Harold Haskew & Associates, Inc.
425 W. Huron, Suite 230
Milford, MI 48381
(248) 684 3410

May 31, 2001

Dean Simeroth, Chief
California Air Resources Board
2020 L. Street
P.O. Box 2815, 4th Floor
Sacramento, CA 95812

Dear Dean,

Attached find my contribution to the California Air Resources Board (CARB) in the matters of permeation and evaporative emissions. This report is submitted in fulfillment of the contract between HH&A and ARB known as ARB Agreement #99-404 with Amendment #1.

Harold Haskew and Associates, Inc. (HH&A) appreciates the opportunity to submit this information, and hope it meets your requirements and expectations.

Thank you.

Harold M. Haskew, P.E.
President

Concerning

Evaporative Emission Effects (Permeation) Created by Ethanol in Gasoline

Submitted to

California Air Resources Board
In Fulfillment of #99-404

May 31, 2001

by
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Created by Ethanol in Gasoline

Overview:

California has banned the use of MTBE in gasolines starting in the year 2003. Federal law (The Clean Air Act Amendments of 1990) require the use of an oxygenate in most of California's gasolines. The only practical other choice for an oxygenate is ethanol. The substitution of ethanol for MTBE (in 2003) in California's gasoline will increase the evaporative emissions (HC) of the existing fleet, mainly because ethanol increases permeation.

Permeation is the migration of molecules through the various elastomers that are included in the vehicle's fuel system.

California's fleet of in-use vehicles in 2003 will contain a mix of new and older vehicles. The older models (some over 30 years old) are thought to have a high sensitivity to the permeation increase from ethanol. While the newer vehicle models have been designed with ethanol's effects considered, there is still a net increase in HC emissions.

There will also be a corresponding increase in emissions due to permeation from the non-road component of gasoline powered equipment, including lawn and garden equipment, and plastic fuel storage containers.

The objective of this report is to outline a process for estimating the increase in evaporative emissions due to permeation created by the ethanol.

This report is organized into sections on:

- Permeation
- Tons per Day
- Vehicle Technology
    - o Carburetor
    - o Throttle Body Injection
    - o Port Fuel Injection
- Plastic Tanks
- Test Program
- Summary
- Appendix
    - RFG2 and RFG3 Specifications
    - Lower Aromatics?

Permeation

The focus of this report is the increase in permeation due to the addition of ethanol. Permeation is the migration of hydrocarbons through any of the materials used in the fuel system. Metals are thought to have zero permeation. Elastomers, used for hoses and seals, are permeable, as are relatively rigid materials like polyethylenes and nylon. Plastic fuel tanks, nylon fuel hoses, and nylon carbon canister bodies all have some degree of permeation.

Published permeation rates show a wide range of values for various materials used in automobiles, and a similar wide range in increases resulting from ethanol. The table below was found in SAE 920163 to illustrate these points. NBR, or Nitrile Butadiene Rubber, was commonly used for hoses and seals in pre-enhanced evap control systems. Nylon is commonly used for chassis fuel lines, vapor hose bundles, and canister bodies.

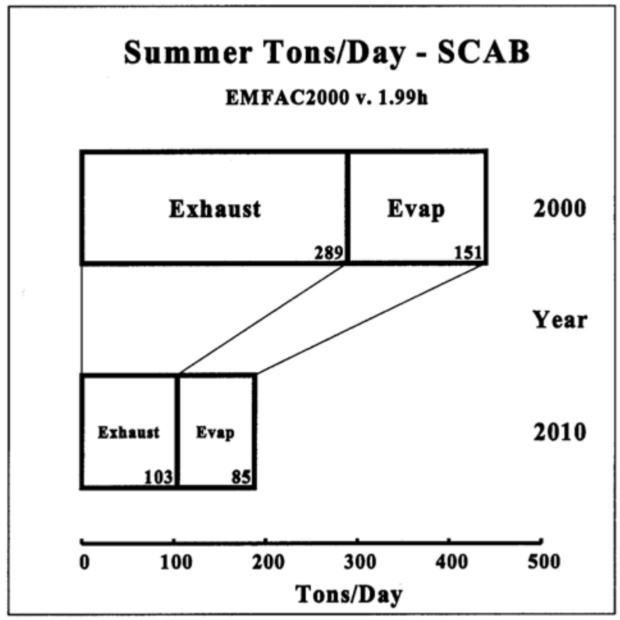
"Viton" is a trade name for a family of floroelastomers made by DuPont. The FKM GFLT is recommended by DuPont for exposure with automotive fuels containing oxygenates.

Table 1 - Part B
Average Permeation Rate (g x mm)/(m2 x day)

Material	Fuel C	10% Ethanol	% Increase
NBR (33% ACN)	669	1028	54
FVMQ (Fluorosilicone)	455	584	28
HNBR (44% ACN)	230	553	140
Nylon 12	5.5	24.0	336
FKM GLT (65% F)	2.6	14.0	438
FKM GFLT (67% F)	1.8	6.5	261
FKM A200 (66% F)	0.8	7.5	838
FKM B70 (66% F)	0.8	6.7	738
FKM B200 (68% F)	0.7	4.1	486
FKM GF (70% F)	0.7	1.1	57
PFA 1000LP	0.1	0.03	-40
FEP 1000L	0.03	0.03	0
ETFE 1000LZ	0.03	0.1	67

Tons per day

The ARB's EMFAC2000 emissions inventory model estimates that the light duty vehicle HC contribution to daily inventory drops from 151 to 85 ton/day in the South Coast Air Basin (SCAB) between the years 2000 and 2010, as shown in the plot to the right. This significant decrease is a hard-fought result of many programs, but still falls short of the overall decrease needed to meet the air quality goals.



Senate Bill 989, a.k.a. the Sher Bill[1], added Section 43013.1 to the Health and Safety Code, and reads (in part) at (b) "The state board shall ensure that the regulations for California Phase 3 Reformulated Gasoline (CaRFG3) adopted pursuant to Executive Order D-5-99 meet all of the following conditions: (1) Maintain or improve upon emissions and air quality benefits achieved by California Phase 2 Reformulated Gasoline as of January 1, 1999, including emission reductions for all pollutants, including precursors, identified in the State Implementation Plan for ozone, and emission reductions in potency-weighted air toxic compounds. …"

The Sher bill sets a very difficult standard for the new fuel. EPA requires oxygenate in the road fuel. The only non-MTBE oxygenate available (ethanol) increases evaporative emissions, by an as yet unquantified amount. No increase is allowed, therefore the magnitude of the permeation increase must be estimated, and offset by reductions in other areas of equivalent tons. The Sher Bill does not appear to limit the impact to just that created by mobile on-road sources -- off-road sources including lawn and garden equipment must also be evaluated.

Grams per day – There are roughly 24 million motor vehicles in California. A one-gram per day increase adds 26 tons per day to the statewide inventory. To convert grams per day per vehicle to tons per day per million vehicles, one would multiply:

1 g/day x 1,000,000 vehicles /2,000 x 454 g/ton = 1.1013 tons/day/million vehicles

If one assumes that California has 24 million vehicles, and ethanol adds one g/day to the fleet, then the statewide increase is 24 x 1.1013 or

26.4 tons/day

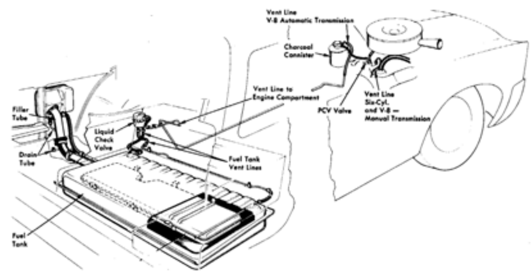
[1] Signed by the Governor on 10/8/99 and filed with the Secretary of State on 10/10/99

The technology of the vehicles in the 2003 time frame

A wide variety of vehicles and vehicle fuel systems will be in place in 2003. A small portion of the vehicles, i.e., the pre 1970 models, will actually pre-date any emission controls. The 1970 through the 1988 model year systems are for the most part carburetor systems with simple control systems. The newest vehicles are the post 1994 models designed to meet the real-time, or enhanced, evaporative regulations. The magnitude or the net change in permeation may be different for the various technologies that are part of California's in-use fleet.

California's EMFAC2000 model has used technology fractions based on fuel system types, i.e.:

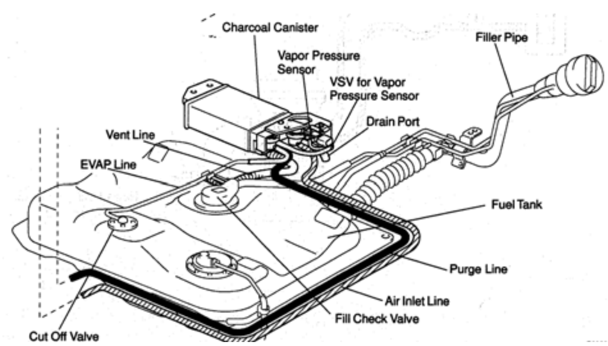
- Carburetor (Carb)
- Throttle Body Injection (TBI), and
- Port Fuel Injection (PFI)



Vapor emission control system components

In a macro sense, all three systems have similar fuel system layout and features. Fuel tanks are typically at the rear of the vehicle, engines are at the front, and chassis line(s) carry the fuel forward from the tank to the engine, and on many models return some fuel back. The differences lie in the pressures used, the durability and performance requirements of the emission regulations, and the demands of the market place.

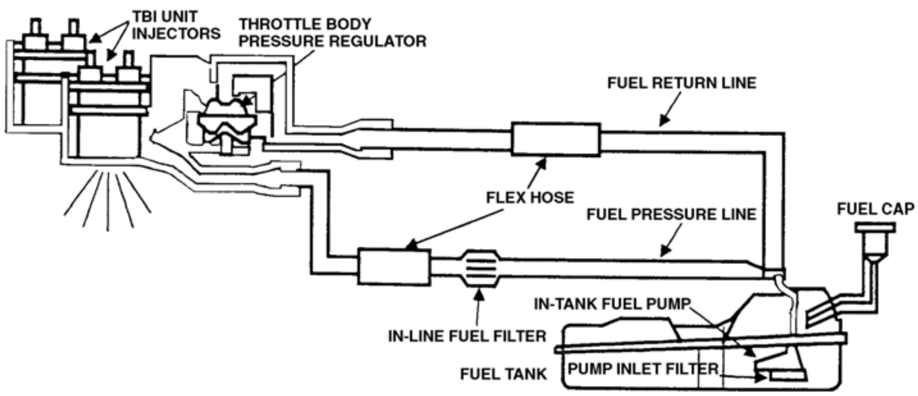
Carburetor Vehicles - Vehicles with carburetors featured low pressure (4 to 6 psi) fuel systems. The fuel tank was typically mounted at the rear of the vehicle. Steel chassis lines ran from the tank to the engine. Mechanical fuel pumps were typically mounted low on the engine, and supplied fuel to the carburetor when the engine was running. Flexible connections (hoses, often of Nitrile Butyl Rubber or NBR) were fitted to allow for service, and relative motion between the elements. It was also common, if not required, on air conditioned models to feature a vapor return line that allowed a small amount of fuel to bleed back to the tank, requiring another chassis line, and another pair of connectors at each end. The chassis fuel supply line, and the vapor return line operated close to atmospheric pressure.



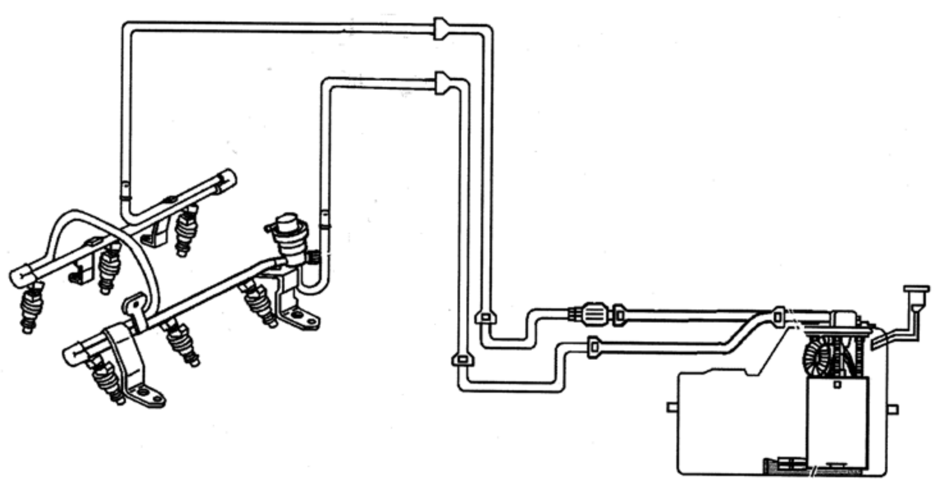
The fuel fill neck was sometimes a separate part from the fuel tank, and had a flexible rubber connection, much like a radiator hose, that joined the two. The major permeable elements consisted of the connections between the fuel tank and the chassis line, the chassis line and the engine, and the fuel fill neck connector, if so fitted. Minor permeable elements were the tank gage sending unit seal, and the mechanical fuel pump diaphragm, which vents to the atmosphere.

Most of these components were in contact with liquid fuel, or saturated fuel vapor, and would therefore be sensitive to fuel changes that affected permeation. Rubber components had very high permeation sensitivity.

TBI - The layout of the Throttle Body Injection (TBI) systems was similar to the carburetor system, except the fuel pump was generally mounted in the tank, and supplied fuel under pressure, e.g., 10 psi, through the chassis line to the engine and the injection unit. An in-line, servicable filter, sometimes using soft hoses to connect it to the chassis line, was typical of the application. An engine mounted pressure regulator was fitted, with a line that returned excess fuel to the tank. The fact that these lines were under pressure, and the durability requirements of regulations and the market place, resulted in higher performance materials, with lower permeation being fitted.



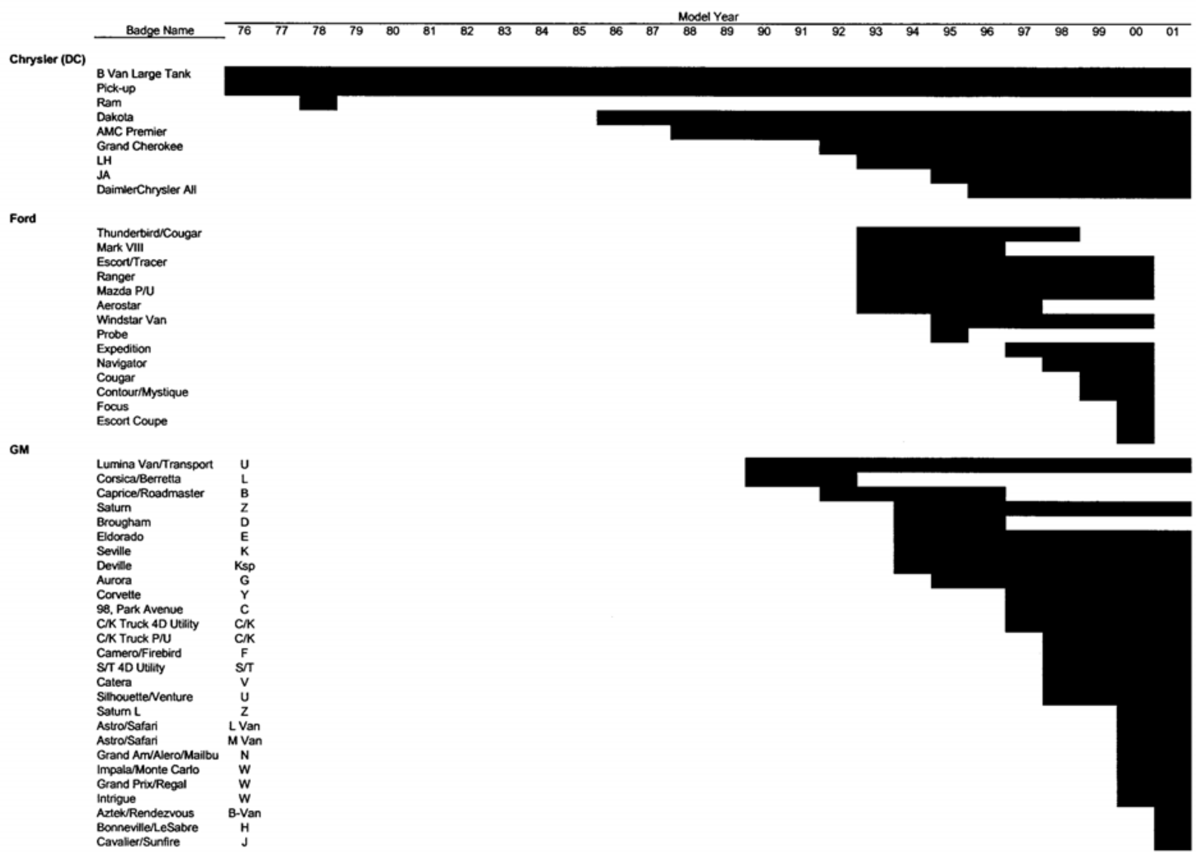
PFI - Port Fuel Injection (PFI) systems became the fuel system of choice during the late 80's and after. PFI systems used much higher system pressures (40 to 60 psi) to provide better fuel atomization at delivery and prevent vapor formation in the lines during hot operation. Given this high pressure, and the rollout of the real-time evaporative emission test requirements in the late 90's, higher grade elastomers were used.



Issues concerning plastic tanks

Vehicles featuring plastic tank were first offered in the US market by Chrysler Corporation as large tank options on trucks in the late 70's. Large volume applications of plastic tanks did not occur until the 90's, when the GM and Ford applications rolled out. Plastic fuel tanks become an issue when permeation is involved, mainly due to the large surface area of the tank.

The chart below and comments that follow were made from information supplied to HH&A by Toyota, Honda, GM, Ford and DaimlerChrysler. Historical records do not appear to be available to verify actual application volumes.



Honda did not use any plastic tanks until 1998, and then at only 5.5% of US volume. Toyota has only offered one model, the 1994-1998 Supra, now discontinued, with a plastic tank.

High-density polyethylene (HDPE) has been the plastic of choice for fuel tanks for a long time[2]. That gasoline would permeate through un-treated HDPE was well-known,

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[2] SAE 920164, "Permeation of Gasoline-Alcohol Fuel Blends Through High-Density Polyethylene Fuel Tanks with Different Barrier Technologies", D.J. Kathios, et al., SAE Congress, Detroit, Feb 24-28, 1992

and barrier treatments (e.g., florination, sulfonation) were developed to reduce permeation losses. Permeation was shown to be highly temperature dependant. SAE 920164 quoted 3 grams per day as the permeation rate for a 22 gallon tank at 20°C, increasing to as much as 30 grams/day at 50°C.

These rates were even higher if ethanol was present.

The more stringent evaporative emissions of the late 90's lead to the development of co-extruded multi-layer fuel tanks with thin, continuous layers of a reduced permeation component in the middle. Permeation from future plastic tanks are thought to be zero by any practical measure.

Portable Fuel Containers – The increase in emissions that result from the addition of ethanol to California's gasoline in 2003 is not limited to motor vehicles. A recent regulation on portable fuel containers[3] addressed the permeation of the in-use plastic cans. The average permeation rate was reported to be 1.57 g/gal/day as a result of their testing. Statewide, this was predicted to be approximately 8 tons/day in 2007. (A later report[4] estimated the inventory as 7.2 tons/day in 1998.) A test report supporting the estimates[5]concluded that alcohol based oxygenated fuel increases permeation rates of the untreated containers by more than 60%. The incremental increase in permeation from plastic containers is therefore estimated to be 8 x .60 or 4.8 tons/day, just for the plastic portable fuel cans.

Lawn and Garden Equipment - The fuel tanks on many lawn and garden products are made of HDPE and should have equivalent permeation characteristics. One might estimate therefore that the off road component of permeation increase is at least 10 tons per day.

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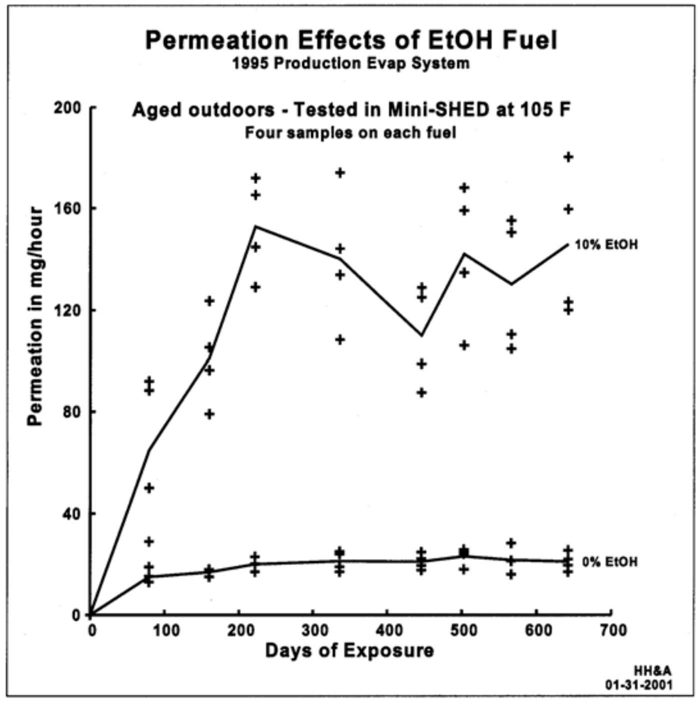
3 "Staff Report: Initial Statement of Reasons for Proposed Rule Making Public Hearing to Consider the Adoption of Portable Fuel Container Spillage Control Regulations", CA ARB Monitoring and Laboratory Division, Release Date August 6, 1999

4 "Public Meeting to Consider Approval of California's Portable Gasoline-Container Emissions Inventory", Mail-out MSC 99-25, September 23, 1999

5 "Test Protocol and Results for the Determination of Permeation Rates from High Density Polyethylene Containers and Barrier Surface Treatment Feasibility Study", Monitoring and Laboratory Division, May 19, 1999

A test program to estimate permeation rates

The quantification of real-time permeation increases with ethanol fuels will require new experimental work, as the existing data is too limited to allow a projection for the entire fleet. A "quick" test program to establish if permeation increases are expected on a class or category of vehicles can be designed.



The data shown in the plot to the right was gathered by a major vehicle manufacturer to estimate the emissions effect of E10 on a 1995 model year fuel system. Eight vehicle fuel systems (with steel fuel tanks) were assembled on "test bucks", filled with test fuel, and allowed to stabilize in the outdoor environment over a period of almost two years.

Periodically the test bucks were brought into a laboratory, allowed to stabilize at 105°F, and then tested for one hour at constant temperature in a mini-SHED. The hourly emission rates for the E10 fuel were over six times higher than the E0 fuel.

The outdoor experience of this test was started in late November. Stabilized emission rates would have been expected to occur sooner if the exposure temperature was higher. The dip measured in permeation for the E10 tests at days ~450 was a result of seasonal temperature exposure (i.e. winter), and has been seen in other data sets.

The hourly permeation rate on the E0 fuel was about 20 mg at 105°F. Over a 65 to 105°F daily test cycle the 24 hour total might be 10 times the 105°F hourly rate, or 0.2 grams per day. That number seems reasonable for an estimate for the permeation contribution to the enhanced evap emission test (approximately 1 gram for the diurnal + hot soak). The E10 increase in permeation would add therefore 10 times the 140 mg difference, or add 1.4 grams per day to the evap emissions total.

It is proposed that a "quick test program" might be designed following a similar protocol. An outline of the proposal is as follows:

- Select a Laboratory to conduct the project and make the measurements.

- Decide on a representative test sample, using 6 samples, like

		1st Choice	2nd Choice
Carburetor			
	Metal Tank	1985 Honda Accord	1984 Chev Suburban
	Plastic tank	!984 Dodge Pick-up	
TBI			
	Metal Tank	1985 Ford Tempo	1989 Chev Suburban
	Plastic Tank	1992 Chev Caprice	1989 Chrysler Sundance
PFI			
	Metal Tank	1994 Toyota Camry	1994 Ford Mustang
	Plastic Tank	1993 Ford Ranger	1994 Toyota Supra

- "Borrow" the selected vehicles from local California sources

- Carefully remove the test components, replace with new service parts, and return the vehicle to the owner.

- Carefully reassemble the test components on fabricated test rigs

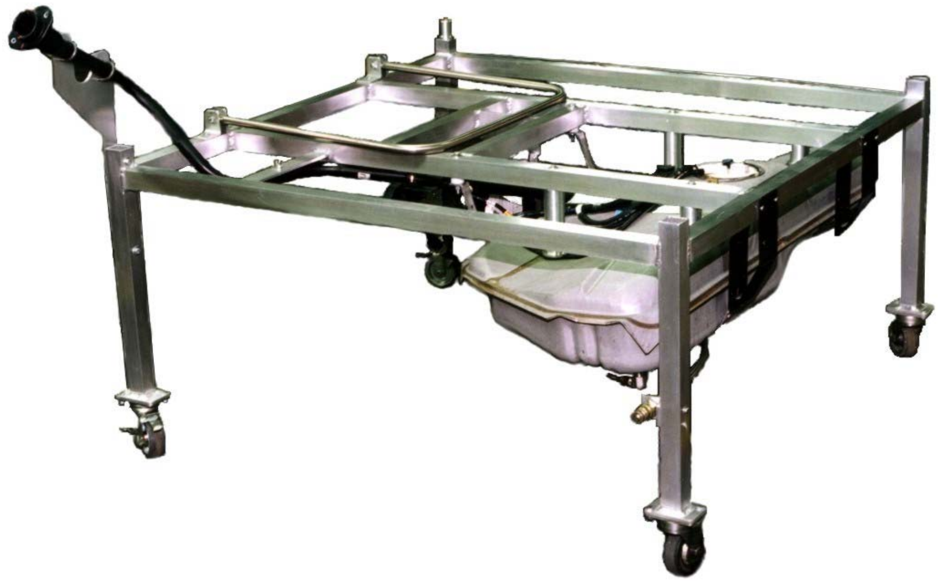
- Fill with CA Phase II fuel, and restabilize for 60 days at 105°F, periodically testing if desired.

- Test each system for 2 days using the CARB 2 day test diurnal protocol

- Drain and fill with CA "Phase 3" (5.7v% EtOH)

- Age the rig at 105°F, testing for emissions each week, for a total of 26 weeks if the emissions continue to increase over the previous reading

The Test Rig



A photo of a typical test rig used by industry is shown above. Such rigs are regularly used for fuel system development. Such a rig is envisioned to study the permeation differences with the ethanol fuel. Dimensions are varied to fit the systems requirements. The one shown above is approximately 4' x 4' and stands 3' off the ground. We will elongate the frame and add the engine fuel system components to this test rig to complete the system

The fuel system components that would be included are:

	Component	Carb	TBI	PFI
1.	Fuel Tank Assembly (Complete)	x	x	x
2.	Vapor Control Canister w/ hoses and parts	x	x	x
3.1	Chassis Fuel Lines (Coiled OK)	x	x	x
3.2	Rear Fuel hose(s)	x	x	x
3.3	Front Fuel Hose(s)	x	x	x
3.4	Servicable Fuel Filter (If Fitted)	x	x	x
4.	Engine Mounted Fuel System Components			
4.1	Carburetor with Air Cleaner	x		
4.2	Fuel Pump to Carburetor Lines	x		
4.3	TBI Assembly with Air Cleaner		x	
4.4	Fuel Rail Assembly with Injectors			x
4.5	Engine Mounted Fuel Pump (If Fitted)	x		

The Test Fuels – The test program envisioned is an "a" and "b" comparison of permeation. The baseline fuel will be a conforming California Phase 2 summer fuel. A supply sufficient for this test program (500 gallons) would be purchased and stored at the test facility, in sealed 55 gallon drums.

The "b" fuel, containing ethanol, will require some effort to procure. The base gasoline that will be mixed with the 5.7v% ethanol to make the Phase 3 conforming fuel is a unique gasoline. It will have very few of the lighter HC and must have a Reid Vapor Pressure (RVP) of 5.7. This is similar to the volatility of the "racing gasolines" used today. A public meeting is suggested to select a vendor for a fuel that represents the composition that is intended for the 2003+ summer product. Several vendors might offer to make conforming product. These could be mixed in equal volumes to make an average future gasoline.

Summary

A test program is suggested to quantify the permeation increase due to ethanol in gasoline, using 6 samples of components from the existing in-use population. It is estimated that such a program could be completed within 9 months from definition and funding. Private laboratories are qualified and available to perform this program, if the ARB laboratory is consumed with higher priority issues.

Appendix A

This table was extracted from the 45 day notice version of the RFG3 rule adopted 12/9/99, at section 2262.

The California Reformulated Gasoline Phase 2 and Phase 3 Standards

Property	***Flat Limits***		***Averaging Limits***		***Cap Limits***	
	CaRFG Phase 2	***CaRFG Phase 3***	***CaRFG Phase 2***	***CaRFG Phase 3***	***CaRFG Phase 2***	***CaRFG Phase 3***
Reid Vapor Pressure[1] (pounds per square inch)	7.00	7.00 or 6.90[2]	Not Applicable	Not Applicable	7.00	6.40 - 7.20
Sulfur Content (parts per million by weight)	40	20	30	15	80	60[3] 30[3]
Benzene Content (percent by volume)	1.0	0.8	0.8	0.7	1.2	1.1
Aromatics Content (percent by volume)	25.0	25.0	22.0	22.0	30.0	35.0
Olefins Content (percent by volume)	6.0	6.0	4.0	4.0	10.0	10.0
T50 (degrees Fahrenheit)	210	211	200	201	220	225
T90 (degrees Fahrenheit)	300	305	290[4]	295	330	335
Oxygen Content (percent by weight)	1.8 - 2.2	1.8 - 2.2	Not Applicable	Not Applicable	1.8 - 3.5[5] 0 - 3.5[5]	1.8-3.5[5,6] 0 - 3.5[5,6]
Driveability Index (DI)[7]	None	1225	Not Applicable	Not Applicable	None	None

Appendix B

Could Lower Aromatics Reduce the Permeation Increase?

Permeation rates in the elastomeric materials used in automobile applications involve three mechanisms, solubility, diffusion, and evaporation. First, the solvent must create some solubility in the surface interface to allow the permeant to enter the material. The second effect is one of diffusion through the polymer. Diffusion is concentration driven, and strongly affected by temperature. Finally, the solvent must evaporate from the outer surface to maintain the diffusion gradient.

Neat ethanol is sometimes shipped in high-density polyethylene (HDPE) drums, and permeation is effectively zero. If aromatics are added to the ethanol, the permeation rate suddenly increases, as HDPE is very soluble in aromatics. California's RFG3 fuel requirements allow up to 25% aromatics under the flat limits. (See Table in Appendix A) This is more than enough to create the start of the permeation. The question is: "Could the permeation increase caused by ethanol be reduced if lower aromatic content fuels were offered?"

Aromatics are an important ingredient in commercial gasoline. One of their most important properties is the increase in octane rating that they provide. An unknown question is how low the aromatic content would have to be to make the permeation increase of ethanol moot?

Discussions with industry contacts suggest that it is the presence of the aromatics that creates the solubility, not especially the concentration. The aromatic content might have to be reduced to near zero to prevent a permeation increase. A suitable test program could be designed around three levels of aromatics, 5, 15 and 25%, with and without ethanol. All six fuels would have to be specially blended to have the properties required by the RFG3 regulations. The evaluation would follow the test protocols outlined in this report.