this reviewer's opinion, existing standards may not be adequate for steady state measurement of certain oxygenated species, particularly alcohols that may be present in dilute quantities in gasoline.

## **11.0 Recommendations**

Establish reliable techniques for determination of the individual contribution of the oxygenated hydrocarbon component to total permeability of gasoline blends in materials of construction commonly found in retail gasoline stations.

Measure directly the permeability of MTBE and other oxygenated hydrocarbons in these materials. From this data and geometrical considerations, estimate the total fugitive emission rates, air and soil, of oxygenated hydrocarbons via permeation through common retail station equipment.

Measure the permeation rate of ETBE relative to MTBE in common polymeric materials. If ETBE is found to be substantially lower, consider the possibility of replacing MTBE with ETBE as the preferred oxygenated component in gasoline.

## APPENDIX A

### Swelling Data

**Table A1** - Volume swell of elastomers exposed to MTBE Blends with gasoline.

Reference	Material	Percent swell by volume								
		Volume percent MTBE in ASTM Fuel C								
		0	5	10	15	20	25	50	75	100
f	Fsi		22	23	24	26				
a	FPM	3	3	3	3	2				3
b,c,d,e	FKM-65	8					26	43	105	153
a	FKM-66	15	17	15	18	20				180
b,c,d,e		5					22	37	84	126
g		6					18			
b,c,d,e	FKM-67	5					17	17	53	87
b,c,d,e	FKM-68	4					16	29	65	88
j		4		6	7					
b,c,d,e	FKM-70	3					3	21	38	59
		2					6			
j		4		4	6					
a	Aflas-57	34	38	36	41	42				57
i	ETP									26
j	U	27		19	24					
a	NBR-34	37	37	38	38	38				36
k	NBR	23		22	19					

a) Westbrook TPR 318-90 (140day)<sup>170</sup>

b,c,d,e) duPont data (7day)

f) Virant, et al, SAE 910102 (60°C)

g) Aliosio Ausimont

i) Stevens, 1997

j) Douhit SAE 881667

k) Lebedev added 9% wash-out

**Table A2** - Volume swell of thermoplastics and thermosets exposed to MTBE/gasoline blends.

Reference	Material	Percent swell by volume	
		Volume Percent MTBE in Fuel C	
		0	15
Douthit	PA - 6,12	0.50	0.20
“	PA - 6,6	-0.50	-0.50
‘	Acetal	1.00	0
‘	HDPE	10.70	10.90
‘	Fiberglass pipe	-0.43	0.87
Davidson			-1.32 to 2.26
‘	Fiberglass tank	-0.02	-.51

**Table A3** - Volume swell of elastomers exposed to ETBE and TAME blends with gasoline.

Reference	Material	Percent swell by volume						
		Volume percent ETBE					Volume percent TAME	
		in ASTM Fuel C						
		0	25	50	75	100	10	100
b,c,d,e	FKM-65	8	8	9	9	10	11	84
b,c,d,e	FKM-66	5	4	5	5	5	6	70
b,c,d,e	FKM-67	5	6	7	7	8	7	41
b,c,d,e	FKM-68	4	4	5	5	5	6	51
b,c,d,e	FKM-70	3	2	3	2	3	2	19
l	U		8			8		

l) Shiblom et al SAE 902132

**Table A4** - Volume swell of elastomers exposed to MeOH/gasoline blends.

Reference	Material	Percent swell by volume								
		Volume percent MeOH in ASTM Fuel C								
		0	5	10	15	20	25	50	85	100
f	FSi	21			30			25	15	5
m		25					26		9	
q		18		22						9
s		16			25			24	13	
r	FKM-65	7			32			75	120	
n	FKM-66	5			46					135
q		1		21						100
	FKM-67	14			30			57	85	
r					14		24	16	13	16
n	FKM-68	5			30					20
r					15			20	22	
	FKM-70				19					
r					7			8	4	
p	NBR-40	29		57	62	57				13
	NBR-34	47				82				
q		51		81						14
s					59			37	15	
s	HNBR-36	23			60			38	14	
	NBR-PVC	28				49				
	NBR-BIIR	95				106				
	NBR-CSM	56				82				
q	U	22		45						11
s	CO	35			80			70	45	
q	ECO	33		77						31
s		40			95			75	50	
q	U	21		58						18
q	Hypalon	61		66						1
q	CIIR	96		81						-4
q	CPE	84		87						-2
q	PS	27		28						3

m) Finney SAE 951066 (60C)  
n) Balzer SAE 910106

o) Baurele Lub eng, 54C  
p) Karg SAE 900196

q) Abu Isa SAE 800786  
r) Stevens SAE 880022

s) Mastromatteo SAE 900195

**Table A5** - Volume swell of thermoplastics and thermosets exposed to MeOH/gasoline blends.

<i>Reference</i>	<i>Material</i>	<i>Percent swell by volume</i>	
		<i>Volume Percent MeOH in Fuel C</i>	
		<i>0</i>	<i>85</i>
	PA - 6,12		
	PA - 6,6		
	Acetal		
	HDPE		
	Fiberglass pipe		
	Fiberglass tank		10

**Table A6** - Volume swell of elastomers exposed to EtOH Blends with gasoline.

<i>Reference</i>	<i>Material</i>	<i>Percent swell by volume</i>								
		<i>Volume percent EtOH in ASTM Fuel C</i>								
		<i>0</i>	<i>5</i>	<i>10</i>	<i>15</i>	<i>20</i>	<i>25</i>	<i>50</i>	<i>85</i>	<i>100</i>
q	FSi	18		19	20					6
s		16		22						
s	FKM-65	7		23						
s	FKM-66	5		21						
q				6	7					2
c					36					
s	FKM-67	14		14						
s	FKM-68	5		17						
c					24					
s	FKM-70	1		12						
c					18					
p	NBR-40	29								
k				22						
s	NBR-36,	23		58						
q	NBR-34	51		68			99			11
s				62						
s	HNBR-36	55		22						
d	NBR-PVC	28		34						
d	NBR-BIIR	95		70						
d	NBR-CSM	56		65						
q	CO	35		50						2
s				65						
s	ECO	40		50						
q	U	21		51		56				19
q	Hypalon	61		81						1

m) Finney SAE 951066 (60C)

n) Balzer SAE 910106

o) Baurele Lub eng, 54C

p) Karg SAE 900196

q) Abu Isa SAE 800786

r) Stevens SAE 880022

s) Mastromatteo SAE 900195

## APPENDIX B

### Permeability Data

**Table B1** - Permeability of some elastomers and ETFE to model fuels containing various concentrations of MTBE.

<i>Reference</i>	<i>Polymer Description</i>	<i>Permeability (gm-mm/m<sup>2</sup>/day)</i>			
		<i>Toluene</i>	<i>Volume percent MTBE in ASTM Fuel C</i>		
			<i>0</i>	<i>15</i>	<i>20</i>
c	NBR-40		192**	176**	
b	FKM-66	88			366
d			7.6	38	
d	FKM-68		7.6	23	
b	FKM-70	9			121
d			3.8	15	
b	Aflas-56	1896			5266
b	ETP-67	16			113
a	ETFE		0.02		0.01*

\* ETBE permeability was found to be 0.05

\* Base gasoline of 73 octane was used rather than Fuel C.

a) Goldsberry SAE 930992

b) Stevens et al. ASC (1997)

c) Lebedev et al.

d) Stevens et al SAE 970307

**Table B2** - Permeability of elastomers to model fuels containing various concentrations of methanol.

<i>References</i>	<i>Elastomer</i>	<i>Permeability (g-mm/m<sup>2</sup>/day)</i>					
		<i>Volume percent methanol in ASTM Fuel C</i>					
		<i>0</i>	<i>10</i>	<i>15</i>	<i>20</i>	<i>2.75 + TBA 2.75</i>	<i>85</i>
a	NBR-33	1212		2419			361
d	NBR-34	541			1400	891	
k		720		1920			336
d	NBR-34/PVC	294			1321	390	
d	NBR-34/BIIR	875			1257	1472	
d	NBR-34/CSM	915			2665	1194	
a	HNBR-45	369		1421			319
a	FVMQ	597		1067			357
a	FKM-A-66	2.2	50	50			122
c		4.0					95
h		1.0					
a	FKM- B-66	2.1		50			250
a	FKM-GLT-65	5.0		97			461
a	FKM-B-68	1.9	25	21	32		13
c		2.0					43
h		1.0					
a	FKM GF	1.7		6			1.7
c		1.0					17
a	FKM GFLT-67	3.2		24			17

**Table B3** - Permeability of thermoplastics to solutions containing various concentrations of MeOH

<i>References</i>	<i>Thermoplastic</i>	<i>Permeability (g-mm/m<sup>2</sup>/day)</i>				
		<i>Volume percent methanol in ASTM Fuel C</i>				
		<i>0</i>	<i>15</i>	<i>20</i>	<i>85</i>	<i>100</i>
e	PTFE	0.06		0.23		0.09
g		0.15				
a	FEP	0.18	0.25	0.13	0.28	
g				0.18		
a	PFA	0.18	0.38	0.05	0.35	0.05
e, g		0.01		0.13		
a	ETFE	0.18	0.43	0.04	0.38	0.03
e		0.02		0.13		
g		0.09				
j	HDPE	36	46			20
j	PA-6 plasticized	5	50			36
f	PA-11					18
f	PA-11 plasticized					40
a	PA-12	8.8	100	1.35	102	
g		1.53				
j		41	27			40
j	PA-12 plasticized	34	53			60
g	PA-12,12			1.35		

**Table B4** - Permeability of elastomers to model fuels containing various concentrations of EtOH.

<i>References</i>	<i>Elastomer</i>	<i>Permeability (g-mm/m<sup>2</sup>/day)</i>				
		<i>Volume percent ethanol in ASTM Fuel C</i>				
		<i>0</i>	<i>10</i>	<i>15</i>	<i>20</i>	<i>85</i>
b	NBR	304	1000			
d	NBR-34	541			1066	
d	NBR-34/PVC	294			700	
d	NBR-34/BIIR	875			995	
d	NBR-34/CSM	915			923	
a	NBR-33	1212	2037			
i			1026			
a	HNBR-45	369	1001			
a	FVMQ	597	857			
a	FKM-A-66	2.2	10.0			21
b		4	100			
c			28.0			
a	FKM- B-66	2.1	11.0			
b			53.0			
a	FKM-GLT-65	5	20.0			
a	FKM-B-68	1.9	5.9			14
b		2	70.0			
c			19.0			
i			4.0			
a	FKM GF-70	1.7	2.2			9
b		1	35.0			
c			12.0			
i			1.1			
a	FKM GFLT-67	3.2	8.4			

**Table B5** - Permeability of thermoplastics to solutions containing various concentrations of ethanol.

<i>References</i>	<i>Thermoplastic</i>	<i>Permeability (g-mm/m<sup>2</sup>/day)</i>	
		<i>Volume percent ethanol in ASTM Fuel C</i>	
		<i>0</i>	<i>10</i>
a	FEP	0.18	0.13
i			0.03
a	PFA	0.18	0.15
a	ETFE	0.18	0.15
a	PA-12	8.8	33

a) Stahl et al. SAE 920163

b) Stevens et al SAE 97037

c) Bauerle Lubrication Eng.

d) Dunn and Pfister SAE 800856

e) Goldsberry SAE 930992

f) Vasselin, Private communication

g) Goldsberry et al. SAE 910104

h) Stevens SAE 880022

i) Fuller & Stevens SAE 960140

j) Weber et al 910304

k) Puisais

**Table B6** - Permeability of hose constructions to model fuels containing alcohols.

<i>Reference</i>	<i>SAE spec hose</i>	<i>Time (days), Permeance (g/m<sup>2</sup>/d)</i>			
		<i>Volume percent ethanol or methanol in ASTM Fuel C</i>			
		<i>0</i>	<i>E10</i>	<i>E15</i>	<i>M15</i>
	30R7 NBR/CSPE	5, 500	5, 630	4, 640	5, 820
	30R8 CO/CO	7, 180	5, 450	5, 400	6, 800
	30R9 FKM lined	12, 4	13, 15	13, 13	9, 90

## APPENDIX C

### Physical and Chemical Description of Common Fuel Resistant Elastomers (Puisais)

<i>Material Trade Names</i>	<i>Structure Vulcanization</i>	<i>Mechanical Properties</i>	<i>Chemical Properties</i>	<i>Thermal Properties</i>	<i>Other Properties</i>	<i>Applications</i>
<i>Chlorinated Elastomers</i>						
<b>Polychloroprene (CR)</b>  Baypren Neoprene Perbunan Santoprene	Polymer of chloro-2 butadiene 1,3 (chloroprene).  <i>Vulcanization</i> By metallic oxides (Zn, Mn)	Good resistance to repeated flexure, abrasion, tearing.  Low residual deformation by compression.	Good resistance to aliphatic hydro-carbons. Poor resistance to aromatic and chlorinated hydro-carbons. Not as resistant to hydro-carbons as NBRs. Excellent resistance to ozone and weathering	Limited thermal resistance (95°C in continuous service), resistance to cold until 20°C (embrittles at -40°C).	Low permeability to gas; good flame resistance; average electrical properties; good adhesion to metals and fibers/cloth.	Petroleum: tank covers, tubes, inflatable reservoirs  Automotive: Spark plug covers; electrical connectors; motor supports; electrical wiring covers
<b>Epichlorohydrin (CO, ECO)</b>  Hydrin Herclor Gechron Epichlomer	Homopolymer: Epichlorohydrin (CO). Copolymer: Epichlorohydrin and ethylene oxide (ECO). Terpolymer: Epichlorohydrin, ethylene oxide, allyl glycidyl ether  <i>Vulcanization</i> Diamine, urea, or thiourea; or 2-mercapto imidazole	Constant hardness over a large temperature range (-20° to 170°C)  low residual compression	Good resistance to oils, gasolines and solvents (low swelling) except in ketones and chlorinated solvents excellent ozone resistance low resistance to water vapor at elevated temperatures.	Good temperature resistance to 135°C excellent flexibility to low temperatures (especially ECO: -40°C)	Low permeation to gas comparable to butyl, superior to polychloroprene and NR low electrical isolation low cost	flexible fuel lines and oil refrigerants; piping systems, diaphragms, pumps.
<b>Polyethylene Chlorosulfone (CSM)</b>  Hypalon Herclor	<i>Vulcanization</i> By magnesium oxide.	Good resistance to tension and abrasion poor tear resistance. Average dynamic properties.	Good resistance to oils and aliphatic hydrocarbons; poor resistance to aromatic hydro-carbons. Excellent resistance to ozone and weathering, acids.	Thermal resistance to 120°-135°C continuous flexible in cold from -18°C to -23°C.	Good electrical properties to 600V; low permeation to humidity and gases; changes colors. Excellent flame resistance.	Petroleum: reservoir membranes; cable covers; airtight gaskets. Automotive: electrical wiring covers; flex hose connections.
<i>Fluorinated Elastomers</i>						
<b>FKM</b>	There are at least many	Good in tensile and to	Excellent chemical	Excellent resistance to	Good electrical properties	oleum:

Compatibility and Permeability of Oxygenated Fuels to Materials  
in Underground Storage and Dispensing Equipment

Viton Fluorel	types of fluorinated elastomers, which are commonly based on copolymers or terpolymers of: vinylidene fluoride, tetra-fluoroethylene, hexafluoropropylene, and perfluoromethylvinylether.  <i>vulcanization</i> oxides, diamines, and bisphenols.	tearing remarkable resistance to compression-set	resistance in a large range of temperatures. Low swelling in oils, fuels, lubricants, aliphatic and aromatic hydro-carbons, mineral acids. Excellent resistance to atmospheric oxidation and weathering sensitive to water vapors poor behavior to esters, methanol, ketones, amines poor resistance to amine based corrosion inhibitors. Increasing Fluorine content generally improves chemical resistance.	temperatures resist oils up to 150°C good cold resistance (dynamic from -20° to -40°C according to grade; static to -54°C)	very low permeation	Wellhead joints; flexible hoses for fuel transport; pumps; cable covers.  omotive: Shafts; rods; valve stems; gasoline filters; fuel injectors; gasoline pumps; carburetor tubing; carburetor valves.
M Kalrez Chemraz	polymer of TFE and of perfluoromethylvinylether.	similar to FKM.	resistant practically to all products, except halogenated solvents.	optional thermal resistance to 290°C (continuous); better resistance to cold than the Viton (usable to -30°C).	flammable; elevated dielectric rigidity; very high cost.	
as	polymer of TFE and propylene.  <i>vulcanization</i> By peroxide in association with triallylisocyanurate, at 150° - 180°C and post cured. By diamine	Good rupture resistance, but mediocre residual compression	Excellent resistance to hydrocarbons, lubricants, hydraulic fluids excellent resistance to hydrogen sulfide and carbon dioxide good resistance to amine-based corrosion inhibitors	Resistance to elevated temperatures (200°C continuous) mediocre resistance to cold.	Exceptional electrical resistance good resistance to blistering mediocre resistance to metal	Petroleum: Exposure to high vapor temperatures; corrosive oils; amine-based corrosion inhibitors; hydrogen sulfide and carbon dioxide;  omotive Hydrocarbons at high temperatures; inferior resistance to gasolines, except gasohols.
FVMQ Fluorosilicone  Silastic FE300	Polymethyltrifluoropropylsiloxane family.  <i>Vulcanization</i> By peroxide	Maximum tensile resistance to 1450 psi.	Good resistance to aliphatic hydrocarbons; poor resistance to aromatic hydrocarbons; moderate resistance to oxygenated compounds.	Good thermal resistance to 175°C. excellent resistance to low temperatures -80°C.		

<i>Material Trade Names</i>	<i>Structure Vulcanization</i>	<i>Mechanical Properties</i>	<i>Chemical Properties</i>	<i>Thermal Properties</i>	<i>Other Properties</i>	<i>Applications</i>
<b><i>Nitrile Elastomers</i></b>						
NBR	NBRs are copolymers of butadiene-acrylonitrile. The butadiene causes the nitrile to be supple and flexible at low temperatures. The acrylonitrile brings about resistance to hydro-carbons and good permeation resistance to gas. <i>Vulcanization</i> By sulfur; by peroxides.	Good static mechanical property. The rupture resistance and the hardness are elevated when the ACN content is higher. Good resistance to abrasion. Inferior dynamic properties.	Good resistance to hydrocarbons. Mediocre resistance to polar compounds. Loses all elasticity in the presence of hydrogen sulfide.	Limited temperature resistance (100° to 120°C). good resistance at low temperatures.		Petroleum Handling and transportation of hydrocarbons; uses in hoses for loading/unloading of tankers.  <i>notive</i> lever joints; airtight joints.
man N n prene N r igum ac ril im						
<b>. Carboxylated Nitriles (XNBR)</b>	polymer of butadiene, ACN, and carboxylic acid..  <i>ization</i> sulfur; by metallic oxides.	<i>erties</i> acterized by exceptional resistance to abrasion; excellent mechanical properties; excellent adhesion to metals.				<i>ications</i> external electrical cable sheaths; turning joints; anti-explosion joints for well shafts.
ac 211-221 Hycar 1072 605 Chemigum NX775						
<b>. Hydrogenated Nitriles</b>	polymer of butadiene-ACN.  <i>ization</i> ly saturated HNBR's are vulcanized by peroxides. Partially saturated HNBR's are vulcanized by sulfur or peroxide.	Excellent static property low retention to compression good dynamic properties excellent abrasion resistance	Excellent hydrocarbon resistance excellent resistance to water vapors at 150°C excellent resistance to amine-based corrosion inhibitors excellent resistance to hydrogen sulfide and carbon dioxide gases	Good heat resistance can be utilized continuously in temperatures to 140°-150°C. good properties at low resistance.	Good resistance to blistering.	
Therban Tornac Zetpol						
<i>Material Trade Names</i>	<i>Structure Vulcanization</i>	<i>Mechanical Properties</i>	<i>Chemical Properties</i>	<i>Thermal Properties</i>	<i>Other Properties</i>	<i>Applications</i>

*Acrylic Elastomers*

<p><b>Alkyl and alkoxyacrylics (ACM)</b>  Hycar</p>		<p>Good mechanical property, excellent resistance to compression set.</p>	<p>Good resistance to hydrocarbons excellent resistance to transmission fluid, hypoid oils.</p>	<p>Thermal resistance to -40°C and 150°-160°C.</p>		
<p><b>Acrylic Ethylene (AEM) (Vamac)</b>  Vamac</p>	<p>A copolymer of ethylene and of methylacrylate, with a monomer created at the vulcanization sites. Vulcanization composed of guanidine and primary diamine</p>	<p>Good tear resistance good resistance to fatigue by flexure good vibration resistance from -30°C to 160°C</p>	<p>Good resistance to oils, to weathering and ozone</p>	<p>Good thermal stability to 170°C good behavior at low temperatures; becomes brittle at -40° to -50°C. good fire resistance</p>	<p>Low permeation to gas; good electrical properties; good adhesion to metals and other supports; moderate costs.</p>	<p><i>Petroleum</i> Cable sheaths due to its good fire resistance; flexible hoses for acid gas service.  <i>Automotive</i> Vamac is used extensively in automobiles due to its thermal resistance to oils; its flexural fatigue resistance; its flexibility at low temperatures; its wear resistance.</p>
<i>Polysulfides</i>						
<p>Polysulfide (S)  Thiokol FA Thiokol ST</p>	<p>A copolymer of  <i>Vulcanization</i> At ambient temperature by zinc oxide.</p>	<p>Poor</p>	<p>Good resistance to aging and ozone. excellent behavior to oils (superior to nitriles), fuels, and hydraulic fluid. insensitive to water, alkalines, and diluted acids</p>	<p>Limited thermal resistance to 135°C, but excellent behavior in cold. Temperature extremes (-55° to 135°C or -75° to 105°C according to grades).</p>	<p>Disagreeable odor; good adhesion to metal</p>	<p>Caulks and sealants</p>

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