Report No. SR88-12-01c

A Study of Excess Motor Vehicle Emissions - Causes and Control

Volume II (Sections VI-X)

The Effect of Gasoline Composition on In-Use Exhaust Emissions

Proposed Test Procedure and Emission Standard Revisions for Medium- and Light-Heavy-Duty Trucks Technical Support Document

Investigation of "Pattern Failure" Vehicles in the California Smog Check Program

Statutory Changes to Implement Recommended Improvements in the California Smog Check Program

Assessment of Options for a Post-1990 I/M Program

ARB Contract No. A5-188-32

prepared for:

State of California
Air Resources Board

December 1988

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PREFACE

This report presents the results of a major research study addressing the causes of excess emissions from California vehicles. The effort produced ten separate reports. This volume contains the last five reports produced under the contract. They are:

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The Effect of Gasoline Composition on In-Use Exhaust Emissions	VI
Proposed Test Procedure and Emission Standard Revisions for Medium- and Light-Heavy-Duty Trucks, Technical Support Document	VII
Investigation of "Pattern Failure" Vehicles in the California Smog Check Program	VIII
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The remainder of the reports produced under this contract are contained in Volume I. For an overview of all of the work produced under the contract, the reader is referred to:

> Executive Summary of Work Produced Under ARB Contract
> "A Study of Excess Emissions - Causes and Control",
> December 1988.

A STUDY OF EXCESS MOTOR VEHICLE EMISSIONS - CAUSES AND CONTROL

VOLUME II

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LIST OF ABBREVIATIONS

RADIAN
CORPORATION

245-050-05

SECTION VI
A STUDY OF EXCESS MOTOR VEHICLE EMISSIONS THE EFFECT OF GASOLINE COMPOSITION ON IN-USE EXHAUST EMISSIONS

FINAL REPORT
ARB Contract No. A5-188-32

Prepared for:

California Air Resources Board
P.O. Box 2815
Sacramento, California 95812

Prepared by

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"The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products."

ABSTRACT

A wide-ranging examination of the effects of gasoline composition on vehicle emissions was performed. The constituents of gasoline can have numerous effects on evaporative and exhaust emissions from gasoline fueled vehicles. For this review, six different fuel composition issues were studied. Additives and impurities such as lead, phosphorus, manganese, silicon, and sulfur were studied to determine their effect on emission control system components. Injector deposits in multi-point fuel injected vehicles were studied to determine their potential impact on exhaust emissions. Gasoline volatility was studied to determine if further reductions in Reid Vapor Pressure (RVP) would reduce vehicle emissions. The effect of RVP reductions on exhaust and evaporative emissions were quantified. The aromatic content of of unleaded gasoline was reviewed to determine the impact on benzene emissions. The effect of aromatic content on both exhaust and evaporative benzene emissions were evaluated. Exhaust and evaporative emission changes due to the addition of oxygenated blending agents, such as ethanol, methanol, and methyl tertiary-butyl ether also were studied. Finally, aftermarket additives such as octane-enhancers, lead substitutes, and pollution control additives, were studied to determine their effect on vehicle emissions.

ACKNOWLEDGEMENTS

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LIST OF ACRONYMS

ARB - California Air Resources Board
AMA - Automobile Manufacturers' Association
ASTM - American Society for Testing and Materials
BTX - Benzene, Toluene, and Xylene
°C - Degrees Celsius
CFR - Cooperative Fuels Research Test Engine
CO - Carbon Monoxide
CRC - Coordinating Research Council
EGR - Exhaust Gas Recirculation
EPA - United States Environmental Protection Agency
°F - Degrees Fahrenheit
FEVI - Front End Volatility Index
FTP - Federal Test Procedures
gm - Grams
gm/gal - Grams Per Gallon
gm/L - Grams Per Liter
gm/mi - Grams Per Mile
gm/quart - Grams Per Quart
H_2 - Hydrogen
HC - Hydrocarbons
H_2S - Hydrogen Sulfide
H_2SO_4 - Sulfuric Acid
I/M - Inspection and Maintenance
kPa - Kilopascals
mg/gal - Milligrams per Gallon
mi/day - Miles per day
MMT - Methylcyclopentadienyl Manganese Tricarbonyl
MON - Motor Octane Number
MPFI - Multi-Point Fuel Injection
MPG - Miler Per Gallon
MTBE - Methyl Tertiary-Butyl Ether
MVMA - Motor Vehicle Manufacturers Association

NIPER - National Institute for Petroleum and Energy Research
NO_x - Nitrogen Oxides
ORI - Octane Requirement Increase
PCV - Positive Crankcase Ventilation
PFI - Port Fuel Injection
ppm - Parts Per Million
psi - Pounds Per Square Inch
PTB - Pounds of Additive Per One-Thousand Barrels
R - Ratio of Reducing to Oxidizing Components in the Exhaust Gas
(R) - Registered Trademark
RON - Research Octane Number
RPM - Engine Speed in Revolutions Per Minute
RVP - Reid Vapor Pressure
SCAB - South Coast Air Basin
SO_2 - Sulfur Dioxide
SO_3 - Sulfur Trioxide
SO_x - Sulfur Oxides
TBA - Tertiary Butyl Alcohol
TBI - Throttle Body Fuel Injection
TEL - Tetraethyl Lead
tm - Trademark
TML - Tetramethyl Lead
VMT - Vehicle Miles Travelled
ZDDP - Zinc Dialkyldithiophosphates

EXECUTIVE SUMMARY

Based on a study of the effects of gasoline composition on motor vehicle emissions, Radian Corporation and Sierra Research have determined that excess emissions could be reduced through the implementation of the following recommendations:

- The maximum allowable lead level for unleaded gasoline should be reduced from 0.05 grams/gallon to 0.005 grams/gallon.
- The use of recycled materials in automotive gasoline should be prohibited unless analysis indicates that such materials are free from contamination by silicon or other metallic compounds known to be catalyst poisons.
- ARB should consider reducing the maximum allowable sulfur content of unleaded gasoline from 300 ppm to 100 ppm.
- The standard for the maximum allowable manganese content of unleaded gasoline should be established at approximately 0.012 grams/gallon.
- ARB should pursue a regulation that would require a minimum level of deposit control additives in unleaded gasoline.
- Because there is potential for achieving further emissions control, ARB should determine the net emissions impact of lowering the Reid Vapor Pressure (RVP) standard below the current 9.0 psi level.
- To avoid excess emissions from intermittent use, the volatility of alcohol-gasoline blends should be controlled to lower RVP than straight gasoline and all such blends should be required to demonstrate no adverse exhaust emissions impact.

- Aftermarket fuel additives containing lead should be prohibited from retail sale at locations which sell other automotive products.

Lead

The current tolerance level of 0.05 grams per gallon for lead in "unleaded" gasoline has not been changed since the mid '70s, despite a twenty-fold reduction in the lead content of leaded gasoline over that period. The legal lead concentration in unleaded gasoline is now up to one-half the legal lead content of leaded gasoline. Lead has been shown to reduce the efficiency of three-way catalytic converters at levels as low as 6 milligrams per gallon. The current tolerance level is also being abused by at least one blender, who regularly markets "unleaded" gasoline with lead levels approaching 0.05 grams per gallon. We recommend that ARB move immediately to reduce this tolerance level by a factor of ten, to 5 milligrams per gallon.

Silicon

Silicon contaminants in gasoline can damage catalytic converters and oxygen sensors by coating them with amorphous silica. There is no evidence that this has yet occurred in California, but incidents have been reported elsewhere in the U.S. The source of the silicon contamination was apparently recycled solvents containing silicone oils. Regulations prohibiting such recycling or requiring chemical analysis of the recycled material would prevent this problem from occurring in California. Combustion of thermal degradation of silicone rubbers, gaskets, sealants, etc. can also result in catalyst or oxygen sensor damage. ARB should examine the extent to which silicones are included in aftermarket products--some regulation of silicones in these products may be warranted.

Sulfur

The sulfur content of unleaded gasoline is presently limited to 300 PPM. In 1978, ARB staff recommended that this be phased down to 100 PPM in

1984, but this recommendation was not adopted by the Board. Reducing the sulfur content of gasoline would contribute to attainment of the SO_2 and sulfate standards in those areas now in violation of them, as well as reducing H_2S emissions from three-way catalysts. A slight increase in catalyst efficiency would also result, thus reducing HC, CO, and NO_x. ARB should re-examine the cost of further reductions in gasoline sulfur content, since the reduction in diesel fuel sulfur in force in the South Coast (and under consideration for the rest of the State) may have affected the costs of gasoline sulfur reduction as well.

Manganese

Manganese (as MMT) may legally be used as an antiknock in leaded gasoline, and is so used in some leaded gasoline sold in California. Due to the phase-out of lead, increased amounts of manganese may be used in the future. Contamination of unleaded gasoline with small amounts of manganese is likely as a result. Manganese increases engine-out HC emissions, but in low concentrations it has no major deleterious effects on catalysts. Thus, cross-contamination of unleaded gasoline with small amounts of manganese is unlikely to have much effect. To ensure against excessive contamination, however, ARB should establish a tolerance level for manganese in unleaded fuel. A tolerance level of 12.5 milligrams per gallon (one tenth the normal level in leaded gasoline) is suggested.

Deposit Control Additives

Multi-point fuel-injected vehicles are susceptible to injector deposits, and these can cause significant emission increases. The extent of the problem depends on vehicle design parameters and fuel composition. Both the automotive manufacturers and the petroleum industry are modifying their products to reduce the occurrence of this problem. Even so, most manufacturers of MPFI vehicles appear to have at least one model which is susceptible to deposits.

As a rough estimate, fuel injector deposits in passenger cars may have been responsible for 3,400 tons of excess hydrocarbon emissions and 34,700 tons of excess carbon monoxide emissions in 1986. Use of deposit control additives in sufficient quantities would reduce and possible remove the excess emissions. The quantity of excess emissions produced due to injector deposits is expected to increase as sales of multi-point fuel-injected vehicles increase in the coming year.

Because of the potential for significant emission increases due to injector plugging, ARB should pursue regulatory action in this area. Currently, it is not feasible to remove the deposit-forming constituents from the fuel because the deposit formation mechanism is not fully understood. At some future time, this may be an option. Because sensitive injectors will be in the fleet for at least another decade, and sales of MPFI-vehicles are expected to increase, mandatory use of detergents and dispersants in unleaded fuel is indicated. Rough cost-effectiveness calculations indicated that the costs per ton of emissions eliminated by mandating the most effective deposit control additives would be less than $8,750 per ton for HC and less than $850 per ton for CO. Due to the conservative nature of these estimates, the actual cost effectiveness could be better.

Establishment of a regulatory requirement for fuel detergency would require the specification of some standard detergency test procedure. No industry standard test procedure for injector deposit control exists at present, although a number of organizations have developed test procedures which might be adopted for this purpose. To assure against creating other problems further downstream, the test procedure would need to address carburetor, intake valve, and combustion chamber deposit formation as well as injector deposits.

Gasoline Volatility

Current ARB regulations limit RVP levels for gasoline during the "smog season" to a maximum of 9 psi. The time of year defined as "smog season" varies from air basin to air basin. This regulation was adopted in order to reduce evaporative emissions during periods of high photochemical reactivity. Reducing this maximum level further would further reduce evaporative emissions. At some point, however, this reduction would be more than offset by increased cold-start emissions due to inadequate fuel volatility. Analysis of limited test data from Chevron Research suggests that this optimal RVP level is probably less than 9, but greater than 6.1 psi for the South Coast Air Basin. Because of the limited data available, however, it is not possible to estimate the actual optimum with any confidence. Additional vehicle testing at different RVP values and ambient temperatures would be required to determine the optimum RVP.

Any drastic reduction in fuel RVP levels could be expected to result in driveability problems, especially under cold-start conditions. This could lead to additional tampering with emission controls, and possible further increases in emissions. This possibility should be taken into account in considering any future reduction in RVP levels.

Alcohol-Gasoline Blends

Increases in hydrocarbon evaporative and exhaust emissions may occur from the use of alcohol/gasoline blends. Intermittent refueling with blended gasolines will cause the tank RVP to increase above the volatility limit of 9 psi. Long-term use of alcohol/gasoline blends may reduce the capacity of the evaporative emission control system and further increase hydrocarbon emissions. Short-term increases in tailpipe NO_x may occur due to the use of alcohol/gasoline blends. If driveability problems associated with blend use are repaired in carburetted vehicles, the NO_x increase could give way to increases in HC and CO emissions.

Increased evaporative emissions may occur from using alcohol/gasoline blends due to volatility differences, evaporative emission control system degradation, and intermittent use. Because of the potential for evaporative hydrocarbon emission increases, ARB should consider additional volatility constraints for blended fuels.

The evaporative emissions increase due to intermittent use could be reduced by requiring blended fuels to have a maximum RVP below 9 psi. Maximum RVPs for blends of Oxinol®, ethanol, and TBA have been calculated. The maximum RVP varies from 5.5 for Oxinol® to 6.5 for ethanol and TBA blends. The reduced volatility would most likely result in decreased vehicle driveability when using the blended fuel. However, when intermittently used, the tank RVP would not be significantly greater than 9.0 psi. The possibility of increased exhaust emissions associated with lower volatility blends should be evaluated as part of the approval process.

Another issue that needs further evaluation is the apparent reduction in evaporative emission control system performance due to blend use. Oxygenated compounds are preferentially absorbed by the charcoal canisters. The higher weight alcohol compounds also more difficult to purge from the canister once they have been absorbed. Increasing the size of the charcoal canister may be one way to mitigate the decreased system performance. Adoption of the on-board vapor control regulation will most likely not mitigate additional evaporative emissions due to decreased system performance. The certification fuel will not contain oxygenates and therefore, the canister will not be sized to compensate for the additional evaporative emissions and system degradation due to oxygenate blends. This degradation needs to be better qualified.

Fuel Additives

Aftermarket fuel additives are currently marketed with claims that they remove water from fuel tanks, clean fuel systems and intake manifolds, enhance the octane rating of gasoline, act as lead substitutes to protect valve seats, and improve the performance of pollution control devices. The potential exists for some of these products to impair the performance of emission control devices and to increase emissions. However, since the ingredients of the majority of these components are unknown, no conclusion regarding their effect on vehicle emissions performance can be made. Of special concern is the fact that additives claiming to contain tetra-ethyl lead are readily available over-the-counter in auto parts stores.

It is recommended that ARB act in conjunction with EPA to re-evaluate their regulation and oversight of the aftermarket additive industry. Some demonstration of effectiveness, and of an absence of adverse emission control impacts, should be required in order for additives to be registered. Public access to additives containing lead and other substances that are known to cause significant detrimental impacts to emission control systems should be minimized. Products not intended for vehicles that use unleaded gasoline should have spouts that are too large to be inserted into the fillpipe restrictor. Products containing lead should not be sold in automotive parts stores since it is illegal to use these products in motor vehicles in California.

1.0 INTRODUCTION

This report presents the results of a wide-ranging examination of the effects of unleaded gasoline composition on vehicle emissions. The hydrocarbons, oxygenates, and additives incorporated in gasoline can have numerous effects on evaporative and exhaust emissions from gasoline-fueled vehicles. These effects range from poisoning of catalytic converters by lead and other additives to increased benzene emissions resulting from higher aromatic contents.

The recent upheavals in the oil market and the Federally-mandated phase-down of lead in gasoline to 0.1 gram per leaded gallon have also led to changes in gasoline composition. The loss of the octane boost due to lead has necessitated changes in refinery processing; and increased use of oxygenated components such as methanol, ethanol, and methyl tertiary-butyl ether, to make up the lost octane. These changes have affected the composition of unleaded as well as leaded gasoline, since the two products are drawn from much the same hydrocarbon pool at the refinery.

The U.S. Environmental Protection Agency has proposed a complete ban on lead additives in gasoline, effective in 1988. The proposed ban, which could become final this year, would have only minor effects on the total octane requirement. It is not clear what the effects of the lead ban on gasoline marketing patterns will be, however. One possibility would be the retention of some form of gasoline which -- while containing no lead-- would still contain other additives which are illegal for use in vehicles with catalytic converters. Such additives could include methylcyclopentadienyl manganese tricarbonyl as an octane-enhancer, and could also include phosphorus or other deposit-forming additives to substitute for lead as exhaust-valve lubricants.

The loss of lead-supplied octane has led to a general increase in the use of aromatic hydrocarbons, such as toluene and benzene in gasoline. The California Air Resources Board has identified benzene as a toxic air contaminant. Current research has shown that levels of benzene in vehicle exhaust are related both to the benzene content of the fuel and to the fuel's content of other aromatic hydrocarbons.

Changes in engine and emissions control technology are also placing new demands on gasoline composition. With the increased use of multipoint fuel injection for improved performance, as well as better hydrocarbon and carbon monoxide control, problems of deposit and varnish formation in the injection system have begun to surface. Certain high-performance engines have also displayed a tendency to form deposits on the intake valves. Automobile manufacturers have expressed concerns about gasoline quality, arguing that fuel injector plugging, vapor lock, and other volatility-related problems can be solved by modifying fuel composition.

To reduce emissions and improve engine performance, auto manufacturers are modifying their engine designs. The modifications include high swirl combustion chambers, increased compression ratios, and increased use of turbochargers. These engine design changes, in turn, are leading to additional demands on the performance properties of unleaded gasoline.

Because of these and other concerns, the California Air Resources Board commissioned Radian Corporation and Sierra Research to study the effects of unleaded gasoline composition on emissions. The study focused on the following issues:

- The effects of additives and impurities, such as lead, phosphorus, manganese, silicon, and sulfur, on emission control system components;

- The effect of injector deposits on emissions from multi-point fuel-injected vehicles;

- The effect of reducing gasoline volatility (as measured by Reid Vapor Pressure or other indices) below an RVP of 9 psi;
- The effect of unleaded gasoline aromatic hydrocarbon content on benzene emissions;
- The effect of using oxygenated blending agents, such as ethanol, methanol, and methyl tertiary-butyl ether on exhaust and evaporative emissions; and
- The effect of aftermarket additives, particularly octane-enhancers, lead substitutes, and pollution control additives, on vehicle emissions.

1.1 Nature and Scope of this Report

This report identifies fuel constituents that can affect vehicular emissions. Effects on both exhaust and evaporative emissions were studied. When possible, a specific mechanism causing an emission variation is identified. In addition, the report identifies areas requiring further study or or in which additional regulatory activity is indicated.

This study included a review of the applicable technical literature to determine typical fuel composition and to identify compounds that affect vehicle emissions. This information was supplemented by contacts with automobile manufacturers, refiners, and aftermarket additive suppliers, where possible. A shelf survey was made of automotive parts stores to determine what types of aftermarket additives are available to the public.

1.2 Structure of the Report

Section Two reviews the basic constituents of gasoline: crude oil components, blending agents, and additives. The properties of these constituents and the extent to which they can be found in unleaded gasoline are described. The emissions impacts of the various components are described. The Federal and State regulations governing fuel composition are also reviewed. Section Two is intended as an overview of gasoline composition and fuel regulations.

Section Three discusses the effects additives and impurities have on emission control system components. The potential for these effects to cause exhaust emission increases also is explored, and recommendations for regulatory action are presented.

Section Four reviews the need for detergent additives to minimize exhaust emissions, especially for vehicles with multi-point fuel injection. The effects of injector plugging vehicle emissions are described. The causes of injector plugging and the design variables that affect plugging are also discussed. Estimates of detergent use in gasoline sold in California and of the cost-effectiveness of detergency regulations are also presented.

The potential effects of further reductions in gasoline volatility on exhaust and evaporative hydrocarbon emissions are evaluated in Section Five. These effects include reduced evaporative emissions, but increase exhaust emissions due to poor cold-start performance. Recommendations for additional research to establish an optimum RVP level are presented.

Section Six analyzes the impact of gasoline constituents and emission control technologies on benzene emissions. Fuel composition variables that affect benzene emissions are described. Methods for reducing benzene evaporative and exhaust emissions are also reviewed.

Section Seven evaluates the impact of the increasing use of oxygenated compounds on total hydrocarbon and carbon monoxide emissions. The effects of oxygenates on emission control system components, gasoline properties, and emissions are described.

Section Eight describes the types of aftermarket additives available in California auto parts stores and similar retailers. The intended functions of these additives are reviewed, and what is known of their potential emission impacts is reported.

2.0 UNLEADED GASOLINE COMPOSITION AND PROPERTIES

Commercial unleaded gasoline is a complex mixture containing varying quantities of hundreds of individual hydrocarbon species. The mixture composition is affected both by the composition of the crude oil from which the fuel is refined and by the chemical processing undergone during refining. Finished gasoline is normally a blend of individual refinery process streams, each having a different chemical composition and properties. By varying the degree of processing of each stream, and the proportion of each stream in the final product, refiners can adjust the physical and chemical properties of the mixture to comply with applicable regulations and quality requirements. Blending agents such as oxygenates, and additives such as detergents, antioxidants, and corrosion preventives may also be added to the mixture to improve the combustion performance, stability, and other properties of the finished mixture.

A gasoline's performance properties and its effects on pollutant emissions are both determined by its composition. These properties are often interrelated. A gasoline with poor oxidation stability, for instance, may cause gum deposits in fuel filters and intake systems, resulting in poor driveability and higher emissions. A gasoline with inadequate antiknock properties (as measured by its "octane" number) may cause destructive engine knock, possibly leading the vehicle owner to advance spark timing or switch to a higher-octane leaded fuel to compensate.

This section reviews the primary constituents of unleaded gasoline and the key performance properties required of it. Gasoline blending agents and additives can have both major effects on gasoline performance and substantial emissions impacts, and are also reviewed in this section. Finally, this section briefly reviews current Federal and State regulations applying to unleaded gasoline.

2.1 Hydrocarbon Constituents of Gasoline

The primary components of unleaded gasoline are hydrocarbons produced from crude oil. Most of the hydrocarbons in gasoline fall into four basic classes:

- Paraffins;
- Naphthenes (also known as cycloparaffins);
- Olefins; and
- Aromatic hydrocarbons.

Each of these hydrocarbon families includes a number of individual chemical species, differing from one another in molecular weight and molecular structure.

Hydrocarbons in the paraffin family are also referred to as alkanes. The molecules in this family have open-chain structures. Members of the paraffin family include butane, pentane, heptane, and isooctane.

The naphthene family often is referred to as cycloparaffins. This family's molecules are saturated ring-structure hydrocarbon compounds. Some of this family's more common members include cyclohexane, cyclopentane, cycloheptane, and 1,1,2 trimethyl-cyclopropane.

The olefin family is composed of open-chain hydrocarbons each containing at least one carbon-carbon double bond. The physical properties of these compounds are quite similar to the paraffin family. Some of the olefin family's more common members include propene, 1-butene, 1-pentene, and 1-hexene. Olefins have high octane ratings, but poor oxidation stability, which can lead to gum and deposit formation.

The aromatic family is composed of hydrocarbons having at least one "benzene"-type unsaturated ring structure. The members of the aromatic family are highly prized as gasoline constituents because of their high octane ratings and excellent stability. Some of the more common members of this family include benzene, toluene, ethyl benzene, and xylene.

Benzene has been identified as a toxic air contaminant by the California Air Resources Board (ARB). In their study of benzene emissions, ARB researchers found benzene in evaporative and exhaust emissions from motor vehicles to be the major source of benzene in the environment (Ames et al., 1986). As discussed in Section Six, evaporative benzene emissions are linked to the benzene content of the fuel, while exhaust benzene emissions are affected by both the benzene content and the content of other aromatics.

2.2 Gasoline Properties

Unleaded gasoline must meet many different performance criteria. As with other petroleum products, optimizing the performance in one area will sometimes degrade performance in another. To produce an acceptable product at reasonable cost, the refiner must make certain compromises. As discussed in Section 2.4, the refiner is also subject to regulatory restraints on product composition, which may impose additional compromises.

The main performance properties for gasoline are octane rating, volatility, and stability. A fuel's octane rating determines its predisposition to knock or preignite. A fuel's volatility determines the cold-start properties and its tendency to cause vapor lock and fuel foaming. Stability is a fuel's ability to resist formation of resin-like insoluble deposits (gum) under adverse storage conditions.

Table 2-1 lists some of the major constituents of gasoline and their properties: octane rating, sensitivity, boiling point, vapor pressure, critical compression ratio, and specific gravity.

TABLE 2-1. PRIMARY UNLEADED GASOLINE CONSTITUENTS AND THEIR PROPERTIES

Family	Formula	Name	Mole Weight	Specific Gravity	Boiling Temp. °F at 1 atm	Vapor Pressure psia at 100°F	Critical[1] Comp. Ratio	Octane Rating		Sensitivity
								Research	Motor	
Paraffin	C_4H_{10}	Butane	58.12	.579	31	51.6	5.5	94	90	4
	C_5H_{12}	Pentane	72.15	.626	97	15.6	4.0	62	63	1
	C_7H_{16}	Heptane	100.20	.684	209	1.62	3.0	0	0	0
	C_8H_{18}	Isooctane	114.22	.692	211	1.72	7.3	100	100	0
Naphthene	C_5H_{10}	Cyclopentane	70.13	.745	121	9.9	12.4	101	85	16
	C_6H_{12}	Cyclohexane	84.156	.779	177	3.3	4.9	84	78	6
	C_6H_{12}	1,1,2 Trimethyl Cyclopropane	84.156	–	126	–	12.2	111	88	23
	C_7H_{14}	Cycloheptane	98.182	.816	246	.85	3.4	39	41	-2
Aromatic	C_6H_6	Benzene	78.108	.879	176	3.29	–	–	115	N/A
	C_7H_8	Toluene	92.134	.867	231	1.03	15	120	109	11
	C_8H_{10}	Ethyl Benzene	106.16	.867	277	.371	13.5	111	98	13
	C_8H_{10}	Xylene-m	106.16	.864	282	.326	15.5	118	115	3
Olefin	C_3H_6	Propene	42.078	.514	-54	226.4	10.6	102	85	17
	C_4H_8	1-Butene	56.104	.595	21	63	7.1	99	80	19
	C_5H_{10}	1-Pentene	70.130	.641	86	19	5.6	91	77	14
	C_6H_{12}	1-Hexene	84.156	.673	146	6	4.4	76	63	13

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[1] Critical compression ratio is that for audible knock; quiet room; 600 RPM; 100°F inlet air; 212°F coolant; spark and A/F ratio for best power (GM tests). This classification will vary with different engines and test conditions and need not correlate with the octane rating.

Source: Obert, (1973)

2.2.1 Octane Rating

Octane ratings for fuels in the United States are specified as the average of the motor and research octane numbers ((R+M)/2). The research octane number (RON) predicts the anti-knock performance of a fuel under full throttle, low engine speed conditions. The motor octane number (MON) predicts the anti-knock qualities of the fuel during full throttle, high engine speed conditions and during part throttle, low and high engine speed conditions. The sensitivity is the difference between a fuel's research and motor octane numbers. A sensitive fuel is more susceptible to knock at full throttle, high engine speed conditions than full throttle, low engine speed conditions.

Octane ratings are measured using a standard single cylinder test engine, the Cooperative Fuels Research (CFR) engine. The research and motor tests are performed using a similar procedure, but with different operating conditions. The octane ratings developed by this method are intended to correlate with resistance to knocking in vehicles on the road. This correlation is not perfect; depending on vehicle characteristics and operating conditions, anti-knock performance on the road may differ from that measured in the laboratory (Society of Automotive Engineers Information Report, Automotive Gasoline - J 312, 1985).

2.2.2 Volatility

The boiling range or volatility properties of a gasoline affect its ability to vaporize under cold-start conditions, and its tendency to foam and cause vapor lock in hot weather. The required boiling range of the fuel varies with the geographic location in which it will be used and the season of the year. In winter, a more volatile fuel is needed to be able to start the engine in cold weather. In the summer months, a lower volatility fuel is required to avoid fuel foaming and vapor lock in hot weather.

Volatility properties are specified in terms of the fraction of the gasoline evaporated at various temperatures, or by its vapor pressure at given temperature. The vapor pressure of gasoline when measured at 37.8°C (100°F) in a container having a vapor-to-liquid ratio of 4 is known as the Reid Vapor Pressure (RVP). RVP is the most commonly used volatility measurement.

Fuel volatibility has a major effect on evaporative emissions. Fuels which boil at lower temperatures have greater vapor pressures and, therefore, produce greater quantities of evaporative emissions. Fuel volatility may also affect the level of exhaust emissions. Fuel volatility effects on both evaporative and exhaust emissions are discussed in Section Five.

2.2.3 Stability

Fuel stability is the measure of a fuel's resistance to the formation of gums and deposits during prolonged storage. Gum deposits can clog fuel filters, carburetor jets, and fuel injectors. These deposits impair driveability and can increase exhaust emissions. Section Four describes the effects of fuel-injector and intake valve deposits on emissions.

2.3 Blending Agents and Additives

In addition to its oil-based constituents, other non-oil-based blending agents and additives are blended with unleaded gasoline for specific purposes. A blending agent is a substance which is added to gasoline in substantial quantities (typically several percent of the finished product), while additives are used in much lower concentrations. Blending agents commonly added to unleaded gasoline include alcohols, ethers, and mixtures of aromatic hydrocarbons such as benzene, toluene, and xylene (BTX). Additives commonly added to unleaded gasoline include anti-oxidants, corrosion inhibitors, metal deactivators, detergents, dispersants, demulsifiers, fluidizer oils, anti-icers, and combustion modifiers.

2.3.1 Blending Agents

The primary blending agents used in unleaded gasoline are oxygenates: methanol, ethanol, and other alcohols; and methyl tertiary-butyl ether (MTBE). Alcohols and ethers are used as blending agents for two primary reasons. First, due to market conditions or favorable tax incentives, blending agents such as methanol and ethanol may be more economical than crude oil components. More commonly, blending agents are used to enhance the octane rating of the gasoline. Most blending agents sold today raise the octane rating per volume of agent blended to a greater extent than does toluene (RON = 120, MON = 109) (Dorn and Mourao, 1984).

As discussed in Section 2.4, the concentration of oxygenates in unleaded gasoline is limited by the U.S. Environmental Protection Agency (EPA). This is due to the differences between oxygenates and hydrocarbon fuels with regard to volatility, stoichiometric air/fuel ratio, water solubility, and materials compatibility. The use of oxygenated blending agents tends to result in leaner combustion, reducing CO emissions but increasing emissions of NO_x. In addition, blends of ethanol and methanol in gasoline can significantly affect evaporative emissions. These effects are discussed in Section Seven.

2.3.2 Unleaded Gasoline Additives

Additives are included in gasoline to improve the performance, distribution, or quality characteristics of the fuel. Performance-enhancing additives are used to improve the engine's operating efficiency, reliability, and durability. Distribution additives are used to deliver a clean product from the refinery, through the entire distribution network, and ultimately to the end-user's equipment. Quality enhancing additives maintain the fuel to specification during transportation, storage, and residence in the end-user's storage facilities. Table 2-2 lists the different types of additives and their typical quantities in unleaded gasoline.

TABLE 2-2. TYPICAL ADDITIVES USED IN UNLEADED GASOLINE

Additive Type	Treatment Range PTB*	ppm
Performance-Enhancing Additives		
Amine Detergent	3 - 30	12 - 120
Polymeric Dispersant	5 - 150	20 - 600
Fluidizer Oils	50 - 250	200 - 1000
Anti-Icers	4 - 15	16 - 60
Distribution Additives		
Corrosion Inhibitors	1 - 10	4 - 40
Demulsifiers	1 - 25	4 - 10
Quality-Enhancing Additives		
Anti-Oxidants	3 - 5	12 - 20
Metal Deactivators	1 - 4	4 - 16

*PTB = Pounds of additive per 1000 barrels.

Source: Tupa and Dorer, 1984.

When using additives, a manufacturer typically adds no more than 1000 parts per million (ppm), or 0.1 percent by weight. Even at this small treatment level, additives can significantly enhance the performance and quality of the fuel. Additive manufacturers normally specify the additive quantity in pounds of additive per 1000 barrels (PTB), as opposed to ppm. A treatment level of 1 PTB corresponds to 4 ppm (Tupa and Dorer, 1984).

2.3.2.1 Performance-Enhancing Additives

Detergents and polymeric dispersants are added to unleaded gasoline to reduce the tendency of deposits to form in the fuel delivery system and intake manifold. Deposits can cause rough idling, stalling, poor acceleration, and reduced fuel economy in carburetted and fuel-injected vehicles. The stability of the gasoline plays a significant role in the formation of deposits.

Fuel-injector and intake system deposits can have major effects on vehicle pollutant emissions, as well as on performance, driveability, and fuel economy. These effects, and the role of detergents and dispersants in preventing them, are discussed in Section Four.

Fluidizer oils are added to gasoline to control gum deposits on intake ports and valves. These deposits can lead to reductions in volumetric efficiency and, potentially, valve burning. The addition of 0.2 to 0.3 percent by volume of mineral oil in the fuel can prevent these deposits (Tupa and Dorer, 1984).

Problems with another type of intake valve deposit have recently been reported (Bitting et al., 1987). High molecular weight materials from the lubricating oil or blowby gas can accumulate and coke on the intake valve when exposed to air and elevated temperatures. Coking on the intake valve and in the intake port can cause increased NO_x emissions and reduced vehicle performance. A further discussion of the effects of intake system deposits can be found in Section Four.

Ice on the throttle blade of a carburetted or fuel-injected engine can build up to a point sufficient to stall the engine during idle conditions. Icing tends to occur during engine warm-up. This problem was more common during the 1950s and 1960s than it is today. The addition of inlet air heater systems to engines and the addition of freeze point depressants or surfactants to fuel has reduced the icing problem (Tupa and Dorer, 1984). An increase in emissions could occur during icing conditions, but this effect would be rare and temporary.

Combustion additives are designed to reduce an engine's tendency to knock during certain operating conditions. Additives that have been used as combustion modifiers include tetraethyl lead (TEL), tetramethyl lead (TML), methylcyclopentadienyl manganese tricarbonyl (MMT), and other metal-based compounds. Under the EPA "substantially similar" requirement, only additives derived from hydrogen, carbon, oxygen, or nitrogen are permitted in unleaded gasoline (Federal Register, Volume 45, No. 199, 1980). Therefore, metal-based, anti-knock combustion modifiers are not permitted in unleaded fuel.

Use of metal-based combustion modifiers such as TEL or MMT in modern engines would result in significant increases in emissions. Lead compounds are known to poison catalysts and oxygen sensors. A more detailed discussion of the effect of combustion modifiers and other additives on exhaust emissions can be found in Section Three.

2.3.2.2 Distribution Additives

Corrosion of fuel tanks, pipelines, storage tanks, and other fuel transporting units could cause significant health and safety hazards if leaks developed in these systems. In addition, particles of rust in the fuel line could clog fuel filters, damage fuel pumps, and clog carburetor jets or fuel-injector orifices. In order to prevent rust-related problems from occurring, corrosion inhibitors are added to unleaded gasoline in low concentrations, typically 4 to 40 ppm (Tupa and Dorer, 1984). Omission of these additives could result in corrosion and damage to fuel systems, most likely resulting in increased emissions.

Detergents and polymeric dispersants form emulsions with water and other contaminants in the fuel. During transportation and distribution, the fuel will come into contact with water and other contaminants. The emulsions formed with the detergents and polymeric dispersants would tend to block fuel filters, and could cause corrosion, carburetor icing, and fuel line freeze-up if not separated from the fuel. To counteract the emulsifying tendencies of detergents and polymeric dispersants, demulsifiers, consisting of chemicals that are highly surface active, are added to the fuel (Tupa and Dorer, 1984).

2.3.2.3 Quality-Enhancing Additives

Anti-oxidants are organic compounds that inhibit oxidation and gum formation in gasoline during storage. The major concern about gum in gasoline is its tendency to form deposits in the fuel delivery system and the intake manifold. The effects of intake system deposits on emissions is discussed in Section Four.

The effectiveness of anti-oxidants depends on the fuel's olefin content. As the fuel's olefin content increases, anti-oxidants lose their ability to resist the formation of gum. Several bench tests determine the oxidation-reducing characteristics of anti-oxidants in specific fuels. To date, no reports of significant emissions impacts due to inadequate anti-oxidant usage have been published.

Copper and its compounds, along with other trace metals, are catalysts that promote the oxidation of gasoline. Metal deactivators are necessary because of the ineffectiveness of anti-oxidants in reducing the oxidation reaction initiated by trace metal contaminants. Chelating agents are used to reduce the copper compounds in the fuel to a compound which does not have pro-oxidation tendencies.

Radian's literature review did not reveal any significant emissions impact due to inadequate usage of chelating agents. If chelating agents are not present, gum can form when the fuel comes into contact with copper. In this instance, the emissions effect expected would be similar to the effect resulting from inadequate use of detergents and polymeric dispersants.

2.4 California Unleaded Gasoline Regulations

The composition of unleaded gasoline is governed by both Federal and State laws and regulations. The EPA has established rules and guidelines for unleaded gasoline based on the authority granted by Section 211 (f)(1) of the

Clean Air Act. In order for unleaded gasoline to be sold, it must be "substantially similar" to the indolene fuel used for emissions certification testing, or receive a waiver from EPA. In order to be considered "similar," the fuel must not contain additives incorporating any elements other than carbon, hydrogen, sulfur, oxygen, and nitrogen. In addition, the fuel may not contain more than 0.05 grams of lead and .005 grams of phosphorus per gallon, and the oxygen content of the gasoline cannot be greater than 2 percent by weight (Federal Register, Volume 45, No. 199, 1980). However, EPA has granted waivers for certain fuels such as gasohol containing up to 3.8 percent by weight oxygen.

The California Air Resources Board also regulates the composition of unleaded gasoline sold in the California. These regulations generally parallel those of the Federal EPA, but contain a number of additional restrictions. These restrictions include limits on the Reid Vapor Pressure (RVP) of the fuel during the "smog season", the degree of unsaturation, and the sulfur content. Like EPA, California prohibits the addition of lead, phosphorus, or manganese to unleaded gasoline, and limits the permissible lead concentration to 0.05 g/gal. The regulations for automotive vehicle fuels are found in California Administrative Code, Title 13, Subchapter 5. The principal limits on gasoline content and the date of adoption of each are listed in Table 2-3.

Bromine Number--To limit the photochemical reactivity of gasoline sold in the South Coast Air Basin (SCAB), ARB regulations limit the Bromine Number of gasoline sold for motor vehicle fuel in the SCAB to a maximum of 30. This limit applies to both leaded and unleaded gasoline. Bromine Number is a measure of the olefin content of the fuel, and olefins have high photochemical reactivity. This limit was originally adopted by the Los Angeles Air Pollution Control Board in 1959, and has not been changed since. It was intended as a "capping" standard--at the time of adoption, no modifications to refinery practice were required in order to comply (Sierra Research, 1987).

TABLE 2-3. SUMMARY OF APPLICABLE UNLEADED GASOLINE REGULATIONS

Regulation	Federal Limit	California Limit	Most Recent California Revision to Limit
Lead Content	.05 gm/gal	.05 gm/gal	1973
Phosphorus Content	.005 gm/gal	.005 gm/gal	1973
Sulfur Content	N/A [1]	300 ppm	1978
Manganese Content	Cannot be added to Unleaded Gas [2]	Cannot be added to Unleaded Gas	1977
Oxygenate Content:			
Methanol	0.03% [2]	N/R [4]	
MTBE	11.0% [2]	N/R	
Isopropanol	7.1% [2]	N/R	
TBA	15.7% [3]	N/R	
Ethanol	10.0% [3]	N/R	
Oxinol-50 (R)	9.5% [3]	N/R	
Reid Vapor Pressure for Oxygenates	N/A	90 psi	1980
Bromine Number	N/A	30	1959
Reid Vapor Pressure	N/A	9.0 psi	1970

Footnotes:

[1] Not Applicable

[2] Limited by EPA "substantially similar" ruling, Federal Register Vol. 45, no. 199, 1980.

[3] Waiver allowing maximum content to be greater than EPA "substantially similar" rule limit.

[4] Not Regulated

ARB has performed a number of surveys to evaluate the Bromine Numbers of gasoline sold in California. A 1974 survey found that the Bromine Number for gasoline sold in the SCAB ranged from 6 to 14. However, surveys of fuel intended for sale throughout California performed in 1984 and 1985 identified some gasolines with Bromine Numbers greater than 30 (Sierra Research, 1987). The Bromine Number of gasoline can be estimated by multiplying the olefin content (in percent) by two (Sierra Research, 1987). The olefin content of gasoline measured during the Motor Vehicle Manufacturers Association (MVMA) Summer-1985 fuel survey ranged from 2 to 16 percent with a mean of 7 percent (Benson and Yaccarino, 1986). This corresponds to a Bromine Number range from 4 to 32 with a mean of 14.

Based on the ARB and MVMA survey results, it appears that the present Bromine Number standard is having only a marginal effect in reducing the photochemical reactivity of gasoline sold in the SCAB. To ensure that gasoline sold in the SCAB is less photochemically reactive than that sold in the remainder of the U.S. would require that the Bromine Number standard be set at a lower level. Any reduction in the Bromine Number standard would require a reduction in the olefin content of some gasolines, however. Since olefins have good octane properties, this could complicate the achievement of required octane levels, and would probably increase the cost of unleaded gasoline. This would need to be taken into account in any regulatory action.

Reid Vapor Pressure--The RVP of gasoline sold in California during the "smog season" is limited to 9 psi. The time of year defined as the "smog season" for the purposes of this regulation varies from air basin to air basin. This regulation was adopted in order to reduce evaporative hydrocarbon emissions during periods of high photochemical activity. As discussed in Section Five, gasolines with lower RVP levels result in less evaporative emissions.

Sulfur--The sulfur content of unleaded gasoline sold anywhere in California is limited to 300 ppm by weight. As discussed in Section Three, this regulation was adopted primarily to limit sulfate emissions from vehicles with oxidation catalysts. Sulfur also reduces the efficiency of catalytic converters somewhat, and contributes to ambient SO_2 and particulate sulfate levels.

Lead and phosphorus--Both California and Federal regulations prohibit the addition of lead or phosphorus to unleaded gasoline, and establish maximum tolerance levels for these contaminants. The present State and Federal tolerance levels for lead and phosphorus in "unleaded" gasoline are the same: 0.05 grams per gallon for lead and 0.005 grams per gallon for phosphorus. These tolerances were established when unleaded gasoline was first introduced in the mid '70s, in order to account for the possible cross-contamination of unleaded gasoline with leaded fuel during transport and distribution. They have not been changed since, despite a 20-fold reduction in the concentration of leaded fuel in the meantime.

Manganese--Both California and Federal regulations prohibit the addition of manganese to unleaded gasoline, although manganese (as MMT) is permitted and occasionally used as an octane improver in leaded fuel. Unlike lead and phosphorus, however, the regulations do not establish a maximum tolerance limit for manganese as a result of inadvertent contamination. This has raised questions for ARB enforcement staff, as it is not clear what level of manganese contamination should be considered to be a violation.

Enforcement--ARB regulations concerning the composition both of leaded and unleaded gasoline are enforced through a program of random sampling and analysis (Jackson, 1987). An ARB mobile laboratory collects approximately 1000 samples per year from retail outlets, distributors, and refiners. These samples are analyzed for RVP, Bromine Number, lead, phosphorus, manganese, and sulfur. Analyses for nickel and cadmium will be added in the future, to accommodate potential ARB regulation of these metals.

To date, these data have been used only for the enforcement of existing gasoline regulations. Regulatory violations are occasionally found in this sampling. Violations of the RVP limit are most common, although sulfur and lead-content violations have also been found (Jackson, 1987). Once a violation is detected, additional sampling is performed to identify the extent of the violation, and to identify the cause and the party(ies) responsible.

In addition to aiding in the enforcement of existing regulations, the data developed in this sampling program could be very valuable in the analysis of air quality data and potential new regulations. Unfortunately, they are not yet available in computerized form, although plans to enter them into a database exist. Statistical analysis of these data would significantly improve our understanding of current gasoline composition in California, and might lead to new insights. It is recommended that ARB pursue this analysis as quickly as possible.

2.5 Unleaded Gasoline Quality

The American Society for Testing and Materials (ASTM) maintains and updates the Standard Specification for Automotive Gasoline, ASTM D439. The standard is used as an industry guideline; unless it is specified by the purchaser, gasoline from a refinery is not required to meet the standard. The standard specifies the composition and performance tests that the gasoline must meet to comply. Typical ASTM guidelines for gasoline are listed in Table 2-4. California regulates the sulfur content and RVP of unleaded gasoline to values that are stricter than the standard. The ASTM standard does not specifically require fuels to have any particular additives or blending agents. It does, however, include tests of oxidation stability and corrosiveness which might require the use of anti-oxidant and anti-corrosive additives in order to pass.

TABLE 2-4. TYPICAL ASTM D439 GASOLINE REQUIREMENTS

Lead Content, Maximum	
Unleaded	0.05 gm/gal, 0.013 gm/L
Leaded	4.2 gm/gal, 1.1 gm/L
Existent Gum, Maximum	5 mg/100 ml
Sulfur, Wt., Maximum	
Unleaded	0.10%
Leaded	0.15%
Oxidation Stability, Minutes	240
Distillation Temperatures[1], °C (°F) at % Evaporated	
10% Max.	60°C (140°F)
50% Min.	77°C (170°F)
50% Max.	116°C (240°F)
90% Max.	185°C (365°F)
End Point, Max.	225°C (437°F)
Distillation Residue, Maximum	2%
Reid Vapor Pressure, Maximum[1]	11.5 psi, 70 kPa
Antiknock Index[2]	
Unleaded	85-90
Leaded	87-93

[1] Varies with location and month of year.

[2] Depends on application.

Source: Dorn and Mourao, 1984

2.6 Summary

In summary, unleaded gasoline is a mixture of hydrocarbons derived from crude oil, with other non-crude, oil-based additives and blending agents added for specific purposes. Gasoline's main performance properties are:

- Octane Ratings;
- Volatility; and
- Stability.

Crude oil components affect the fuel's performance with regard to octane rating, volatility, and stability. Non-crude oil components are used to maintain the quality of the fuel during distribution and storage, and to reduce knocking and the formation of deposits.

Gasoline constituents and additives also affect the emissions performance of motor vehicles. Octane ratings below those required to reduce "knock" may lead to emission increases due to misfueling or spark advance modifications. Insufficient use of certain additives can lead to gum formation causing increased fuel and intake system deposits that result in exhaust emission increases.

Because of these and other potential emission impacts, both the EPA and the State of California regulate the composition of unleaded gasoline. To add to the fuel components other than hydrogen, carbon, oxygen, sulfur, or nitrogen, an EPA waiver is required. In addition, California regulates the RVP of fuel sold in the state during "smog season"; the Bromine Number; and the sulfur, lead, phosphorus, and MMT content of the fuel. EPA and ARB standards for the lead, phosphorus, and sulfur content of unleaded fuel were established in the mid '70s, and have not been changed since. As discussed in Section Three, these issues should be re-examined by ARB.

The Bromine Number limit was originally adopted to restrict the photochemical reactivity of gasoline sold in the SCAB. The current Bromine Number limit has only a marginal effect on the photochemical reactivity of gasoline sold in the SCAB compared to other California Air Basins, and has not been changed since 1959. It is recommended that ARB re-evaluate this limit to determine whether a lower value would be feasible and cost-effective for reducing the photochemical reactivity.

3.0 EFFECT OF IMPURITIES ON EMISSION CONTROL SYSTEM COMPONENTS

Elemental impurities such as lead, phosphorus, sulfur, and manganese may enter unleaded gasoline by a number of routes. Sulfur is a normal constituent of crude oil, and small quantities of it carry through the refining process to wind up in gasoline. Recycling of solvents, etc. can also result in contaminants carrying through--as with silicone oils in several recent cases.

"Unleaded" gasoline may also be contaminated by additives such as lead, phosphorus, and manganese, due to mixing with leaded gasoline during distribution and storage. Under California law, gasoline containing up to .05 grams (50 milligrams) of lead and .005 grams (5 milligrams) of phosphorus per gallon may legally be sold as "unleaded". These limits were established in 1973, when leaded gasoline contained more than two grams of lead per gallon. Beginning in January 1988, leaded gasoline will be limited to an average of 100 mg/gal of lead. Thus, a 50:50 mix of leaded gasoline and "sterile" (lead free) fuel could legally be sold as "unleaded".

Impurities in unleaded gasoline are of concern primarily due to their effects on vehicle emission control systems. However, lead, and the sulfur dioxide (SO_2) and sulfates formed from the combustion of sulfur in gasoline are also significant pollutants themselves. All areas of California are now in attainment of the State and Federal ambient lead standards, but the South Coast air basin marginally exceeded the State sulfate standard, and the South Central Coast air basin exceeded the SO_2 standard in 1986.

The emission control system components which are most sensitive to gasoline impurities are catalytic converters and oxygen sensors. The efficiency of these components may be temporarily or permanently reduced by lead, phosphorus, sulfur, and amorphous silica (formed from the combustion of silicones) in the exhaust. Other components of a modern-day emission control system include the air management system, evaporative emission control system, electronic spark control, electronic fuel-injection, exhaust gas recirculation (EGR) system, and heated air intake. These are considered relatively insensitive to contaminants in the fuel. The only known adverse effect of contaminants on any of these systems is on the EGR system, which may be clogged or plugged by large amounts of lead or other ash-forming contaminants.

Radian's literature review identified the following gasoline impurities as having the potential to impair the performance of catalytic converters and/or oxygen sensors:

- Lead;
- Phosphorus;
- Silicon (in the form of silicones);
- Sulfur; and
- Manganese.

The routes of contamination, concentrations, and effects of each of these contaminants on emissions are discussed below.

3.1 Lead

When catalytic converters were first developed, lead anti-knock additives were shown to cause severe poisoning of catalytic converters. To permit the use of catalytic converters for emissions control, EPA mandated the sale of unleaded gasoline at service stations in 1974. At that time, ordinary "leaded" regular gasoline contained more than two grams of lead per gallon. Recognizing that some cross-mixing between leaded and unleaded fuel was inevitable, EPA and ARB established a permissible lead tolerance of 0.05 grams per gallon (50 mg/gal) (California Administrative Code, Title 13, Subchapter 5). This tolerance level remains in effect, even though the permissible lead content in leaded gasoline has declined 20-fold since that time, to 100 mg/gal at present.

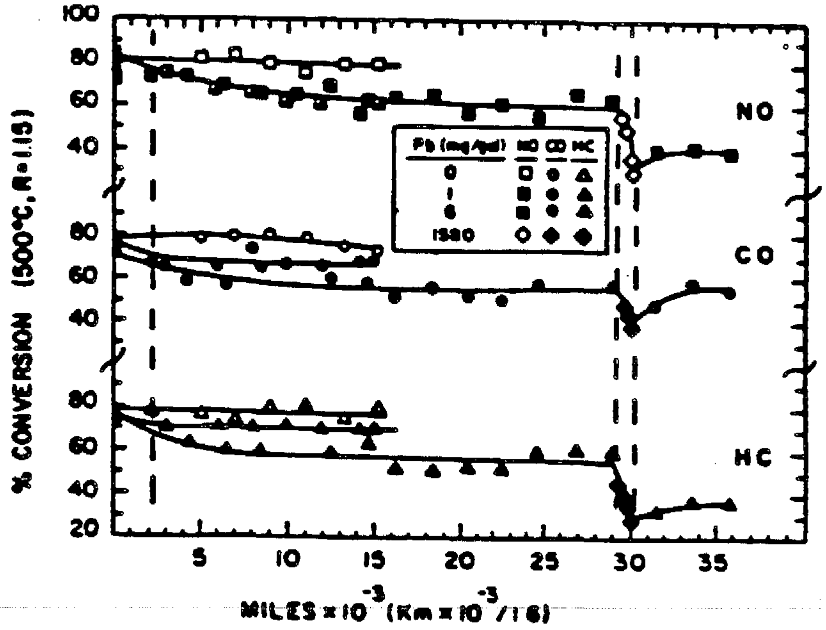
The effects of high concentrations of lead on emission control system components are well known and extensively documented (Hammerle and Graves, 1983; Duncan and Braddock, 1984; McIntyre and Faix, 1986). Lead affects the ability of a catalytic converter to reduce oxides of nitrogen (NO_x) and to oxidize hydrocarbons (HC) and carbon monoxide (CO). In the catalytic converter, lead appears to have two distinct poisoning mechanisms. At catalyst operating temperatures below 550°C, a barrier of lead sulfate builds up and appears to reduce the diffusion of exhaust gas constituents to the noble metal sites. At temperatures between 700 and 800°C, the active platinum sites appear to be poisoned by lead oxide, or lead. Lead buildup on the catalyst at 750°C appears to be due to deposition of a lead oxide vapor. The lead oxide appears to buildup uniformly throughout the wash coat and poisoning occurs from the interaction of the lead oxide with platinum (Hammerle and Graves, 1983).

Lead also reduces the operating capability of oxygen sensors by apparently blocking the diffusion of exhaust products to the surface of the sensor. Oxygen sensors poisoned by lead cannot output a rich signal (greater than 0.5 volts). The mixture control system in a modern three-way catalyst equipped vehicle works on a feedback principle, varying the air fuel mixture in response to the lean/rich signal from the oxygen sensor. Since the the feedback system receives only a "lean" signal, it will drive the actual air/fuel ratio rich. This can dramatically increase CO and HC emissions. When exposed to exhaust from an engine operating on gasoline containing 1.5 grams of lead per gallon, oxygen sensor performance is affected after 48 to 120 hours (Hammerle and Graves, 1983).

Lead concentrations of 0.5 gm/gal have been shown to cause premature degradation of three-way catalytic converters (Duncan and Braddock, 1984). Additional work by McIntyre and Faix (1986) has shown significant catalyst deterioration due to misfueling with high-lead gasoline even where misfueling episodes were infrequent. This work showed that catalytic converters which are "poisoned" by use of leaded gasoline can recover some of their efficiency if they are subsequently operated on unleaded fuel. This recovery is not complete, however--HC and NO_x conversion efficiencies do not return to their pre-poisoning levels.

In the 70's, lead levels above two grams per gallon were common in leaded gasoline. At present, however, Federal regulations limit the lead concentration of leaded gasoline to 0.1 gm/gal. Relatively little work has been done to examine the effects of these lower lead levels on emission controls. However, the work that does appear in the literature (EPA, 1975; Williamson et al., 1979; Williamson et al., 1985) shows significant long-term effects even at very low levels of lead contamination.

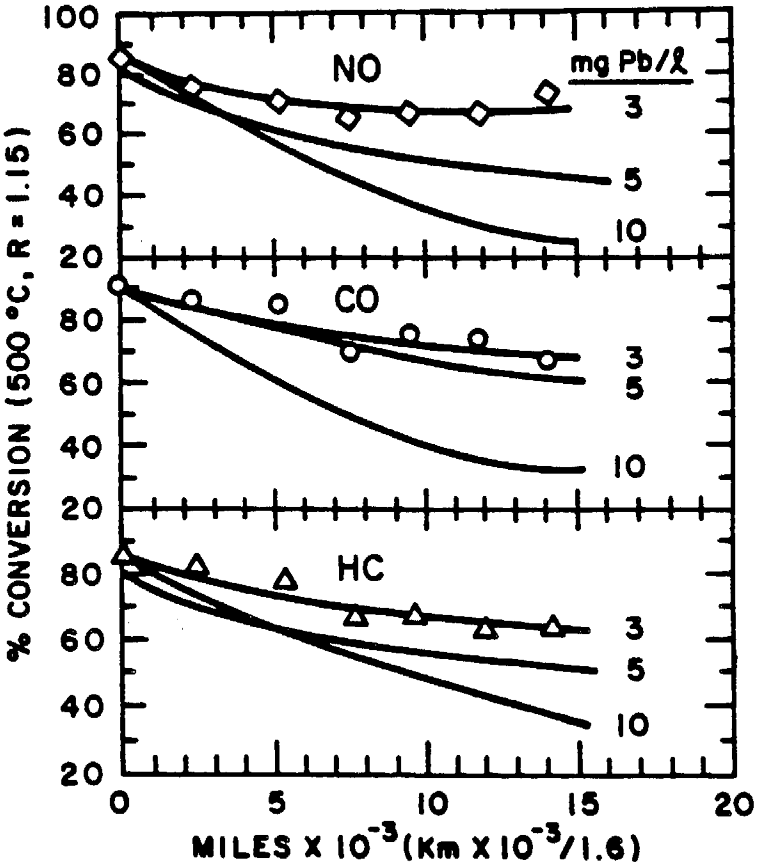
Williamson and co-workers (1979) examined the effects of low levels of lead contamination on three-way catalyst activity in the laboratory. Catalysts were aged on a pulse-flame reactor simulating conditions in use, and exposed to differing levels of lead contamination of the fuel. Conversion efficiency was measured under modulated conditions simulating closed-loop operation. Figure 3-1 shows the results for lead levels of 0, 1, and 6 mg/gal lead contamination as a function of simulated mileage, as well as the effects of a one-time misfueling with high-lead (1.58 gm/gal) gasoline. As this figure shows, conversion efficiency with the contaminated fuel decreases and then levels off at a lower level. For the zero-lead fuel, the loss in conversion efficiency is negligible, but at 6 mg/gal HC conversion efficiency drops from about 80 percent to less than 60 percent.



Source: Williamson et al., 1979

Figure 3-1. Effect of Lead Levels on Converter Durability - Pulsator Aging

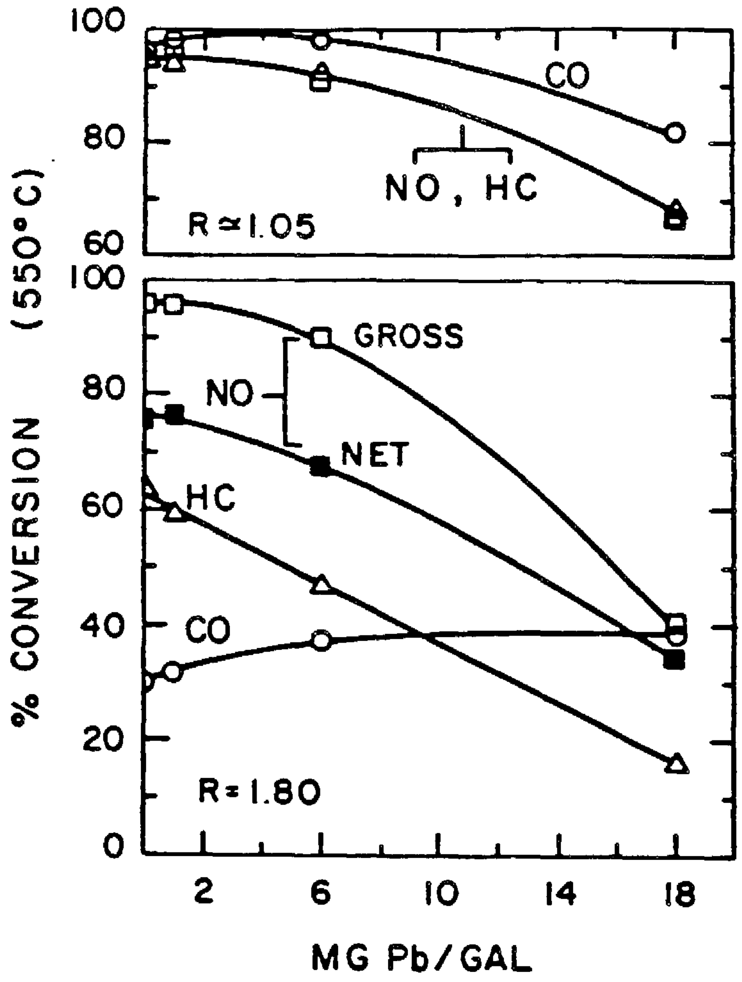
The extent of efficiency loss is affected by the operating conditions. Figure 3-2 shows similar data from a later paper by Williamson et al. (1985), using a European test cycle which included more high-speed, high-load operation. The trends are similar to those in Figure 3-1, but the loss in efficiency is greater and occurs more rapidly.



Source: Williamson et al., 1985

Figure 3-2. Effect of Lead Levels on Converter Durability - European Test Cycle

Figure 3-3 shows the effects of lead contamination levels ranging from 0 to 18 mg/gal on steady-state catalyst efficiency under mildly rich and rich operating conditions after 25,000 simulated miles of operation. The parameter R shown in the figure is the ratio of reducing to oxidizing components in the exhaust gas, the value of R=1.05 shown in this figure reflects a slightly rich mixture, while R=1.80 is a very rich one.



Source: Williamson, et al., 1979

Figure 3-3. Effect of Lead Levels on Steady-State Catalyst Operation

As Figure 3-3 indicates, the loss in catalyst efficiency under these conditions is significant, reaching more than 35 percent at 18 mg/gal for HC and NO under slightly rich conditions. The loss is even greater at the richer conditions tested. It should be noted that even 18 mg/gal (the highest lead concentration tested by Williamson et al.) is about one third the current standard of 50 mg/gal for lead in "unleaded" gasoline. Thus, even "unleaded" gasolines may legally contain lead concentrations which are known to cause substantial loss of catalyst efficiency.

It appears that some gasoline marketers may be abusing the present lenient standard for lead in unleaded gasoline. ARB compliance staff (Jackson, 1987) have found that gasoline from one particular blender is often at or near the statutory limit, even though (as noted above) this would require approximately a 50:50 leaded with sterile unleaded fuel. Apparently, this blender is mixing heavily contaminated gasoline from pipeline ends, etc. with unleaded and marketing the result as unleaded fuel.

Given the significant emissions impacts of even small amounts of lead in gasoline, there is no reason to tolerate such abuse of the regulations. It is recommended that ARB move immediately to reduce the permissible level of lead in unleaded gasoline by at least a factor of ten (to 5 mg/gal), and that it consider further reductions if statistical analysis of the Compliance Division's gasoline sampling database indicates that they are warranted. Since the present leaded gasoline contains less than a twentieth of the lead concentration that it had when the present tolerance levels were set, this immediate factor-of-ten reduction should cause no hardship for those who are not presently abusing the system.

3.2 Phosphorus

Phosphorus is sometimes used in leaded gasoline at concentrations about 1/10th that of lead. The maximum legal quantity of phosphorus in unleaded gasoline sold in California is 5 mg/gal. This permitted level was set at the same time and for the same reasons as the lead tolerance.

Significant quantities of phosphorus (up to .17 mass percent, or about 1.5 gm/quart) are found in engine oils (Caracciolo and Spearot, 1979). Most phosphorus in the exhaust stream comes from the engine oil, not from the fuel. At 20 MPG and 5 milligrams of phosphorus per gallon of fuel, a catalyst would be exposed to about .25 grams of phosphorus from the fuel per 1000 miles. This is about one-sixth the phosphorus from the engine oil, assuming a moderate oil consumption level of one quart per 1000 miles. Since ARB's compliance division has not detected violations of the phosphorus standard in unleaded gasoline (Jackson, 1987), it can be concluded that the great bulk of the phosphorus going into the catalyst comes from the oil.

Phosphorus is a catalyst poison, acting to block the diffusion of exhaust gas constituents to the noble metal sites in the catalyst. Once they have been poisoned by phosphorus, catalysts cannot be reactivated by thermal treatments (Joy et al., 1985).

The effect of currently permitted levels of phosphorus in fuel on emissions is probably minor. Williamson et al. (1979) found little clear effect on emissions at phosphorus levels up to 8.2 mg/gal. In any event, these effects would be small compared to those of phosphorus in the oil. A number of studies found in the literature have evaluated the impact of oil-derived phosphorus on emission control system performance (Caracciolo and Spearot, 1979; Williamson et al., 1984; Joy et al., 1985). Sierra Research will be evaluating these data under Task 4 of this contract. Any recommendations for regulatory action on phosphorus will be presented in that report.

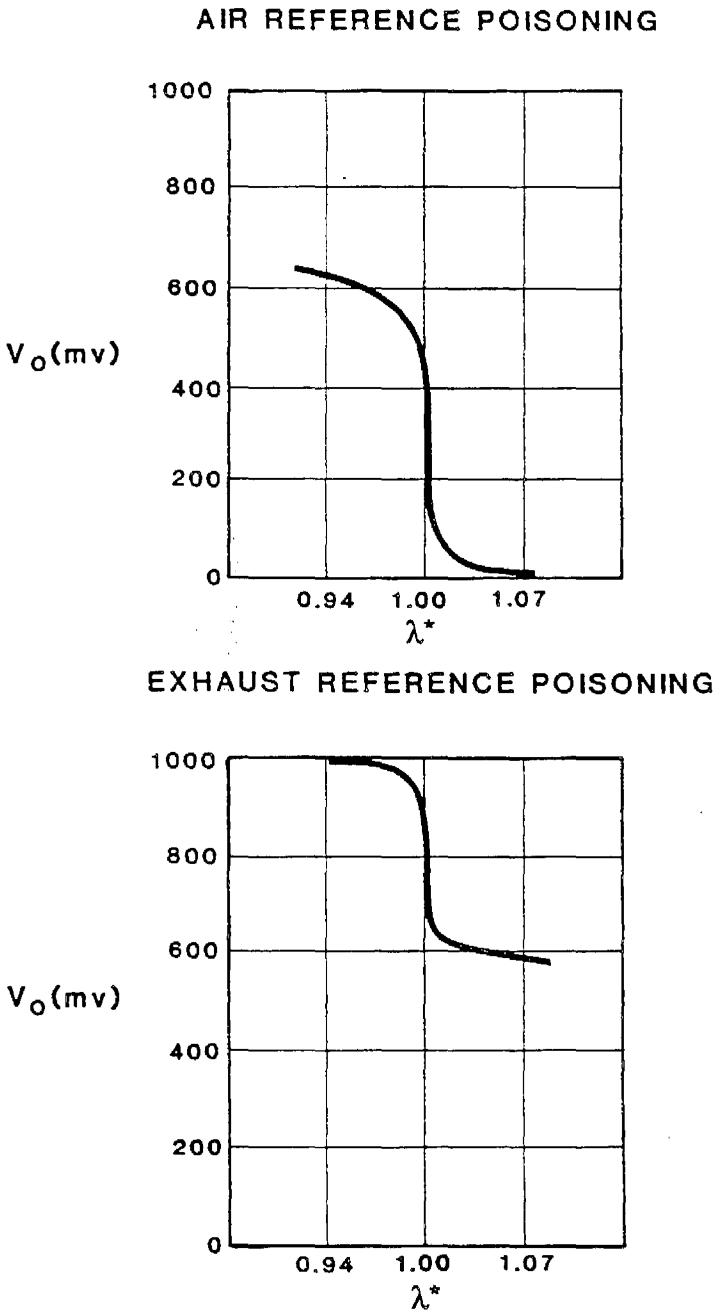
3.3 Silicon

Silicon is a common element in the earth's crust, and (in the form of crystalline silicates) is probably found at low levels in all petroleum-derived fuels due to contamination with dust, etc. At low levels, these silicates should have little effect on emission controls. Silicon in synthetic silicones, however, can be very damaging. Instances of fuel contaminated with silicones have occurred in Detroit, Michigan, and in northern Florida (Holleboom et al., 1986). Radian is not aware of any documented problems with silicone-contaminated fuels having been sold in California.

Silicones, when exposed to extreme temperatures in the combustion chamber, decompose to form amorphous silica. Amorphous silica deposits on oxygen sensors and catalytic converters and blocks diffusion of the exhaust gas constituents to the catalyst. Once in the exhaust stream, small amounts of silica produce rapid and irreversible damage to the catalytic converter. In laboratory tests, aging of three-way catalysts using fuel doped with 20 ppm silicon as silicones resulted in three-way catalyst conversion efficiencies of less than 40 percent for all three constituents after only 15,000 simulated miles (Gandhi et al., 1986).

Silica deposits also significantly reduce oxygen sensor performance. By coating the outer electrode with silica, the mass transfer of exhaust components is reduced. This increases the oxygen transfer from the air reference side to the outer electrode at a given air/fuel ratio. The result is an increase in the output voltage of the sensor at a given air/fuel ratio. Also, the response time for the sensor to toggle from rich-to-lean increases. Figure 3-4 shows the effect of silica poisoning on oxygen sensor output voltage.

In addition to the poisoning of the outer electrode, the inner electrode of an oxygen sensor can become poisoned. This type of poisoning occurs when silicone rubbers become overheated and contaminate the air reference. When the air reference side is poisoned, the voltage output of the sensor decreases at a given air/fuel ratio. This occurs because the diffusion of the oxygen ions from the inner to the outer electrode is inhibited. This can result in negative voltage outputs from the oxygen sensor (Holleboom et al., 1986). In this case, the electronic control system is driven to an excessively rich condition, causing large increases in hydrocarbon and carbon monoxide emissions.



$$^{*}\lambda = \frac{\text{Actual Air/Fuel Ratio}}{\text{Stoichiometric Air/Fuel Ratio}}$$

Figure 3-4. Zirconia Oxygen Sensor Response

To date, silicone contamination has been reported only in a few isolated instances; it does not appear to be a widespread problem. These instances are disturbing, however, as there appears to be no clear regulatory mechanism for preventing a recurrence. Regulations requiring chemical analysis of recycled solvents and/or prohibiting their mixture with process streams intended for unleaded gasoline may be indicated. ARB should also examine further the potential effects of silicone rubbers, gasket sealants, etc. in the automotive aftermarket on catalytic converters and oxygen sensors.

3.4 Sulfur

In California, state regulations limit the sulfur content of unleaded fuel to less than 300 ppm. This limit was added to the California Administrative Code primarily because of concern about sulfuric acid emissions from vehicles with catalytic converters. When converters were introduced in the mid-1970s, concerns regarding the conversion of sulfur dioxide (SO_2) into sulfuric acid (H_2SO_4) were voiced. Precious-metal catalysts can oxidize SO_2 to sulfur trioxide (SO_3), which combines with water in the exhaust to form sulfuric acid. EPA, at the time, believed that significant increases in the ambient sulfate concentrations might occur as a result of catalytic converter use. These concerns have subsequently been found to have been overstated. Although oxidation catalysts do produce some sulfates, this effect is much less than was originally feared (ARB, 1978).

Two other motivations for limiting sulfur in unleaded gasoline were its detrimental effects on catalyst efficiency and its contribution to overall SO_2 and sulfate levels. For 1985, ARB's emission inventory shows that sulfur in gasoline accounted for about 58.5 tons of SO_x per day, out of a total statewide inventory of 484 tons per day. About 30.2 tons, or more than half the total, came from unleaded gasoline. For the South Coast Air Basin (which marginally violated the State sulfate standard in 1986), sulfur in gasoline accounted for 27.5 out of a total of 137 tons per day.

Sulfur in gasoline can act as a poison for catalytic converters. Sulfur compounds may either form a barrier, so that the exhaust constituents cannot reach the noble metal catalyst, or it may react chemically with the base metals to modify the catalyst's composition. Sulfur is known to react chemically with the base metals in catalytic converters. This is one reason catalysts containing only base metals are not functional in automotive applications.

Tests with the levels of sulfur found in gasoline have shown that increased sulfur slightly reduces catalyst efficiency. This effect, though small (of the order of a few percent), is statistically significant (Furey and Monroe, 1981). The poisoning due to sulfur is reversible. Once the sulfur in the fuel is removed, the catalyst returns to its previous performance level. Sulfur poisoning tends to affect HC and NO_x conversion more significantly than CO conversion.

In three-way catalysts under rich operating conditions, sulfur in the exhaust stream is converted to hydrogen sulfide (H_2S) when it reaches the catalyst. Under lean operating conditions, SO_2 and SO_3 form in the catalyst. In addition, at temperatures below approximately 600°C and under lean operating conditions, sulfur reacts with metals in the catalyst (Diwell et al., 1987). The sulfur stored in the catalyst is released when the temperature rises above 600°C or the air/fuel ratio switches from lean to rich. During rich operation, the previously stored sulfur is rapidly released from the catalyst and reacts with H_2 to form H_2S. The quantity of H_2S released under these conditions can be significantly greater than would be anticipated based on the fuel sulfur content (Henk et al., 1987). This is apparently responsible for the pronounced "rotten egg" odor sometimes produced by three way catalyst vehicles.

During normal operation, the mixture in a three-way catalyst vehicle cycles continuously between lean and rich conditions. If sulfur is stored under lean conditions, and released as H_2S in rich conditions, then a large fraction of the sulfur in gasoline used by three-way catalyst vehicles could be emitted as H_2S. In addition to being malodorous, this gas is also extremely toxic, which could be a concern in some circumstances. The offensive odor is normally detectable at well below toxic concentrations, however, so the toxic threat is not a major one. This odor may create an incentive to tamper with catalytic converters, however, and is thus undesirable from an air-quality as well as a quality-of-life standpoint. H_2S emissions from three way catalysts can be reduced by adding metals such as nickel to the washcoat formulation, or by reducing the sulfur content of the fuel.

A reduction in the sulfur content of unleaded gasoline appears desirable for all of the reasons discussed above. Such a reduction would directly reduce SO_2, sulfate, and H_2S emissions; and would slightly increase the efficiency of catalytic converters, thus helping to reduce HC, NO, and NO_x. In a 1978 report on this issue (ARB, 1978), ARB staff recommended that sulfur be phased down in stages from 500 ppm to 100 ppm in steps of 100 (the Board subsequently adopted only the first three steps). Since that time, the adoption of a diesel fuel sulfur standard of 500 ppm for the South Coast may have altered the economics of lowering gasoline sulfur. It is recommended that ARB re-examine this issue to determine whether further reductions in gasoline sulfur would be cost-effective under the current circumstances.

3.5 Manganese

Methylcyclopentadienyl manganese tricarbonyl (MMT) has been suggested as a lead substitute. This performance-enhancing, anti-knock additive has been known for many years. It is used occasionally as an octane-enhancing additive in leaded gasoline in the U.S., including some gasoline sold in California. To produce the same anti-knock properties as 1.0 gram of TEL, 1.3 grams of MMT are required (Obert, 1973). Manganese is also helpful in protecting exhaust valve seats from destructive recession. With the expiration of lead credits in 1988, future leaded gasolines may contain larger amounts of MMT. Use of MMT is prohibited in U.S. unleaded gasoline, although Canada permits its use in unleaded fuel.

The use of MMT is known to increase engine-out HC emissions somewhat, but its effect on emission control system components (e.g. catalytic converters and oxygen sensors) is controversial. In 1979, the Coordinating Research Council (CRC) undertook a study with representatives from EPA, ARB, automotive manufacturers, and oil companies to determine the effects of MMT on emission control system components of 1977 and 1978 California vehicles. Sixty-three vehicles accumulated over 3 million miles during the testing program. The study showed that use of MMT at dosage levels of 8.3 and 16.5 mg/liter (0.03 gm/gal and 0.0625 gm/gal) resulted in increased engine-out and tailpipe HC emissions. An increase in tailpipe HC emissions of .09 gm/mi occurred at 50,000 miles using MMT at .03 gm/gal; an increase in tailpipe HC emissions of .11 gm/mi occurred at 50,000 miles using MMT at .0625 gm/gal (Benson et al., 1979). MMT did not adversely affect the emissions of NO_x or CO. The converter efficiencies were not affected by the use of MMT. In fact, HC converter efficiencies were 2 percent to 3 percent higher for vehicles which used MMT for 50,000 miles compared to vehicles which used fuel without MMT for the same mileage (Benson et al., 1979).

In more recent work, MMT usage and its effect on catalytic converters was studied using a combustor. The combustor burned a stoichiometric mixture of 75 percent isooctane and 25 percent heptane. An amount of MMT equivalent to an MMT dosage of 0.0625 gm/gal was added to this mixture. The HC and CO conversion efficiency of the catalyst was not negatively affected by the use of MMT; however, the NO_x conversion efficiency steadily deteriorated until, at approximately 15,000 miles, its efficiency dropped to 60 percent. At the end of the study, the catalyst's NO_x efficiency had dropped below 30 percent (Duncan and Braddock, 1984).

Other MMT studies have been performed to determine its impact on catalytic converters. Those studies have generated mixed results. Plugging of the converter has been reported in some studies; other studies did not find negative impacts due to MMT usage (Williamson et al., 1982). A recent study indicates that MMT can reduce the phosphorous deposits from oil-based ZDDP.

The study concluded that combustion of MMT to Mn_3O_4 served as a scavenger for transporting away fuel and oil-derived catalyst poisons including phosphorous, zinc, and lead (Williamson et al., 1982).

MMT is occasionally used in leaded fuel sold in California, and it can thus be expected that some contamination of unleaded fuel with MMT will occur. To date, however, this has not been observed in ARB's sampling (Jackson, 1987). With the phase-down of lead in leaded gasoline, there will be increased economic incentives for the use of MMT, and its use may become more widespread. There is presently no defined maximum tolerance level for manganese in unleaded gasoline, although its deliberate addition is prohibited. To facilitate enforcement, some such tolerance level should be defined. As the available data indicate that manganese has fairly minor effects on catalyst activity, this limit need not be particularly strict. A limit of 0.0125 grams per gallon, one-tenth the recommended concentration in leaded fuel (Weaver, 1984), is recommended.

3.6 Summary, Conclusions, and Recommendations

The current tolerance level of 0.05 grams per gallon for lead in "unleaded" gasoline has not been changed since the mid '70s, despite a twenty-fold reduction in the lead content of leaded gasoline over that period. The legal lead concentration in unleaded gasoline is now one-half the legal lead content of leaded gasoline. Lead has been shown to reduce the efficiency of three-way catalytic converters at levels as low as 6 milligrams per gallon. The current tolerance level is also being abused by at least one blender, who regularly markets "unleaded" gasoline with lead levels approaching 0.05 grams per gallon. We recommend that ARB move immediately to reduce this tolerance level by a factor of ten, to 5 milligrams per gallon

The current tolerance level for phosphorus in unleaded gasoline is 0.005 grams per gallon. This tolerance was set at the same time as the lead tolerance, and is probably unnecessarily high. However, phosphorus at this level does not result in clear damage to the catalytic converter. In addition, even if all unleaded gasoline contained the maximum legal amount of phosphorus, the resulting contamination would be small compared to the effects of phosphorus from the engine oil. Thus, there would be little or no benefits from a change in the tolerance level for phosphorus.

Silicone contaminants in gasoline can damage catalytic converters and oxygen sensors by coating them with amorphous silica. There is no evidence that this has occurred in California, but incidents have been reported elsewhere in the U.S. The source of the silicon contamination was apparently recycled solvents containing silicone oils. Regulations prohibiting such recycling or requiring chemical analysis of the recycled material might be required if more such problems are reported. Combustion of thermal degradation of silicone rubbers, gaskets, sealants, etc. can also result in catalyst or oxygen sensor damage. ARB should examine the extent to which silicones are included in aftermarket products--some regulation of silicones in these products may be warranted.

The sulfur content of unleaded gasoline is presently limited to 300 PPM. In 1978, ARB staff recommended that this be phased down to 100 PPM in 1984, but this recommendation was not adopted by the Board. Reducing the sulfur content of gasoline would contribute to attainment of the SO_2 and sulfate standards in those areas now in violation of them, as well as reducing H_2S emissions from three-way catalysts. A slight increase in catalyst efficiency would also result, thus reducing HC, CO, and NO_x. ARB should re-examine the costs and cost-effectiveness of further reductions in gasoline sulfur content, since the reduction in diesel fuel sulfur in force in the South Coast (and under consideration for the rest of the State) may have affected the costs of gasoline sulfur reduction as well.

Manganese (as MMT) may legally be used as an antiknock in leaded gasoline, and is so used in some leaded gasoline sold in California. Due to the phase-out of lead, increased amounts of manganese may be used in the future. Contamination of unleaded gasoline with small amounts of manganese is likely as a result. Manganese increases engine-out HC emissions, but in low concentrations it has no major deleterious effects on catalysts. Thus, cross-contamination of unleaded gasoline with small amounts of manganese is unlikely to have much effect. To ensure against excessive contamination, however, ARB should establish a tolerance level for manganese in unleaded fuel. A tolerance level of 12.5 milligrams per gallon (one tenth the normal level in leaded gasoline) is suggested.

4.0 FUEL INJECTOR AND INTAKE SYSTEM DEPOSITS

Fuel and intake system deposits in gasoline engines are not a new problem--the need for detergents to maintain carburetor and intake system cleanliness has been recognized for many years. With the recent expansion in the use of multi-point fuel injection systems, fuel-injector deposit formation has come to be recognized as a major problem as well. Public attention was drawn to this issue in 1985, when General Motors Vice-Chairman Howard H. Kehrl addressed the issue in a 1985 letter to major oil company executives. In the letter, Mr. Kehrl asked about the oil companies' plans for improving the quality of the fuel, and thereby reducing injector deposits. It was stated that repairing vehicles with injector deposits had become a major warranty problem for General Motors and other automobile manufacturers.

Since that time, a great deal of research in the area of fuel injector deposit formation and prevention has been published. The use of proper doses of detergent/dispersant additives has been shown to prevent fuel injector deposits; with larger doses, existing deposits can be removed. Gasoline formulations containing such detergents are now marketed (with extensive advertising) by most major oil companies. However, not all gasolines contain the appropriate detergents in the proper quantities, and deposits may thus continue to be a problem. In addition, it has been found that some presently-used detergents may actually exacerbate another problem: that of deposit formation on the intake valves.

Both fuel injector and intake system deposits increase exhaust emissions, in some cases substantially. Use of multi-point fuel injection systems is common now, and is expected to become increasingly common in the future. A case can be made, therefore, for ARB regulations to ensure adequate fuel detergency to prevent deposits. This section describes the effects of deposits that occur in automotive engines and fuel-injection systems, the mechanism of injector deposit formation, and the additives that can be used to remove deposits and keep engines and fuel systems clean. In addition, the types and quantities of detergents used in California gasoline are estimated, and potential regulatory actions in this area are discussed.

4.1 Deposit Effects on Emissions and Performance

In multi-point fuel-injected engines, deposits in the injector annulus can cause misfires, rough operation, loss of power, and hard starting. These deposits reduce the effective flow area of the injector and cause the cylinder to run lean. Because of feedback in the control system, the effect of injector deposits does not follow the apparently logical path. One would expect the leaning effect to cause an increase in NO_x and a decrease in HC and CO. However, severe injector deposits actually cause an increase in HC and CO emissions.

The increase in HC and CO emissions can be attributed to the response of the electronic fuel control system and to the reduction in vehicle power due to the deposits. Differences in deposit formation between injectors cause each individual cylinder to operate at a different air/fuel ratio. The oxygen sensor attempts to maintain the air/fuel ratio at stoichiometry. If the oxygen sensor maintains the average air/fuel ratio of all cylinders at stoichiometry, an emissions increase will occur. The cause of this increase can be seen in Figure 4-1. The cylinders operating richer than stoichiometry produce a greater increase in HC and CO emissions than the reduction produced by the cylinders operating leaner than stoichiometry.

Another potential effect is the variation in power produced by the rich and lean cylinders. Cylinders having extremely plugged injectors do not produce the same amount of power as properly fueled or rich cylinders. Extremely plugged injectors result in reduced power from the engine at a given throttle opening. The driver is forced to step deeper into the throttle to produce the power desired. Opening the throttle further causes additional air and fuel to enter the engine, thereby increasing the total mass of HC and CO emissions produced by the vehicle. In addition, modern emission control

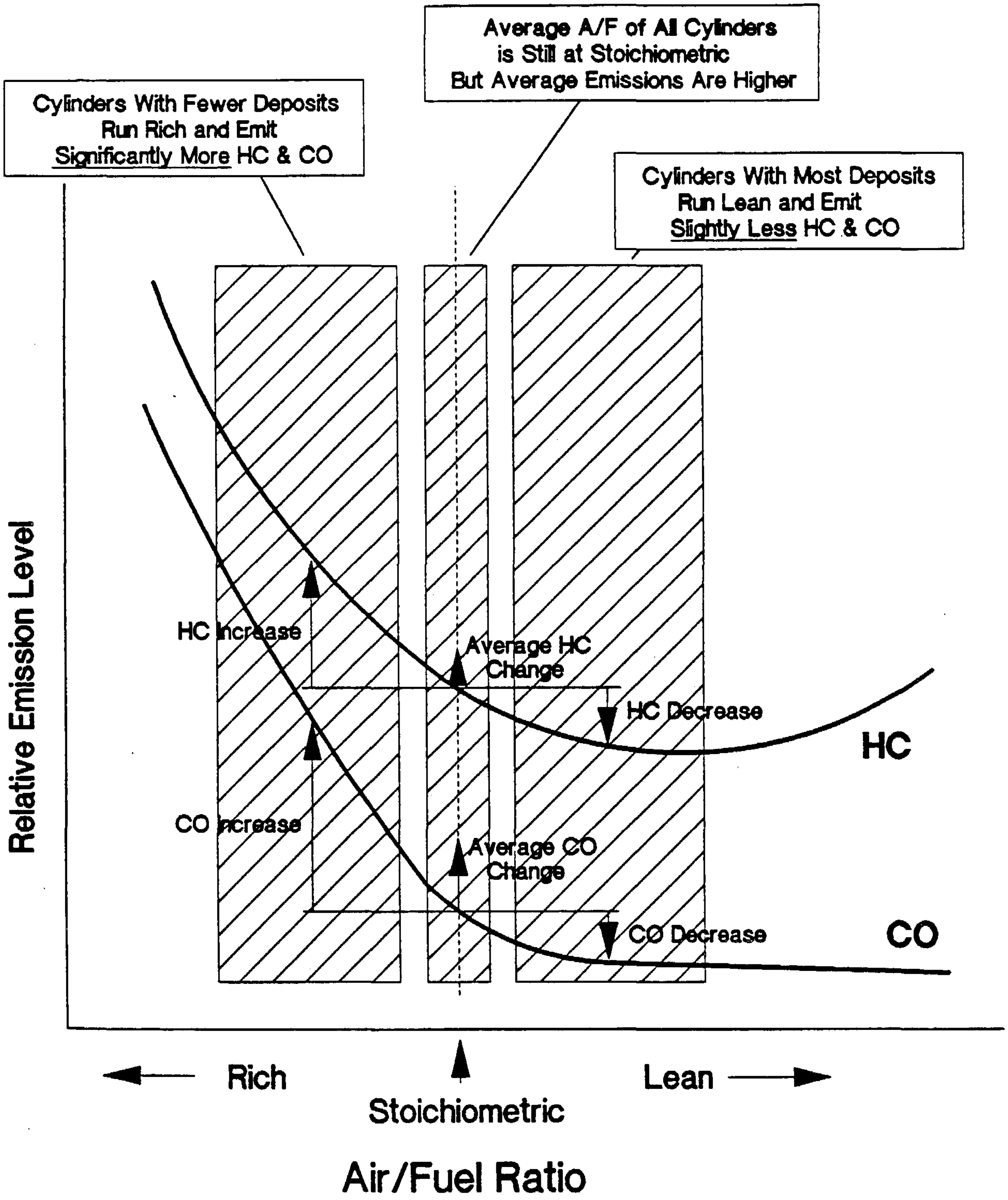


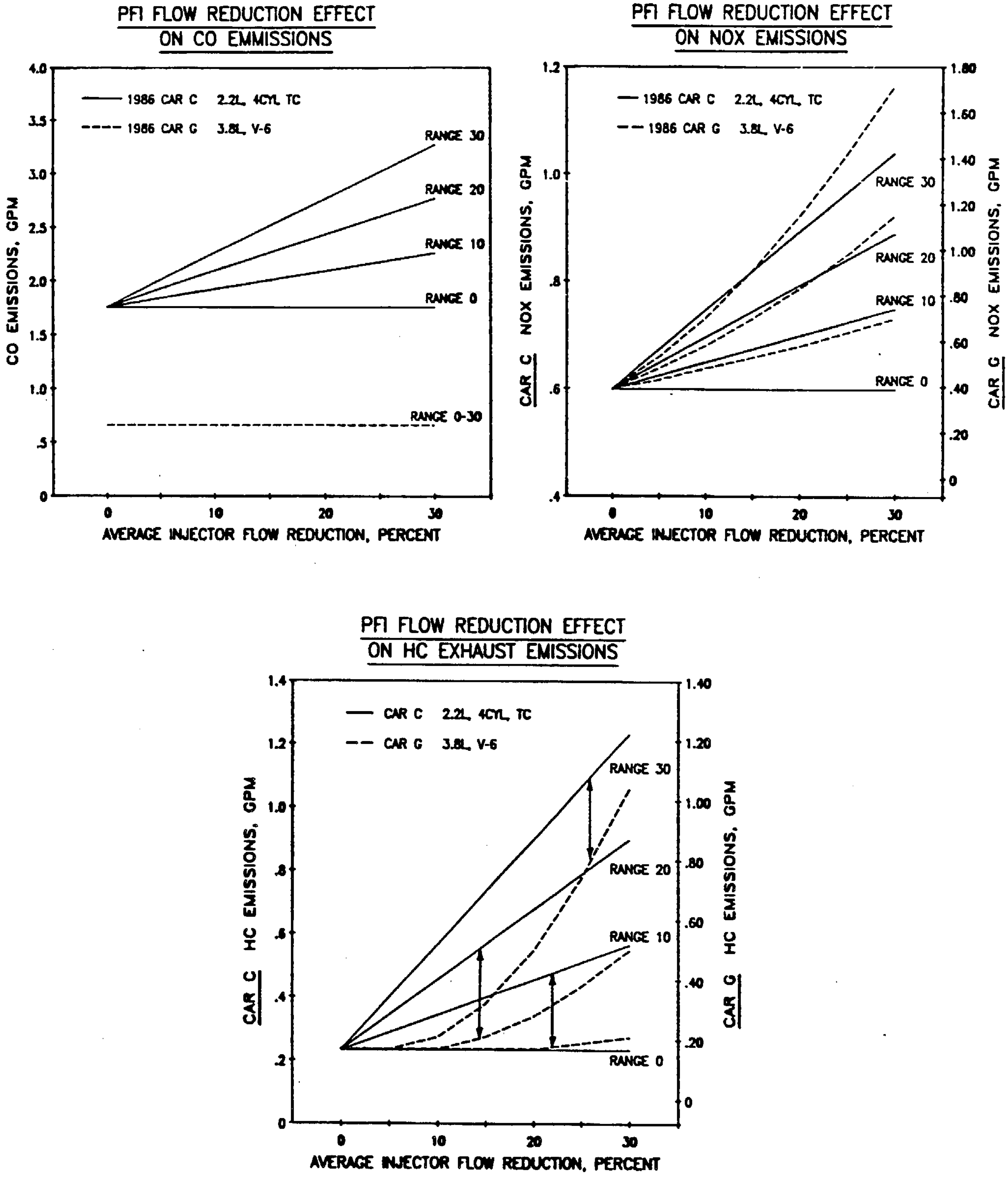
Figure 4-1. Effect of Injector Deposits on Exhaust Emissions

systems have algorithms which richen the air/fuel ratio at high throttle openings. This effect would also cause an increase in HC and CO emissions.

Data from Tupa (1987) show that <u>differences</u> in the degree of restriction from injector to injector are more important in determining emissions impacts than the average restriction for all injectors. Tupa and co-workers measured emissions from two cars: a 2.2 liter, four cylinder, turbocharged vehicle (car C) and a 3.8 liter V-6 (car G). These data are shown in Figure 4-2. As this figure shows, where all injectors were restricted equally, restrictions up to 30% had little effect on emissions. Where some injectors were more restricted than others, however, emissions of HC, CO, and NO_x increased dramatically. The greater the range of injector restriction, the larger the increase in emissions.

Intake valve deposits can also lead to increased emissions. The major effect observed to date is on NO_x (Gething, 1987). Gething showed that valve deposit weights of 12 grams can cause an increase in NO_x of up to 0.35 gm/mi. The cause of the increase in NO_x emissions is not fully understood. Two mechanisms have been proposed as explanations for the increase in NO_x emissions. First, the valve deposit could increase intake flow velocities, thereby increasing the turbulence level in the cylinder, resulting in increased temperatures and pressures during combustion. Also, the deposits may block the flow of the residual exhaust gas into the intake manifold during the valve overlap period. This reduction in internal exhaust gas recirculation (EGR) also could lead to increased NO_x emissions.

Severe intake valve deposits could also produce an increase in HC and CO emissions. As the valves grow more restricted, a larger and larger throttle opening is required to achieve the same power level. At some point, the throttle will open enough to trigger the "full throttle" response in the electronic control system. Typically, this response includes richening the mixture for best power and switching to open-loop control. The result is a large increase in HC and CO emissions.



Source: Tupa, 1987.

Figure 4-2. Effect of Injector Deposits on Emissions

Combustion chamber deposits, if severe, can cause an increase in HC emissions and an increase in the octane number required for the vehicle to operate without knocking. Formation of these deposits is theorized to be one of the significant causes of increases in HC emissions from aging vehicles operating on leaded gasoline. Combustion chamber deposits do occur in vehicles operating on unleaded gasoline, but the average increase in HC emission due to combustion chamber deposits tends to be lower for unleaded vehicles than for leaded vehicles (Weaver, 1986).

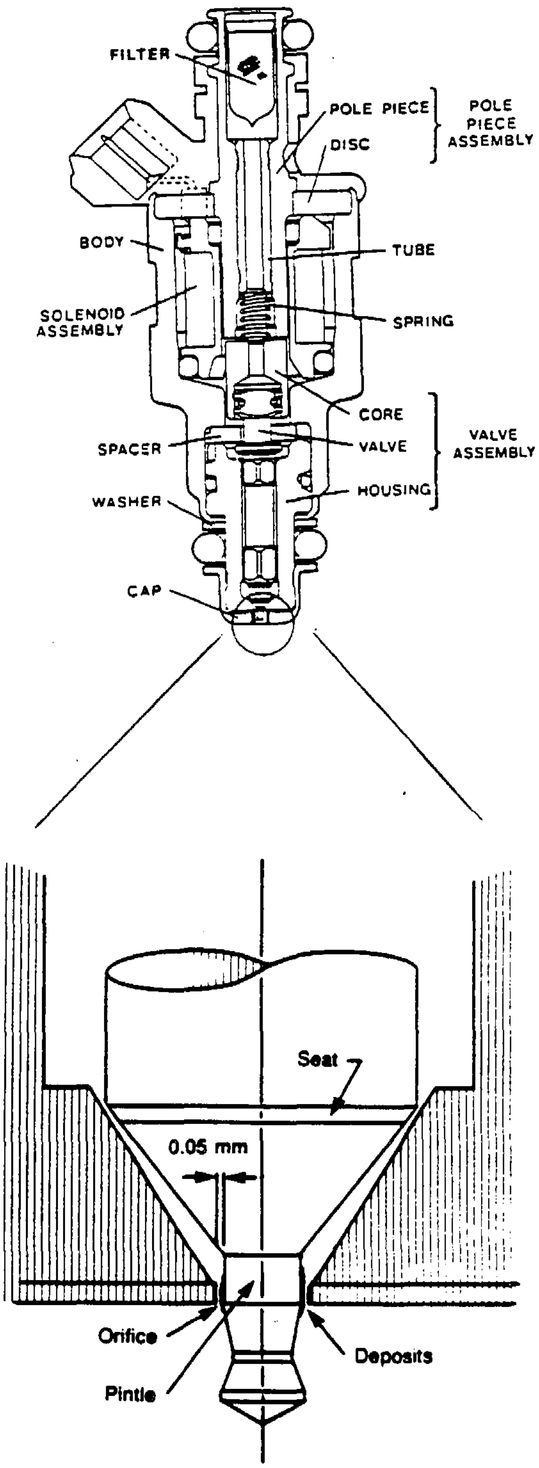
4.2 Causes of Fuel-Injector Deposit Formation

The pintle-type fuel injector shown in Figure 4-3 is the most popular injector used by automotive manufacturers. This type of injector meters fuel in the annular region near the pintle tip. When the injector is metering fuel, the clearance in this region is approximately 50 micrometers. Due to the minimal metering area, these injectors are extremely sensitive to the presence of deposits in the annular region.

A number of factors, most of which are not fuel related, impact the formation of injector deposits. Underhood temperatures, driving cycles, vehicle design, and fuel composition all determine whether a given vehicle will develop deposits. The key variable in this determination appears to be temperature of the injector tip during the hot soak period (Tupa, 1987).

4.2.1 Fuel-Injector Deposit Formation Hypothesis

The current generally accepted hypothesis is that injector deposits are built up during the hot-soak period after a vehicle is driven. During the soak period, fuel weeping from the injector heats at the pintle, evaporates and leaves a "gum" residue. When the engine is started, particles from the EGR system, the PCV system, or the fuel system, collide with the gum and stick there to form deposits. As time goes by, these deposits accumulate until significant reductions in the flow from the injector occur (Tupa, 1987).



Source: Lenane, 1986

Source: Benson and Yaccarino, 1986

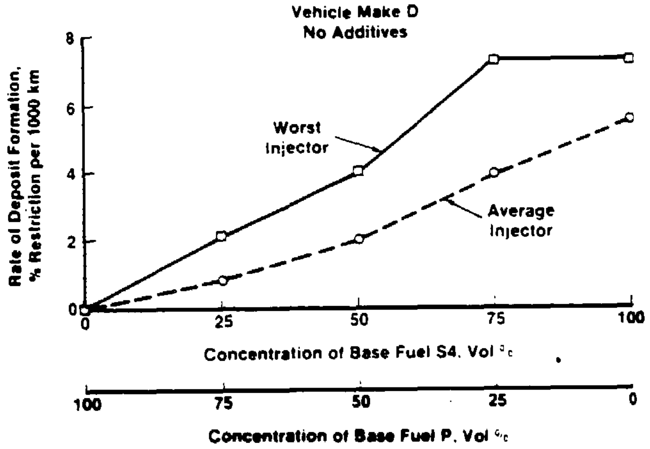
Figure 4-3. Pintle-Type Fuel Injector

By studying the composition of injector deposits, a better understanding of deposit formation and of methods to prevent it can be developed. Deposits on injector pintles generally contain carbon, hydrogen, nitrogen, oxygen, sulfur, sodium, lead, and zinc. The organic fraction is predominantly partially oxidized hydrocarbons. These hydrocarbons most likely originate from the fuel. The inorganic fraction consists of sulfates and oxides of several metals. These metals most likely originate from oil additives and the vehicle's fuel system. The sulfur most likely comes from the fuel. This composition of the deposits lends credence to the theory of fuel weeping from the injector and "sticking" to the pintle (Taniguchi et al., 1986).

4.2.2 Effect of Fuel Composition on Fuel-Injector Deposit Formation

The formation of injector deposits is related to fuel composition. The most severe deposit-forming fuels tend to be catalytically cracked gasolines, which are highly olefinic. Because of their unsaturated chemical structure, olefins are relatively unstable, and thus form gums easily. Figure 4-4 shows the rate of deposit formation for several different fuel compositions. The different fuel compositions were created by combining two fuels in different percentages. The percentage of each fuel included in the different mixtures are shown at the bottom of Figure 4-4. Listed in Table 4-1 are the chemical properties of the two base fuels used to create the different fuel compositions shown in Figure 4-4. As the olefinic content of the fuel increases, the rate of deposit formation for the average injector and the worst injector increases.

Our understanding of the fuel components that cause injector deposits is not yet complete. The formation of these deposits is an extremely complex phenomenon. It is not yet possible, therefore, to estimate deposit formation rates accurately from fuel composition data. Limited testing of the fuel constituents indicates that olefin content, sulfur content, and polar material content contribute to deposit formation (Taniguchi et al., 1986). Polar compounds found in gasoline include phenols, pyrroles, and anilines. Alcohols are also polar compounds which are sometimes added to unleaded gasoline.



Source: Taniguchi et al., 1986

Figure 4-4. Deposit Formation for Different Fuel Compositions

TABLE 4-1. TEST FUEL SPECIFICATIONS

Fuel Code	S4	P
Gum, mg/100 mL		
Unwashed	8	2
Washed	5	1
Induction Period, Min.	>1440	>1440
Composition, FIA, Vol %		
Olefins	23	3
Aromatics	24	31
Saturates	53	66
Sulfur, ppm	417	36
Total Nitrogen, ppm	144	6
Diolefins, Vol % by GC	0.27	0.04
Mass % by MA	0.32	0.12
Distillation, °C		
10%	57	44
50%	114	91
90%	187	155
EP	218	198

Source: Taniguchi et al., 1986

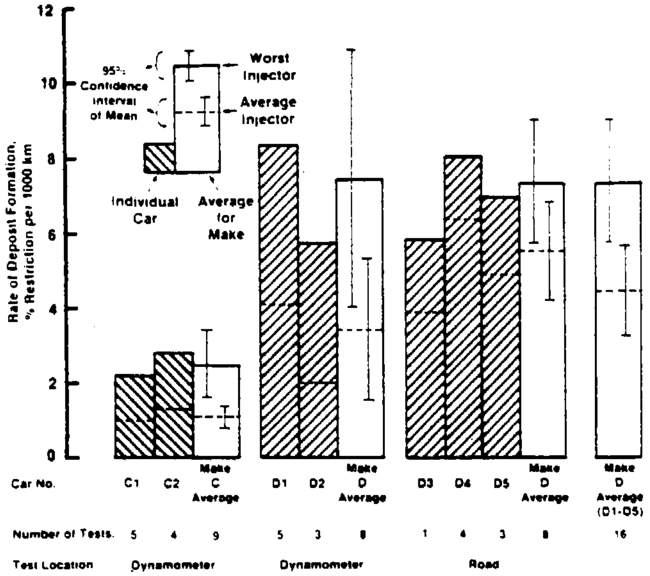
4.2.3 Effect of Fuel-Injector Tip Temperatures on Deposit Formation

Different makes of vehicles exhibit varying rates of deposit formation. Figure 4-5 displays the variation in deposit formation rates for different vehicles using the same fuel and driving cycle. Differences in fuel-injector tip temperatures among vehicle makes are theorized to be the reason for the variation in deposit formation rates.

Temperature profiles for different injectors on a given vehicle are displayed in Figure 4-6. As can be seen, injectors 2 and 3 reached the highest temperature of the four injectors. Injector 4 remained the coolest of all the injectors. In 91 percent of the deposit formation tests performed on this vehicle, injectors 2 and 3 reached the restriction point first. In no instance did injector 4 become restricted prior to the other injectors. These data support the conclusion that injector tip temperature is related to injector deposit formation (Taniguchi et al., 1986). Tupa (1987) has also published data showing a strong positive correlation between deposit formation rates and the ambient temperature during testing. These data also support the conclusion, since injector tip temperature would be lower at lower ambient temperatures.

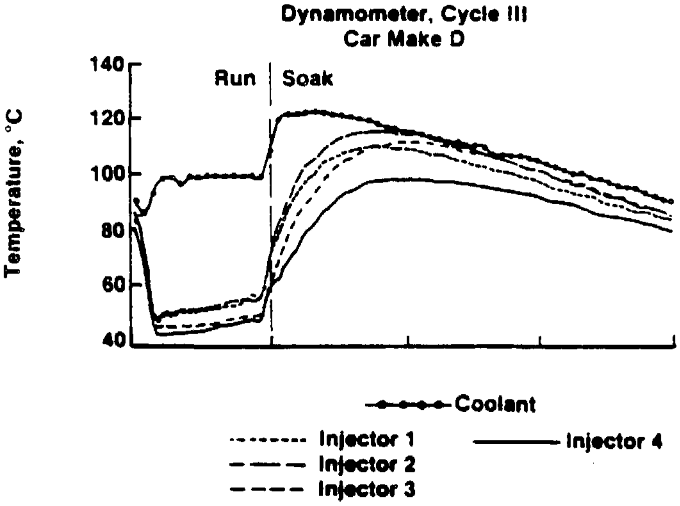
4.2.4 Effect of Driving Cycle on Fuel-Injector Deposit Formation

Deposit formation rates vary depending on a vehicle's driving cycle. These rates have been measured for a number of different driving cycle/soak periods. The independent variables studied included the engine run time and soak time. Table 4-2 lists the deposit formation rate for the four different run/soak schedules that were used by Taniguchi et al. (1986). The testing resulted in significantly increased deposit formation rates for the relatively long soak period, with a relatively short run period. All other run/soak schedules resulted in lower deposit formation rates.



Source: Taniguchi et al., 1986

Figure 4-5. Deposit Formation in Different Vehicles



Source: Taniguchi et al., 1986

Figure 4-6. Injector Temperature Profiles

TABLE 4-2. DEPOSIT FORMATION RATES FOR DIFFERENT RUN/SOAK CYCLES

Run Time (min.)	Soak Time (min.) 15	30	45	
15	.40 (.24)		4.7 (2.5)	Worst Injector (Average Injector)
30		.94 (.62)		
45			.08 (.03)	

Deposit Formation Rate = Percent Flow Restriction/1000 km

Source: Taniguchi et al., 1986

Automotible manufacturers use an accelerated durability driving test schedule (the "AMA Cycle") to demonstrate emissions durability during certification. In some cases the 50,000 miles of vehicle durability can be completed in three months. This accelerated schedule contains none of the hot soak/run cycles which cause fuel injector deposits. In most cases, the vehicle stops only long enough to have an emissions test performed or to change drivers. Thus, the certification durability schedule will not create injector deposits in vehicles which may be susceptible to deposit formation. Deterioration factors developed using this driving schedule would underestimate in-use emissions from vehicles which are susceptible to injector deposit formation.

4.3 Detergent/Dispersant Effects

Detergent and polymeric dispersant additives are used in gasoline to prevent deposit build-ups and remove pre-formed deposits from carburetors, fuel-injectors, and intake systems. Detergents can effectively remove deposits from carburetors and fuel injectors, but may decompose at high temperatures such as those found on the intake valve, resulting in increased intake valve deposits (Tupa, 1987; Taniguchi et al., 1986). Polymeric dispersants are used to remove and to disperse deposits. Polymeric dispersants tend to be more stable at higher temperatures and can be used at greater concentrations than detergents (Tupa and Dorer, 1984).

4.3.1 Classification of Detergent Additives

There are not generally-accepted industry guidelines for classifying detergent additives by performance. Each additive manufacturer tends to use a different classification approach, generally one which reflects well on that manufacturer's products. Chevron Research Company (whose affiliate, Chevron Chemical, is also an additive manufacturer) has developed a classification methodology based on the formulation and performance of different detergent additives. Chevron's classifications, along with the effects attributed to the different classes of detergent additives, can be found in Figure 4-7.

Chevron's classification system consists of three generic classes:

- Carburetor/Injector Detergents;
- Detergent-Dispersants; and
- Deposit Control Additives.

Carburetor and injector detergents have performance properties similar to the original carburetor detergents. These detergents are relatively inexpensive. They are effective in preventing deposits from forming in carburetor throttle bodies. These additives are not effective at keeping critical air bleeds and intake systems clean (Chevron Research Company, 1985).

Generic Class	Throttle Body	Idle Air Bleeds	Manifold Warm-Up Hot-Spot	Intake Ports	Intake Valves	PCV Valve	Combustion Chamber[3]	Port Fuel Injectors
Carburetor/Injector Detergents	■			X	X			■[1]
Detergent-Dispersants	●		●	●	●[4]	●	X	■[1]
Deposit Control	■	■	■	●	●	●	X[2]	■[1]
	■	■	■	■	■	■	X[2]	■

[1] Clean-Up at Higher Concentrations or in Mild Fuels Only
[2] Not Applicable to All Chemistry
[3] Unleaded Fuel Only
[4] Not All Formulations Provide Keep-Clean Performance

☐ No Benefit
● Keep-Clean Performance
■ Keep-Clean Plus Clean-Up Performance
X Detrimental

Source: Chevron Research Company, 1987

Figure 4-7. Detergent Additive Classification and Performance

Carburetor/injector detergents will prevent fuel injector deposits, but this requires additive concentrations greater than those previously used to maintain carburetor cleanliness. At these higher concentrations, carburetor/injector detergents accelerate deposit formation on intake valves and ports, however. This has been confirmed by a number of researchers (Tupa, 1987; Taniguchi et al., 1986; Jewitt et al., 1987)

Additives classed as detergent-dispersants by Chevron provide keep-clean performance for intake manifolds, throttle bodies, and other critical systems. These additives are apparently the ones described as "polymeric dispersants" by Tupa. According to Chevron, detergent-dispersants can also can provide keep-clean performance for fuel-injectors and possibly clean up fuel-injector deposits in mild fuels. Use of detergent-dispersants tends to increase the formation of combustion chamber deposits (Chevron Research Company, 1987).

According to Chevron, deposit control additives are the most effective detergent additives currently on the market (Chevron uses such additives in its own gasoline, and markets them to other refiners). Two classes of deposit control additives exist. Both classes provide keep-clean and clean-up performance for throttle-bodies and fuel-injectors. The first class of deposit control additives also provides keep-clean performance for intake ports, intake valves, and PCV valves. The second class of deposit control additives provides keep-clean and also clean-up performance for all systems including intake ports, intake valves and PCV valves. These additives can be used in mild fuels and production fuels while still maintaining fuel and intake system cleanliness.

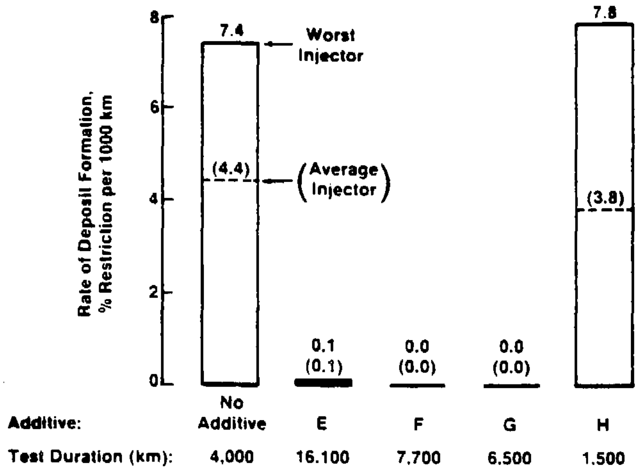
These classifications are used to define the performance characteristics of the different additives in use today. The specific additive formulations are proprietary; additive manufacturers generally do not divulge their formulations. In published literature, additives are typically identified as additive A, B, C, etc. It is difficult, therefore, to determine whether a specific set of tests was performed using carburetor detergents or deposit control additives.

4.3.2 Keep-Clean Additives and Dosages

In all papers Radian reviewed, additive manufacturers reported that they were able to clean up and keep clean pintle-type injectors under the most severe conditions (Lenane and Stocky, 1986; Abramo, Horowitz, and Trewella, 1986; Taniguchi et al., 1986; Tupa, 1987). However, in independent testing performed by an oil company (Jewitt et al., 1987), a number of commercial additive formulations failed to prevent injector deposits. Some of these additives also contributed to excessive intake valve deposits. Unfortunately, Jewitt et al. did not specify the chemistry or source for each of their additives, identifying them simply as additive A, additive B, etc.

One study, Taniguchi et al. (1986), presented the results of injector keep-clean tests, and specified the additive formulation tested. This study showed that under the most severe conditions, a polyether amine additive, a polybutene amine additive, and an alkyl succinimide additive were able to keep pintle-type fuel-injectors clean when used at proper dosage levels. These additives are all polymeric dispersants. One additive, an amino amide detergent, was not able to maintain injector cleanliness under the severe testing conditions. Figure 4-8 shows the rate of deposit formation for the test fuel with and without the various additives.

EFFECT OF ADDITIVES ON DEPOSIT FORMATION



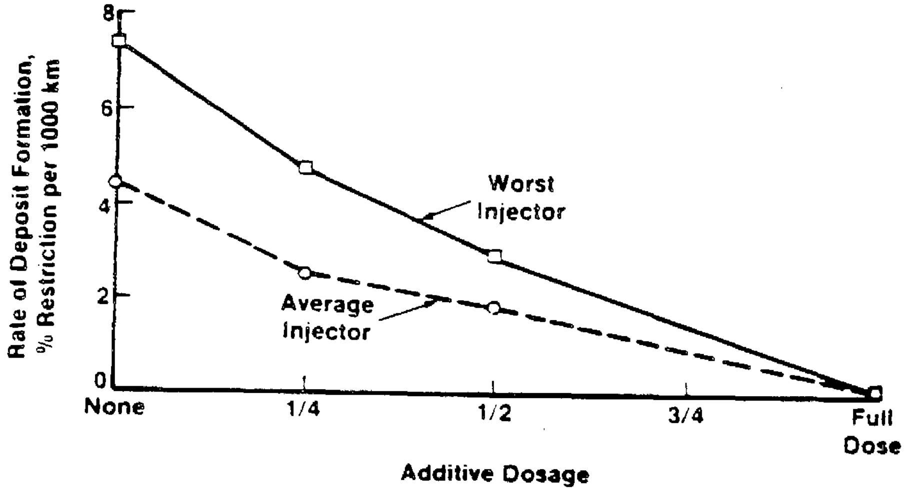
GASOLINE ADDITIVES TESTED

Code	Chemistry
E	A Polyester Amine
F	A Polybutene Amine
G	An Alkyl Succinimide
H	An Amino Amide

Source: Taniguchi et al., 1984.

Figure 4-8. Effect of Additives on Deposit Formation

One additive was tested at various dosage levels. This was done to determine whether lower dosages could be used to keep injectors clean. Figure 4-9 shows the rate of deposit formation for the various additive dosages that were used. Testing was performed at one-quarter, one-half, and full dosage. As shown by the figure, reduced dosages resulted in increased injector deposit formation. The deposit formation rate was reduced with additive usage; with the full dosage, no deposit formation occurred (Taniguchi et al., 1986).



Source: Taniguchi et al., 1986

Figure 4-9. Effect of Additive Concentration on Deposit Formation

Note: Polyether Amire Additive added to a severe deposit forming fuel.

This testing shows that not all additives are effective at maintaining injector cleanliness. In addition, the full dosage of additives which are effective must be used. If dosages less than those specified by the additive manufacturer are used, deposit formation will occur. It is likely that the effective dose is a function of fuel chemistry, and that this will be different for different fuels.

4.3.3 Clean-Up Additives and Dosages

The work of Taniguchi et al. (1986) and others (e.g. Tupa, 1987) shows that the additives used to maintain injector cleanliness can also be used to clean up fouled injectors. Taniguchi et al. found that additive doses which were effective for keep-clean performance in severe fuels could remove injector deposits when used in normal production fuels. The amino amide additive, which did not effectively prevent deposits in severe fuels, was an ineffective deposit-removing additive when used in the production fuel.

These same additives were unable to remove the deposits when used at the same dosage in an attempt to clean up fouled injectors while using the severe fuels. The effective detergents appeared able to stop additional deposit formation; however, they were not effective enough to remove the deposits. A concentrated additive was added to the severe fuel to determine if this additive would clean up the injector. When used at a high dosage level, the additive concentrate was sufficient to clean the injector (Taniguchi et al., 1986).

This study showed that when additives are used at the manufacturer-specified treatment levels in severe base fuels, they are not effective at removing deposits. Only by adding a concentrated additive can the deposits be removed when a severe fuel is used. These concentrated additives are sold in the automotive aftermarket by a number of firms, including most of the major oil and auto companies. They are intended to be added to the gas tank by the vehicle owner.

4.3.4 Intake Manifold and Combustion Chamber Deposits

In addition to removing injector deposits, detergents and polymeric dispersants also must maintain the cleanliness of the intake system and combustion chamber. In testing performed to date, polyether and polybutene amine polymeric dispersants have been shown to reduce intake system deposits (Lewis et al., 1983). Other detergents and dispersants (alkyl succinimides, amino amides, and a polybutene succinimide) do not reduce intake system deposits as effectively. In some tests, intake valve deposits were greater for fuel containing an amino amide and fuel containing an alkyl succinimide, than for fuel containing no detergents or dispersants (Taniguchi et al., 1986). This effect has been observed by many workers in the field (Tupa, 1987; Jewitt et al., 1987; Gething, 1987).

Some deposit control additives increase the formation of combustion chamber deposits. Chevron Research estimated the octane requirement increase due to these combustion chamber deposits to be between 0.5 and 1.0 octane numbers compared to gasoline without these additives. An increase of this magnitude would not be expected to cause significant emissions increases, although it might result in knocking by some marginal engines. Most engine manufacturers incorporate sufficient allowance for octane requirement increase (ORI) due to combustion chamber deposits (Weaver, 1984).

4.3.5 Detergent/Polymeric Dispersant Performance Tests

Two types of tests are used to evaluate the performance of detergents. One test is the Coordinating Research Council (CRC) standard test for measuring detergent effectiveness. This test, widely accepted in the industry, is known as the CRC Carburetor Cleanliness Detergent Test. The second test type has been developed to evaluate the formation of fuel-injector deposits. Although there is general agreement on the most vulnerable engines and the important features of the test cycle, these tests have not yet been codified into an industry standard.

Because detergent use can potentially increase deposit formation rates in intake systems, detergent testing should evaluate the ability to maintain the cleanliness of all critical intake and fuel system components, including the intake valves and ports and the combustion chamber. While some tests of intake valve deposit formation have been reported (Bitting, 1987; Jewitt et al., 1987), these tests are not yet universally accepted. No industry standard test procedure to evaluate the overall cleanliness performance of detergent additives has yet been developed.

4.3.5.1 CRC Carburetor Detergency Test

Carburetor detergency effectiveness is measured using a standard test procedure. The method measures the effectiveness of gasoline additives in reducing the formation of carburetor throttle-body deposits. The test is conducted on a dynamometer with a Ford six-cylinder, 240 cubic-inch engine. Crankcase blowby gas is directed to the air cleaner to accelerate the deposit build-up. EGR also is used to increase the quantity of contaminants entering the engine. The engine is operated at idle (700 RPM) for three minutes followed by seven minutes at 2,000 RPM. This cycle is repeated for 20 hours.

The carburetor on the Ford engine has been modified so the throttle bore is removable. The removable throttle bore is an aluminum sleeve which is weighed before and after the test. The difference in weight is the deposit that accumulated during the test.

This test, although useful for additive manufacturers, does not correlate with injector deposit formation in pintle-type injectors. The operating environment of the pintle-type injector is much more severe than the carburetor bore on the CRC detergency test. Due to the difference in operating environments, additive manufacturers have developed specific detergency tests for pintle-type injectors. The differences include the use of MPFI engines, the use of a modified test schedule including significant hot-soak time, and the use of severe fuels.

4.3.5.2 Typical Fuel-Injector Detergency Test

Deposit formation testing with fuel-injected vehicles is typically performed on a chassis dynamometer. The vehicle is cycled between a high-speed cruise and an engine-off soak period. Generally, the soak period lasts 45 minutes, while the cruise period lasts 15 minutes at vehicle speeds near 55 mph.

The fuel used during the test generally has a high olefin content. The deposit forming tendency is increased by using the less stable fuel. The test is performed using a vehicle so that injector temperatures will be representative of in-use conditions. In most cases, the test is performed until the injector deposits have stabilized, or a specified time period has elapsed.

When testing the effectiveness of detergents in pintle-type fuel-injectors, most additive manufacturers use the previously described procedure. However, no single standard test (vehicle, driving cycle, and fuel composition) has been generally accepted for evaluating the effectiveness of detergents on pintle-type fuel-injectors.

4.3.6 Detergent/Polymeric Dispersant Usage

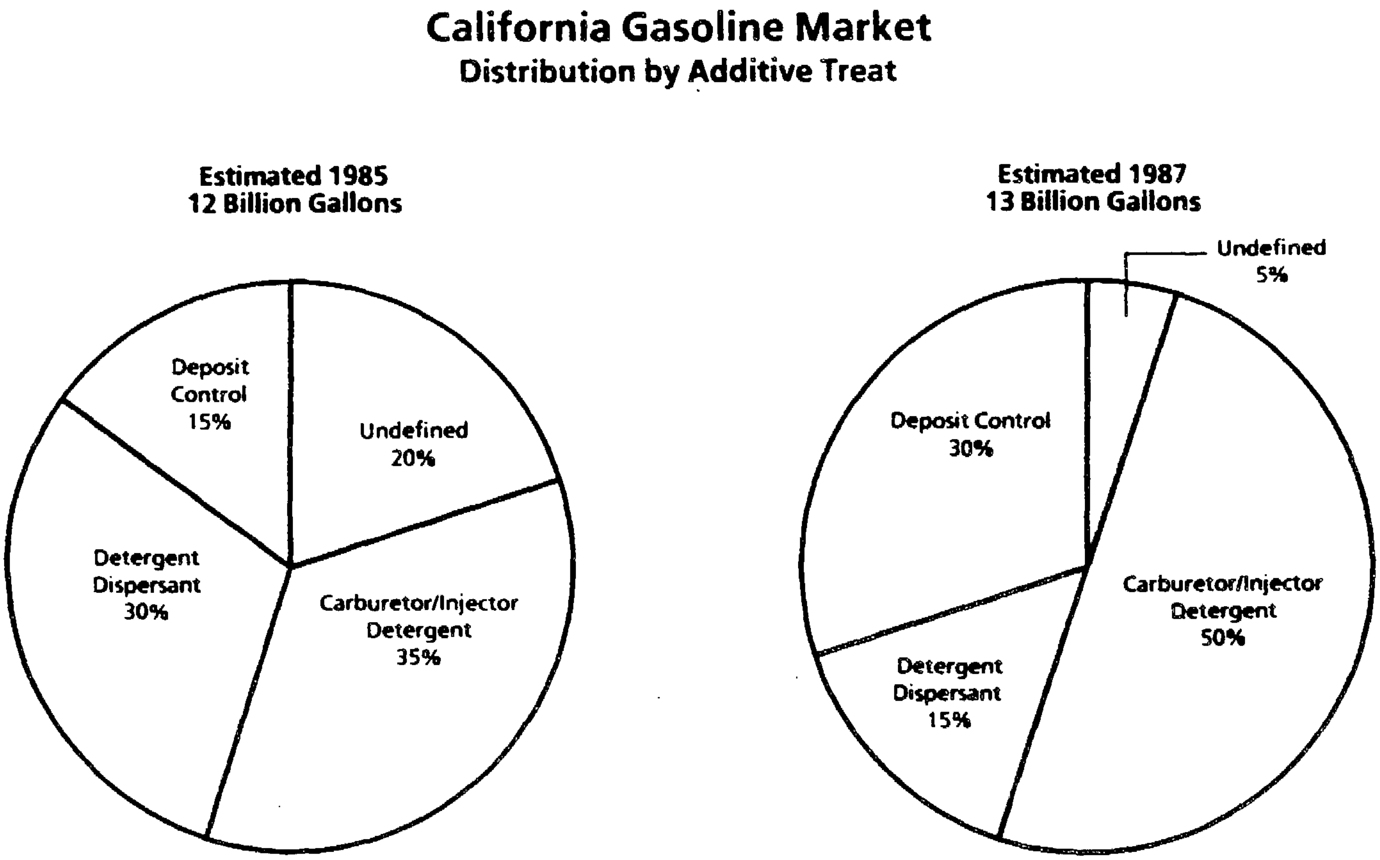
Until the recent publicity concerning fuel-injector deposit formation, detergent usage in unleaded gasoline had been declining. Because of economic considerations, a number of refiners reduced detergent levels to cut costs. According to an account manager with Lubrizol, the majority of oil companies use a treatment in the range of 8 pounds of additive per 1,000 barrels (PTB) or 32 ppm. In addition, he estimated that 30 percent of the oil companies in operation in the U.S. did not use any detergent additive at all (Keebler, 1986).

Chevron has estimated detergent/polymeric dispersant use for the California gasoline market for 1985 and 1987. The Chevron estimates can be found in Figure 4-10. Chevron uses three classifications (described in Section 4.3.1) for detergent additives based on the additives' effectiveness and chemistry. For 1985, Chevron estimated that 20 percent of the gasoline sold in California contained no detergents. Due to the publicity over injector deposits, this segment was estimated to have decreased to 5 percent during 1987. However, Chevron estimates that only 30 percent of gasoline sold in California in 1987 contained deposit control additives. Fifty percent of the gasoline sold in California was estimated to contain only carburetor detergents--the least effective form of detergent additive. Detergent-dispersant additives were estimated to account for the remaining 15 percent.

By Chevron's estimates, use of deposit control additives has increased by 100 percent from 1985 to 1987. Detergent/dispersant use has decreased by an estimated 50 percent during the same period, while carburetor/injector detergent use during the same time period has increased by over 40 percent (Chevron Research Company, 1987).

The increased use of carburetor/injector detergent, while potentially reducing the formation of injector and carburetor deposits, cannot be expected to reduce existing deposits. In addition, the greater use of these additives could result in increased intake valve and port deposits, thereby potentially increasing NO_x emissions.

In order for a detergent to be acceptable in the marketplace, it must work for carburetors as well as fuel-injection systems. Carburetted engines will be present in California for a number of years to come. In the limited testing reported to date, additives formulated for cleaning fuel-injectors also keep carburetors clean (Lenane and Stocky, 1986; Jewitt et al., 1987).



	Overall Additive Effectiveness
Carburetor / Injector Detergent	Low
Detergent Dispersant	Medium
Deposit Control	High

Source: Chevron Research Company, 1987

Figure 4-10. Estimated Gasoline Detergent Use in California

4.4 Fuel Factors

The South Coast Air Basin (SCAB) has placed limits on the degree of unsaturation of motor vehicle fuel (refer to Section 2.4). Unsaturated components include olefins and diolefins, which tend to be unstable and produce gum. Theoretically, reducing the quantity of unstable components in the fuel should reduce injector deposits. As discussed in Section 2.4, however, the bromine number regulation in the SCAB is so high that it has only a marginal effect on the quantity of olefins and diolefins found in gasoline in the SCAB. Any reduction in the maximum bromine number permitted in the SCAB could be expected to reduce the concentration of olefins and diolefins currently found in unleaded gasoline, and thus to reduce the formation of injector deposits. The degree of this improvement is uncertain, however.

4.5 Estimated Excess Emissions due to Injector Deposits

To assist in evaluating the cost-effectiveness of a fuel detergency regulation, Radian has developed a rough estimate of the impact of injector deposits on excess emissions in California in 1986. Estimates of the number of fuel-injected vehicles in California, the number of vehicles with injector deposits, and the increase in emissions due to injector deposits, along with emission factors and VMT data from EMFAC7C were used to predict the impact of injector deposits on excess emissions.

Estimates for the number of fuel-injected vehicles were developed from ARB and EPA fuel system sales fraction data (Lyons and Kenny, 1987; Heavenrich et al., 1986). California passenger car sales were used for model years 1983 through 1986. Estimates of California passenger car sales were determined using EPA national sales figures for model years 1975 through 1982. The total number of vehicles in California estimated using this method is approximately the same as the California Department of Transportation estimate for 1986: 12,841,000.

Sales of fuel-injected vehicles in California, including both MPFI and TBI vehicles, were estimated to be 12 percent of the total vehicle sales for model years 1975 through 1979. These sales were estimated to increase at a rate of 6 percent per year from 1979 until 1983. The data presented by Lyons and Kenny (1987) was used for model years 1983 through 1986. The Lyons and Kenny data were not segregated by the type of fuel-injection system: throttle-body or MPFI. Because injector deposits have not been identified as a serious problem in throttle-body fuel-injected vehicles, these vehicles were segregated from the MPFI vehicles. The California sales fraction of MPFI vehicles was assumed to be the same as the national sales fraction, taken from Heavenrich et al. (1986).

The number of fuel-injected vehicles on the road in California in 1986 was estimated to be 2,190,000 vehicles, or 17.2 percent of the 1986 passenger car population. The number of vehicles on the road was assumed to be the same as the number of MPFI vehicles sold during the period from 1975 through 1986.

Model-year specific emission factors for these vehicles were calculated using EMFAC7C. The MPFI emission factors for vehicles without injector deposits were assumed to be the same as those predicted by EMFAC7C. Vehicles with injector deposits were assumed to have emissions greater than those predicted by EMFAC7C.

The percentage of MPFI vehicles with injector deposits was estimated to be 5 percent of the entire MPFI fleet. These vehicles were assumed to emit 200 percent more hydrocarbons and 200 percent more carbon monoxide than vehicles without injector deposits. The estimate of the total number of vehicles with injector deposits was obtained from Chevron Research Company.

From discussions with automobile manufacturers, Chevron has estimated the occurence of fuel-injector deposits by geographic region. For

California, 5 percent is a conservative (high) estimate based on the data presented by Chevron. These estimates reflect the number of vehicles being serviced because of performance problems due to injector deposits. These vehicles would be expected to be emitting significant quantities of excess emissions. Because different vehicles respond differently to injector deposits, Radian conservatively estimated the emissions increase for both HC and CO at 200 percent.

Making these assumptions, the excess emissions due to injector deposits are estimated to be 3,400 tons per year for HC and 34,700 tons per year for CO in 1986. These values are equivalent to 9.3 and 95.1 tons per day for HC and CO, respectively, or about 1 percent and 1.5 percent of total passenger-car emissions of these pollutants. The calculations used to arrive at these values can be found in Appendix A. Because the sales of fuel-injected vehicles are expected to increase significantly during the coming years, excess emissions due to injector deposits could be expected to increase in the future.

4.6 Cost-Effectiveness of Fuel Detergency Requirements

Based on the results discussed above, excess emissions due to fuel injector deposits could essentially be eliminated by a requirement that all unleaded gasoline sold incorporate one of the higher-performing additives that are currently known. This requirement should also help to reduce the incidence of carburetor and intake valve deposits, further reducing total emissions. The cost of this action would depend on the cost of the detergents involved. Unfortunately, these costs are not publicly available. Speaking in very approximate terms, one additive manufacturer indicated that the costs of the most effective additive treatments are less than one cent per gallon, while the least expensive (and least effective) treatments are about one tenth this cost.

Table 4-3 shows our cost and cost-effectiveness calculations, based on the rough cost information cited above. About three-quarters of the motor gasoline sold in California is unleaded (California Energy Commission, 1987).

As shown in Figure 4-9, Chevron estimates that 5 percent of the gasoline sold in California contains no detergent additives, 50 percent contains carburetor detergents only, 15 percent contains detergent-dispersants, and 30 percent contains deposit control additives. We assumed that the same percentages would apply to the unleaded gasoline component (i.e. that there are no important differences in additive usage between leaded and unleaded). Using these assumptions and the Chevron estimate of 13 billion gallons per year total gasoline sales, we calculated the volumes of unleaded gasoline sold in California, broken down by additive type. These volumes are shown in Table 4-3.

We then calculated the added costs of treating all unleaded gasoline with deposit control additives. For the volume of fuel which presently contains no additives, this cost was taken as one cent per gallon. For fuel which presently contains carburetor detergent or detergent/dispersant additives, the added cost for upgrading to deposit control additives was taken as 0.9 cents per gallon. For fuel which is already treated with deposit control additives, no additional costs would be incurred. These assumptions result in a total cost increase of about $84 million per year. Allocating half of this cost to HC reduction and half to CO results gives a cost of $8,750 per ton of HC and $857 per ton of CO eliminated. These costs are toward the high end of the range of cost-effectiveness values for HC and CO control programs adopted in California to date.

The cost-per ton values shown in Table 4-3 should be considered as order-of-magnitude indicators only. Both the estimated costs and the estimated benefits are highly uncertain, and a number of factors have been left out of the calculation. Some of the factors omitted include: potential emissions benefits in non-MFPI cars and in trucks, savings in repair costs due to improved engine cleanliness, savings on purchase of aftermarket additives, and

TABLE 4-3. DETERGENT COST-EFFECTIVENESS ANALYSIS

Current Estimated California Gasoline Detergent Use	
No Detergents	468×10^6 gal
Carburetor/Injector Detergents	$4{,}680 \times 10^6$ gal
Detergent/Dispersants	$1{,}406 \times 10^6$ gal
Deposit Control Additives	$2{,}813 \times 10^6$ gal
Estimated Detergent Costs	
Carburetor/Injector Detergent	$.001/gal
Detergent/Dispersants	$.001/gal
Deposit Control Additives	$.01/gal
Total Cost Increase to Use Only Deposit Control Additives	$59,500,000
Estimated HC Reduction	3,400 tons
Estimated CO Reduction	34,700 tons
Cost-Effectiveness:	
HC	$8,750/ton ($4.38/lb)
CO	$857/ton ($0.43/lb)

potential fuel consumption benefits. In addition, due to the vagueness of the available cost data, the costs of treatment may have been overestimated.

All of these effects, had they been included in the analysis, would have tended to lower the costs per ton, perhaps significantly. Thus, the most that can be said about the cost-effectiveness of requiring deposit control additives is that it appears to be within the range of cost-effectiveness values for other HC and CO control strategies that have been adopted.

4.7 Summary, Conclusions, and Recommendations

Multi-point fuel-injected vehicles are susceptible to injector deposits, and these can cause significant emission increases. The extent of the problem depends on vehicle design parameters and fuel composition. Both automotive manufacturers and the petroleum industry are modifying their products to reduce the occurrence of this problem. Even so, many current MPFI vehicles models appear to be susceptible to deposits.

The components of the fuel which cause injector deposits are being determined by researchers at this time. Olefins, alcohols, and polar material all are suspected of contributing to the problem. Injector deposits can be minimized by using specific detergents and polymeric dispersants. Not all detergents are alike. Some classes of detergents, when used at the concentrations required to prevent injector deposits, can cause increases in intake valve and port deposits, which also result in increased emissions.

As a rough estimate, fuel injector deposits in passenger cars may have been responsible for about 3,400 tons of excess hydrocarbon emissions and 34,700 tons of excess carbon monoxide emissions in 1986. Use of deposit control additives in sufficient quantities would reduce, and possibly eliminate, these excess emissions. The quantity of excess emissions produced due to injector deposits is expected to increase as sales of multi-point fuel-injected vehicles increase in the coming year.

Because of the potential for significant emission increases due to injector plugging, ARB should consider regulatory action in this area. Presently, it is not feasible to remove the deposit-forming constituents from the fuel, since the deposit formation mechanism is not fully understood. At some future time, this may be an option. Because sensitive injectors will be in the fleet for at least another decade, and sales of MPFI-vehicles are expected to increase, mandatory use of detergents and dispersants in unleaded fuel may be indicated. Rough cost-effectiveness calculations indicate that the costs per ton of emissions eliminated by mandating the most effective deposit control additives would be within the range of cost-effectiveness values for other HC and CO control strategies that have been adopted; and probably less than about $8,750 per ton for HC and $850 per ton for CO.

It is recommended that ARB investigate further the costs and emissions benefits of establishing a minimum detergency standard for unleaded gasoline. This investigation should focus on obtaining better estimates of treatment costs and emissions benefits, including the benefits for carburetted and throttle-body fuel-injected vehicles as well as those with multipoint injection. Savings in repair costs due to reduced deposit formation could be important, and should be quantified as well. As a first step in this investigation, we recommend that ARB hold a workshop on the issue.

Establishment of a regulatory requirement for fuel detergency would require the specification of some standard detergency test procedure. No industry standard test procedure for injector deposit control exists at present, although a number of organizations have developed test procedures which might be adopted for this purpose. To assure against creating other problems further downstream, the test procedure would need to address carburetor, intake valve, and combustion chamber deposit formation as well as injector deposits.

5.0 THE EFFECT OF GASOLINE VOLATILITY ON EXHAUST HYDROCARBON EMISSIONS

Evaporative emissions from gasoline vehicles are directly (but not linearly) related to the volatility of the gasoline used. Evaporative emission control systems were designed to work with certification test fuel, which has a Reid Vapor Pressure (RVP) of 9 psi. Higher-volatility fuels result in higher evaporative emissions than measured in the certification tests. Extremely volatile fuels may result in the evaporative control canister becoming saturated with hydrocarbons, so that additional emissions are not absorbed but emitted to the atmosphere. This phenomenon is known as "break through".

Gasoline volatility may also affect exhaust emissions, by means of two competing mechanisms. In highly volatile gasolines, an increased quantity of hydrocarbons is stored in the evaporative canister. Purging the canister richens the mixture, and can increase HC and CO emissions. However, gasoline with too low a volatility rating can impair cold-start performance, resulting in increased HC and CO emissions in the first bag of the FTP.

The Reid Vapor Pressures of both winter and summer-grade gasolines in most of the U.S. have been gradually increasing during the past 10 years (Dickson and Woodward, 1986). In California, however, RVP is limited by regulations to a maximum of 9 psi in most air basins during the summer months. California has thus been spared the increase in evaporative emissions that would have resulted from these more volatile fuels. EPA has recently proposed a similar limit to take effect nationwide.

This section reviews literature describing gasoline volatility and its impact on exhaust and evaporative hydrocarbon emissions. Since there is little motivation at present to increase the summertime RVP limit in California to more than 9 psi, this section focuses on the possible impacts of decreasing this limit instead. As discussed below, the limited data available suggest that further reducing summertime RVP levels to about 6 psi would probably result in small net increase in HC emissions, as well as degraded driveability. Data to assess the effects of a smaller RVP reduction (e.g. to 8 or 7 psi) are not available.

5.1 Effect of Gasoline Volatility Reductions on Exhaust Emissions

Reducing the RVP of gasoline below the current summertime maximum of 9 psi would reduce the quantity of hydrocarbon vapors generated in the fuel system, and thus reduce the quantity of vapors required to be purged from the evaporative emissions control system. A reduction in purge vapors would be expected to reduce exhaust hydrocarbon and carbon monoxide emissions. This phenomenon has been seen when reducing the RVP of fuel from above 10 psi to 9 psi (Stebar et al., 1985), and could be expected to continue at lower RVP levels as well. Below some RVP level, however, this trend would be offset by a countervailing effect.

Adequate gasoline volatility is required for effective cold starting of gasoline engines, especially at low temperatures. At a sufficiently low RVP level, cold-start performance would be impaired, causing increased HC and CO emissions. Thus, at any given ambient temperature, there is some optimum RVP level which minimizes exhaust HC and CO emissions overall. This optimum level is undoubtedly a function of the ambient temperature. At low ambient temperatures, the optimum RVP would be expected to be higher.

Chevron Research Company conducted tests to evaluate the effect of reducing summertime RVPs in the South Coast from approximately 8 psi to 6 psi. FTP emissions tests were performed on 19 vehicles, including several different types of emission control systems. Tests were performed at two ambient temperatures: 75°F (as specified for the FTP) and 55°F (a typical early morning temperature in the SCAB during the "smog season"). Only vehicle exhaust emissions were measured during the tests; evaporative emissions tests were not performed.

Table 5-1 shows the results of emissions testing at 75°F with fuels of 8.5 and 6.5 psi, respectively. For the 1970's model vehicles tested, the reduction in RVP from 8.5 psi to 6.5 psi resulted in increases of 3.7% and 6.4% in average HC and CO emissions, respectively (Welstand, 1983).

Table 5-2 shows the results of emissions testing of the same vehicles at 55°F ambient temperature, at the same RVP levels of 8.5 and 6.5 psi. In addition, testing was also performed on some later-model vehicles at 55°F, using fuels with RVPs of 8.4 and 6.1 psi. As Table 5-2 shows, the change in HC and CO emissions due to the lower RVP fuel was greater at 55° than at 75°F for the older model vehicles. At 55°F the average exhaust HC and CO increases for the older model vehicles were 15 percent and 10 percent, respectively. For the newer vehicles, the average exhaust HC and CO increases at 55°F were 10 percent and 9 percent, respectively.

In addition to the effects on exhaust emissions, drivers of the test vehicles reported degraded driveability with the lower RVP fuels. The number of stalls during the testing also increased when the volatility of the fuel was reduced. The degraded driveability might result in additional emission increases, since drivers might tamper with their vehicles to reduce the driveability problems.

5.2 Effect of Gasoline Volatility Reductions on Evaporative Emissions

The quantity of evaporative emissions produced by a vehicle is dependent on a number of factors. These factors include: the state of maintenance of the evaporative emission control system, the type of evaporative emission control system, the RVP of the fuel, and the ambient temperatures encountered. A reduction in RVP below the 9 psi level used for certification fuel would be expected to reduce evaporative emissions.

In work for the Coordinating Research Council (CRC), Radian has developed a model to predict vehicular evaporative emissions as a function of various factors (Kishan et al., 1987). Factors included in the model are the

TABLE 5-1. EFFECT OF VOLATILITY REDUCTION ON FTP EXHAUST EMISSION 75°F AMBIENT TEST TEMPERATURE

Vehicle	HC 8.5 RVP gm/mi	HC 6.5 RVP gm/mi	HC gm/mi	HC %	CO 8.5 RVP gm/mi	CO 6.5 RVP gm/mi	CO gm/mi	CO %
1973 Plymouth	0.875	0.869	+0.012	+ 1.4	13.1	12.5	-0.6	- 4.6
1973 Pontiac[1]	1.188	1.213	+0.025	+ 2.1	20.9	27.0	+6.1	+29.2
1973 Pontiac[2]	1.82	1.54	-0.28	-15.4	9.2	11.6	+2.4	+26.1
1974 Volkswagen	2.45	2.71	+0.26	+10.6	24.8	26.2	+1.4	+ 5.6
1975 Chevrolet	0.668	0.821	+0.153	+22.9	5.85	6.77	+0.92	+15.7
1975 Ford	0.504	0.623	+0.119	+23.6	12.1	8.5	-3.6	-29.8
1975 Pinto	0.150	0.139	-0.011	- 7.3	2.98	2.72	-0.26	- 8.7
1976 Oldsmobile	0.130	0.139	+0.009	+ 6.9	1.38	0.79	-0.59	-42.8
Average	0.971	1.007	+0.036	+ 3.7	11.29	12.01	+0.72	+ 6.4

[1] Original carburetor.

[2] New carburetor.

Source: Welstand, 1983

TABLE 5-2. EFFECT OF VOLATILITY REDUCTION ON FTP EXHAUST EMISSION 55°F AMBIENT TEST TEMPERATURE

Vehicle	HC				CO			
	8.5 RVP gm/mi	6.5 RVP gm/mi	gm/mi	%	8.5 RVP gm/mi	6.5 RVP gm/mi	gm/mi	%
1973 Plymouth	1.020	1.118	+0.098	+ 9.6	20.6	17.6	-3.0	-14.6
1973 Pontiac[1]	1.480	1.593	+0.113	+ 7.6	24.6	28.5	+3.9	+15.9
1973 Pontiac[2]	1.72	1.69	-0.03	- 1.7	13.7	17.5	+3.8	+27.7
1974 Volkswagen	2.48	2.90	+0.42	+16.9	30.7	31.8	+1.1	+ 3.6
1975 Chevrolet	0.692	1.070	+0.378	+54.6	6.27	8.36	+2.09	+33.3
1975 Ford	0.608	0.775	+0.167	+27.5	20.7	24.8	+4.1	+19.8
1975 Pinto	0.320	0.331	+0.011	+ 3.4	9.54	10.0	+0.46	+ 4.8
1976 Oldsmobile	0.279	0.371	+0.092	+33.0	6.00	6.66	+0.66	+11.0
Average	1.075	1.231	+0.156	+14.5	16.51	18.15	+1.64	+ 9.9

Vehicle	HC				CO			
	8.4 RVP gm/mi	6.1 RVP gm/mi	gm/mi	%	8.4 RVP gm/mi	6.1 RVP gm/mi	gm/mi	%
1982 Ford Escort	0.427	0.460	+0.033	+ 7.7	10.725	12.603	+1.878	+17.5
1983 Honda Accord	0.644	0.714	+0.070	+10.9	5.625	6.177	+0.552	+ 9.8
1982 Chev. Cavalier	0.362	0.381	+0.019	+ 5.2	6.058	6.324	+0.266	+ 4.4
1981 Datsun 210	0.430	0.511	+0.081	+18.8	6.421	6.943	+0.522	+ 8.1
1982 Oldsmobile Ciera	0.245	0.280	-0.015	- 6.1	7.612	7.825	+0.213	+ 2.8
1981 Dodge Aries	0.393	0.476	+0.083	+21.1	12.876	15.639	+2.763	+21.5
1983 Datsun Maxima	0.725	0.807	+0.082	+11.3	5.693	6.715	+1.022	+18.0
1983 Olds. Cutlass	0.328	0.348	+0.020	+ 6.1	5.560	5.483	-0.077	- 1.4
1982 Toyota Corolla	0.274	0.358	+0.084	+30.7	3.423	3.407	-0.016	- 0.5
1983 Lincoln Town Car	0.296	0.316	+0.020	+ 6.8	4.782	5.159	+0.377	+ 7.9
1983 Toyota Pickup	0.312	0.340	+0.028	+ 9.0	4.119	4.704	+0.585	+14.2
1983 Mazda GLC	0.580	0.601	+0.021	+ 3.6	11.546	11.424	-0.122	- 1.1
Average	0.418	0.462	+0.044	+10.5	7.037	7.770	+0.663	+ 9.4

[1] Original carburetor.
[2] New carburetor.

Source: Chevron Research Company, 1987

RVP of the fuel, the type of fuel system (carburetted or fuel-injected), state of maintenance (problem free or malfunctioning), ambient temperature during the hot soak, initial diurnal tank temperature, and diurnal temperature rise. The model predicts the evaporative emissions based on the previously listed factors.

The Radian model is based on evaporative emissions data over an RVP range from 9 to 11.7 psi. This model was extrapolated to lower RVP levels by extending the correlation equations for the 9 to 11.7 psi range. The results of this extrapolation are shown in Figures 5-1 through 5-4. Figure 5-1 shows projected evaporative emissions as a function of RVP for problem-free carburetted vehicles, while Figure 5-2 shows the same data for malfunctioning carburetted vehicles. Figures 5-3 and 5-4 show similar estimates for fuel-injected vehicles. These figures indicate that further reductions in fuel RVP (below 9 psi) would result in additional evaporative HC emission reductions. Each figure shows the estimate of diurnal emissions alone, and diurnal plus hot soak emissions for two different hot-soak temperatures.

As shown in the figures, the projected reduction in evaporative emissions due to lowering fuel RVP is dependent upon the fuel system type and its state of maintenance. The greatest reductions in emissions would be expected for the malfunctioning vehicles--i.e. those with a problem that would impair evaporative emission control system performance. Total emissions from problem-free vehicles are much lower than for malfunctioning vehicles, and thus the reduction in emissions with RVP is lower as well.

5.3 Estimated Effect of Reducing RVP on Total Hydrocarbon Emissions

To compare the expected evaporative emissions decrease to the exhaust emissions increase, fleet composite exhaust and evaporative hydrocarbon emission factors were calculated. The exhaust hydrocarbon emission factor was estimated by aggregating the model year specific emission factors found in Appendix A. The emission factors were weighted by sales fraction and VMT fraction. The fleet composite exhaust hydrocarbon emission

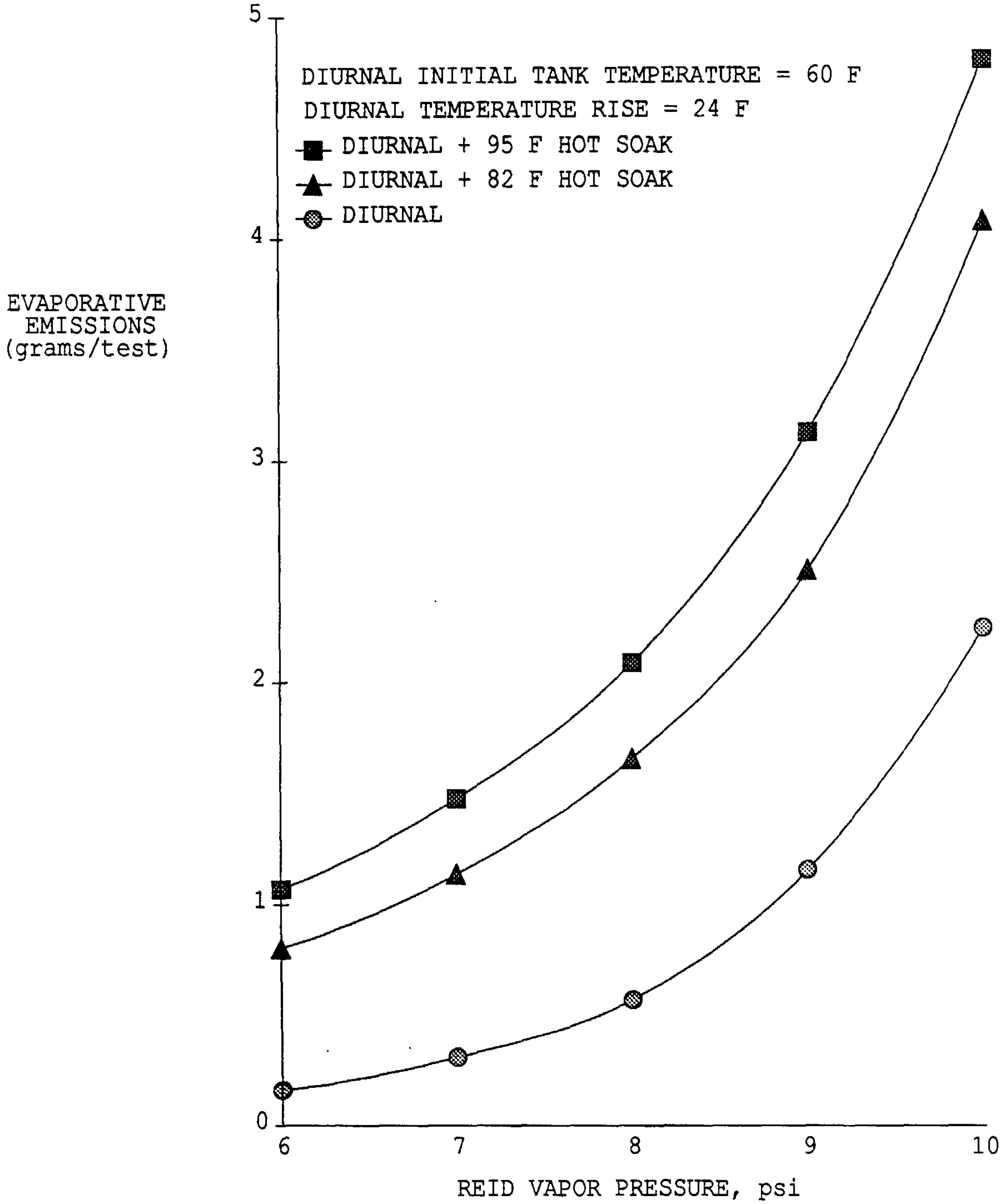


Figure 5-1. Evaporative Emissions from Problem-Free Carburetted Vehicles

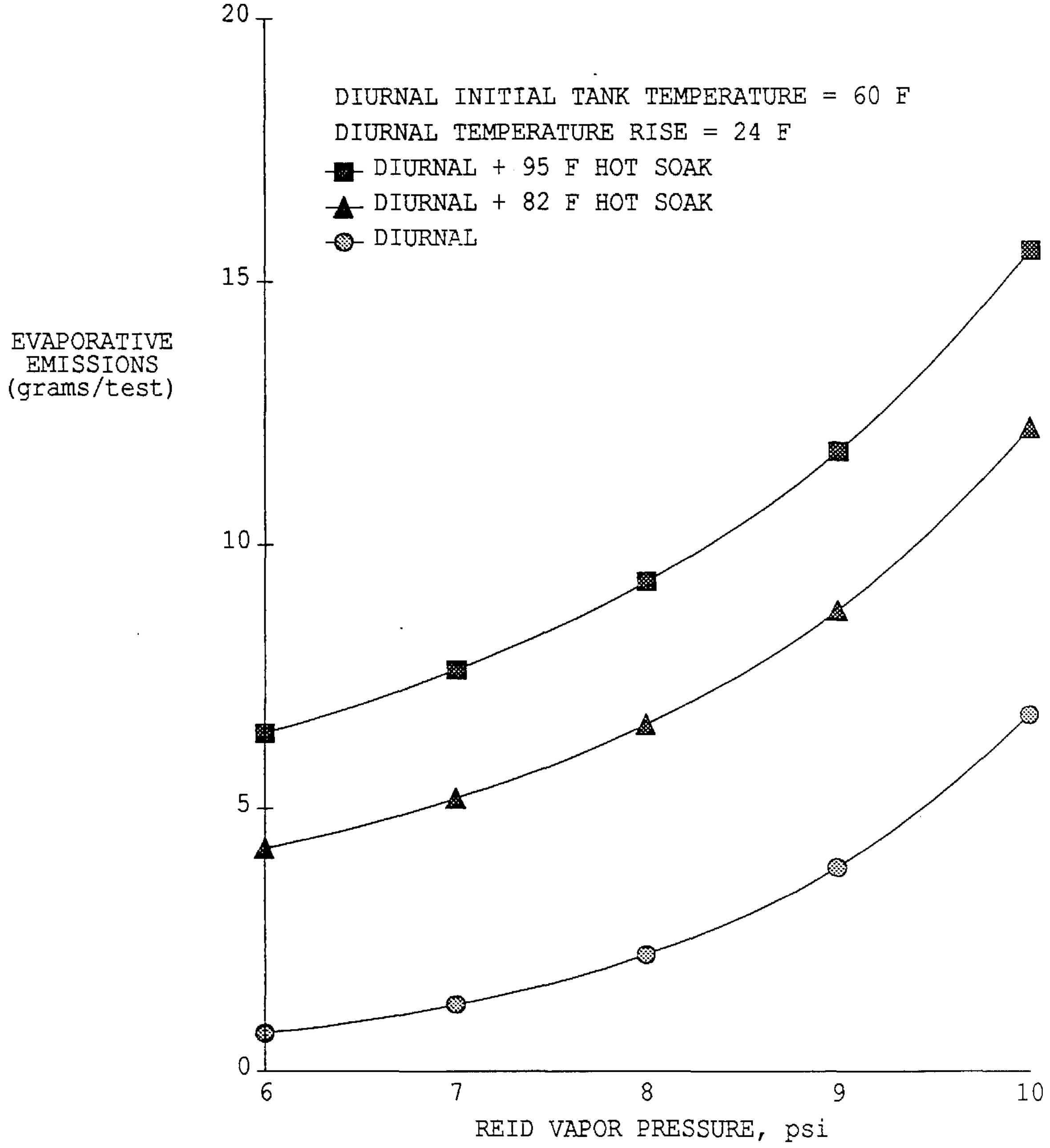


Figure 5-2. Evaporative Emissions from Malfunctioning Carburetted Vehicles

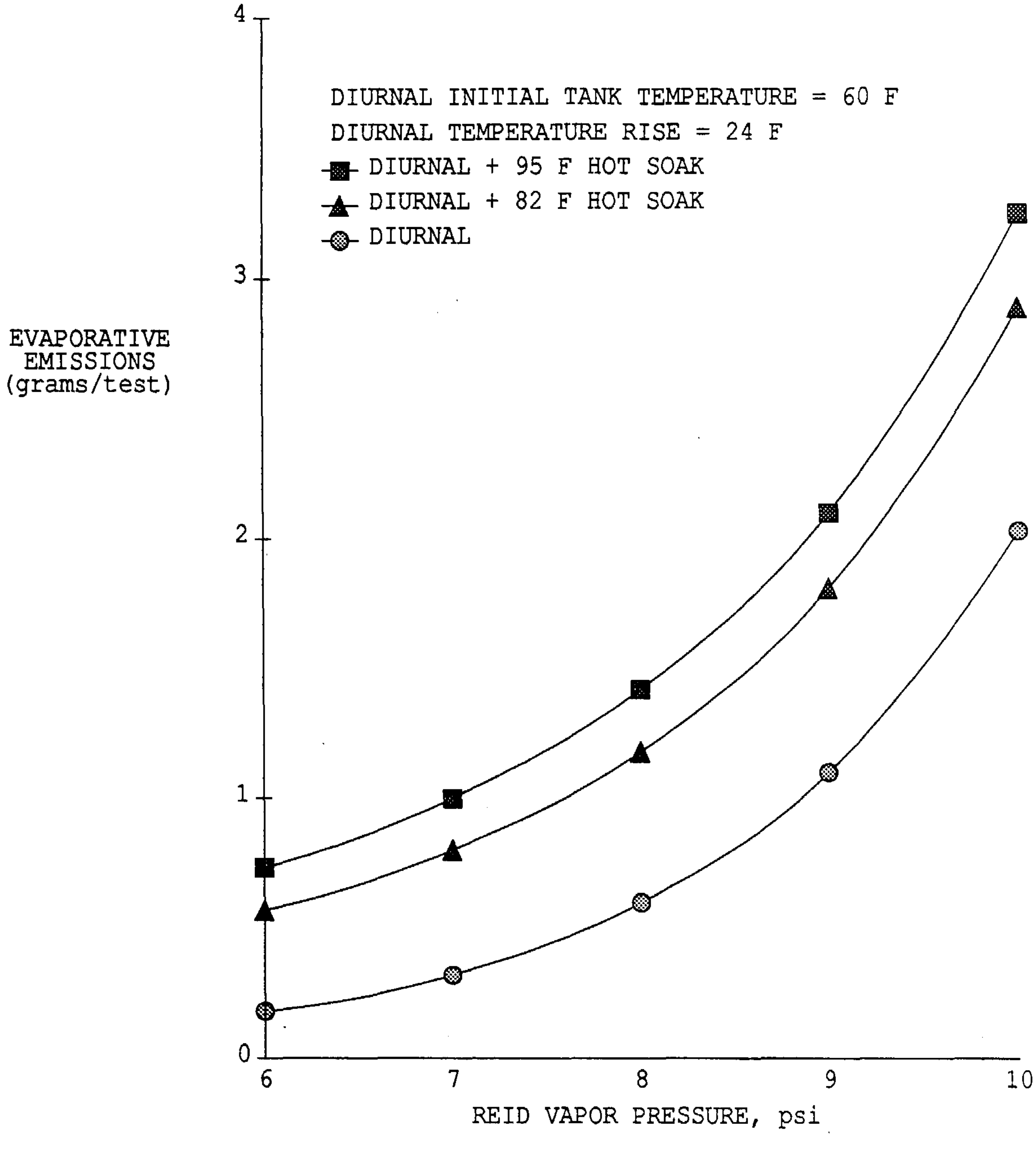


Figure 5-3. Evaporative Emissions from Problem-Free Fuel-Injected Vehicles

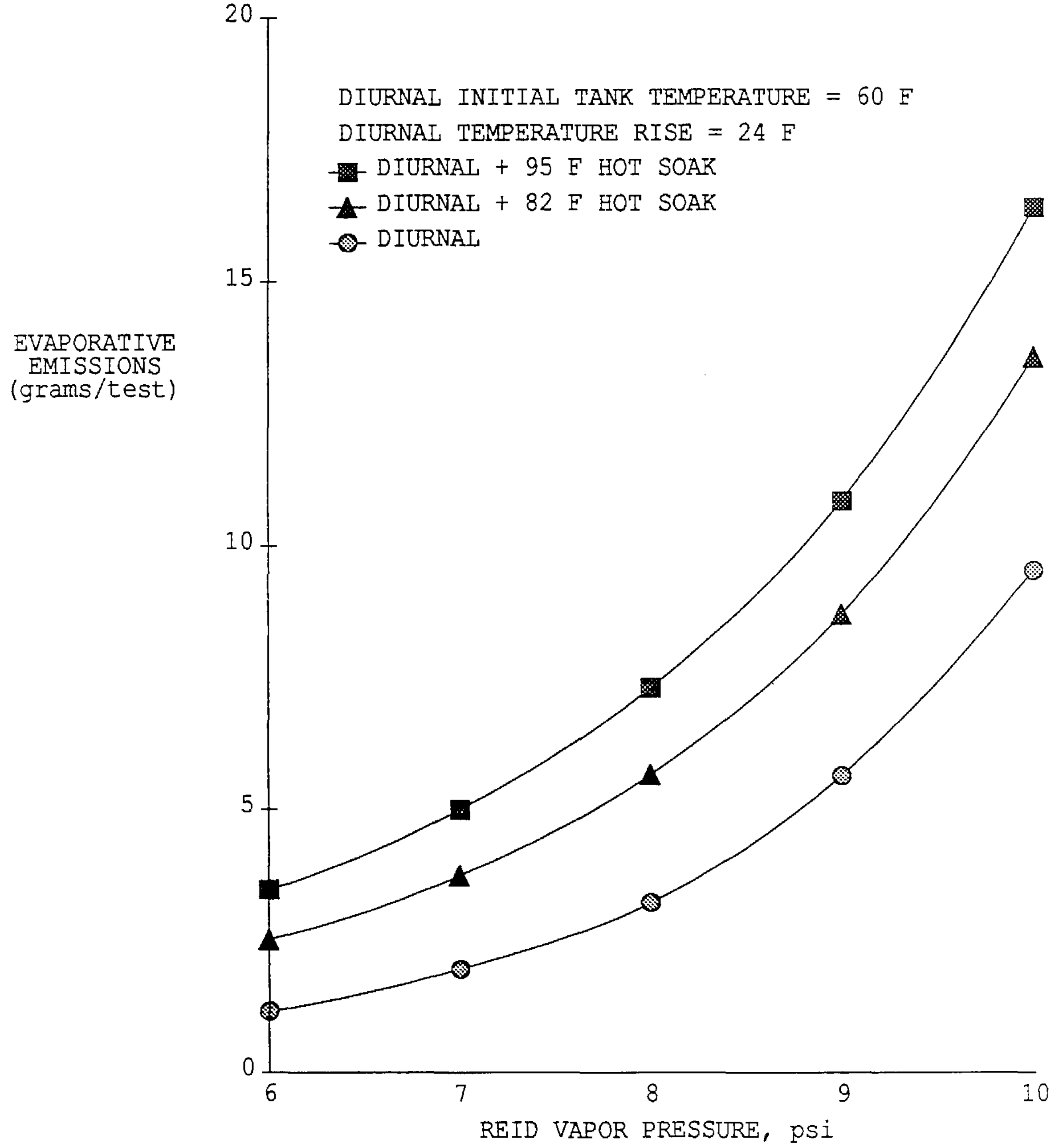


Figure 5-4. Evaporative Emissions from Malfunctioning Fuel-Injected Vehicles

factor was determined to be 1.45 gm/mile. The calculation methodology can be found in Appendix B.

Evaporative hydrocarbon emission factors were calculated using the MOBILE3 methodology:

$$\text{Evaporative Emissions} = \frac{([\text{hot soak (gm)}] \times 3.05) + \text{diurnal (gm)}}{31.1 \text{ mi/day}}$$

Fleet composite hot soak and duirnal emission factors were calculated by aggregating the carburetted and fuel-injected evaporative emissions presented in Figures 5-1 through 5-4. Carburetted vehicles were estimated to be 71 percent of the California fleet; fuel-injected vehicles, throttle-body and MPFI, were estimated to be 29 percent of the fleet. Twenty five percent of the carburetted vehicles and 10 percent of the fuel-injected vehicles were assumed to be malfunctioning (EPA, 1985). Two composite evaporative emission factors were calculated: one assuming that all hot soaks occurred at 82°F, and a second assumed 95°F hot soaks. The resulting composite evaporative emission factors are listed in Table 5-3.

TABLE 5-3. FLEET COMPOSITE EVAPORATIVE HYDROCARBON EMISSION FACTORS

Fuel RVP (psi)	Evaporative Hydrocarbon Emission Factor (gm/mi)
82°F Hot Soak	
9.0	.242
8.0	.185
7.0	.147
6.0	.120
95°F Hot Soak	
9.0	.337
8.0	.266
7.0	.215
6.0	.177

Figure 5-5 displays the fleet composite exhaust hydrocarbon emission increase and fleet composite evaporative hydrocarbon emission decrease for the two different hot soak temperatures. The exhaust emission increase was assumed to be 10 percent. This is the exhaust hydrocarbon emission increase determined by Chevron when testing 1980 and later model year vehicles at an ambient temperature of 55°F. As shown in Figure 5-5, a net HC increase of 0.02 gm/mi up to 0.05 gm/mi would be anticipated as a result of reducing the RVP from 8.4 to 6.1 psi.

5.4 Summary, Conclusions, and Recommendations

Current ARB regulations limit RVP levels for gasoline during the "smog season" to a maximum of 9 psi. Reducing this maximum level further would further reduce evaporative emissions. At some point, however, this reduction would be more than offset by increased cold-start emisssions due to inadequate fuel volatility. Analysis of limited test data from Chevron Research Company suggests that this optimal RVP level is probably less than 9, but greater than 6.1 psi for the South Coast Air Basin. Because of the limited data available, however, it is not possible to estimate the actual optimum with any confidence. Additional vehicle testing at different RVP values and ambient temperatures would be required to determine the optimum RVP.

Any drastic reduction in fuel RVP levels could be expected to result in driveability problems, especially under cold-start conditions. This could lead to additional tampering with emission controls, and possible further increases in emissions. This possibility should be taken into account in considering any future reduction in RVP levels.

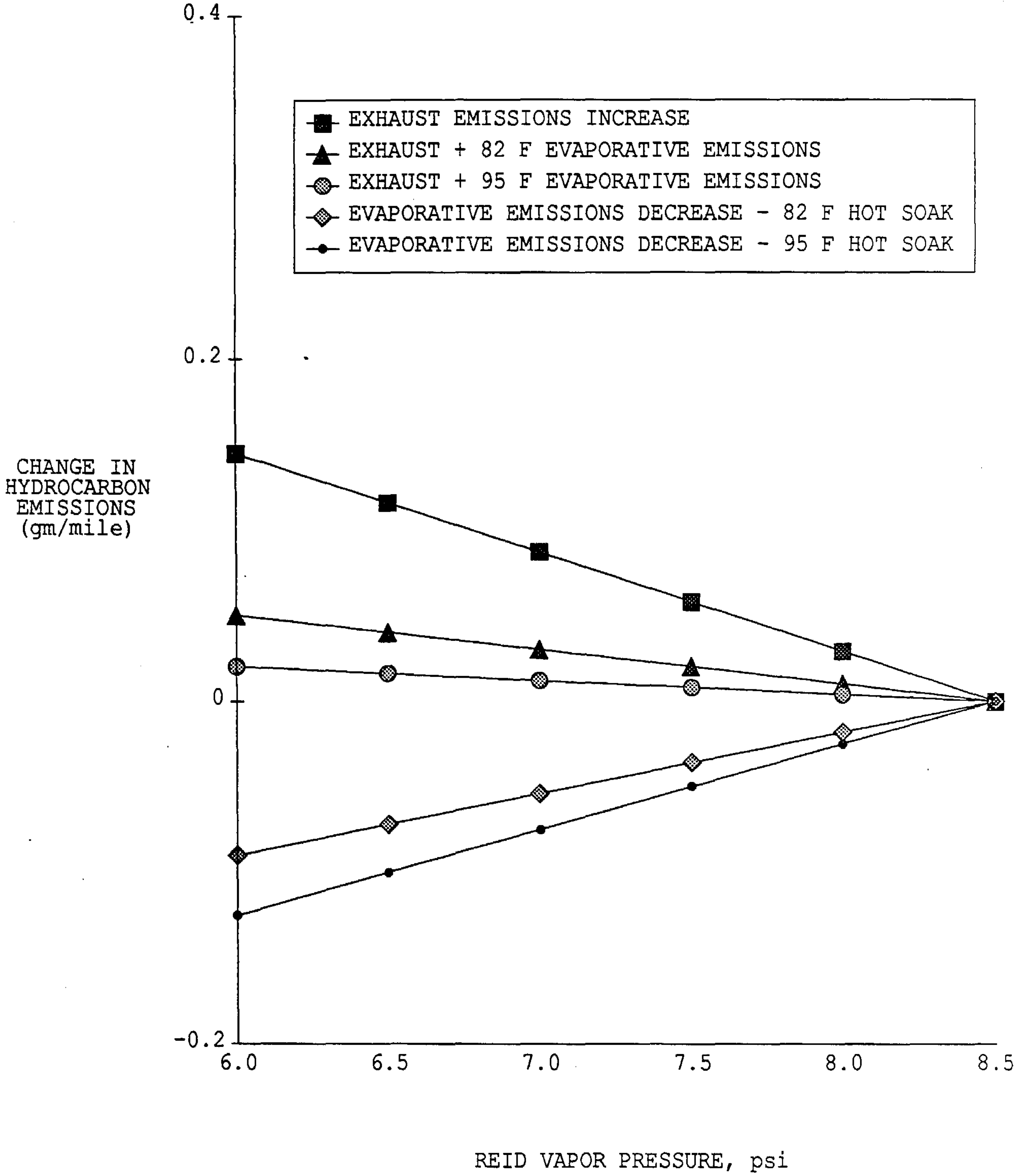


Figure 5-5. Effect of Volatility on Exhaust, Evaporative, and Total Hydrocarbon Emissions

6.0 THE EFFECTS OF FUEL BENZENE AND AROMATICS ON BENZENE EMISSIONS

In January 1985, the California Air Resources Board (ARB) identified benzene as a toxic air contaminant. Emissions from mobile sources are the largest source of benzene in the state. For example, on- and off-road vehicles contributed 93 percent of the total benzene emissions in California in 1984--19,800 tons/year of the total 21,400 tons/year (Ames et al., 1986). Benzene is present in exhaust emissions from gasoline vehicles, and in evaporative emissions from gasoline which contains benzene. Approximately 1.4 percent, by volume, of the gasoline sold in California in 1984 was benzene. In 1990, it is anticipated that benzene content of gasoline in the state will be 1.9 percent by volume (Ames et al., 1986).

The amount of benzene present in the evaporative emissions from gasoline vehicles is linearly related to the amount of benzene present in the fuel. For exhaust emissions, the benzene content appears to be related both to the benzene content of the fuel and to its content of other aromatic hydrocarbons. Some benzene also appears to form during the combustion process, even in the absence of benzene or other aromatics in the fuel. To date, however, the relationship between aromatic content, benzene content, and exhaust benzene emissions has not been determined conclusively. At this time, the Research Division of the ARB is funding a study at the National Institute of Petroleum and Energy Research (NIPER) to identify aromatic compounds that are benzene precursors. This study scheduled to be completed early in 1988.

At present, the most effective means for reducing benzene emissions appears to be reducing total exhaust and evaporative HC emissions. Benzene typically constitutes 3 to 4 percent of total exhaust HC emissions, and reductions in total HC emissions produce a corresponding reduction in benzene.

6.1 Evaporative Benzene Emissions

Evaporative emissions of benzene appear to be linearly related to the benzene content of gasoline. Black et al. (1980) measured evaporative emissions from vehicles using fuels having different benzene contents. Table 6-1 lists the important fuel parameters and the benzene fraction of the evaporative emissions. As demonstrated in the table, the percentage of benzene in the evaporative emissions is approximately the same as the percentage of benzene in the fuel (Black et al., 1980).

TABLE 6-1. EFFECT OF FUEL BENZENE CONTENT ON EVAPORATIVE BENZENE EMISSION

	Fuel RVP and Benzene Content			
Fuel	A	A-1	B	B-1
RVP (psi)	8.4	8.4	9.8	9.8
Benzene (Wt.%)	.28	7.1	1.52	7.1

	Wt. % Benzene in the Evaporative Emission			
Fuel	A	A-1	B	B-1
Vehicle				
77 Mustang			1.8	6.2
78 Monarch	0.5	5.7		
79 LTD-II			2.2	7.1

Source: Black et al., (1980)

If a vehicle switches from a fuel containing benzene to one that does not contain benzene, the evaporative emissions will contain benzene until all the benzene is purged from the charcoal canister and the fuel tank vapor volume. In vehicle testing, two to three additional Federal Test Procedures (FTPs) are required to purge the canister and the fuel tank vapor volume of residual benzene (Seizinger et al., 1986).

The studv by Seizinger et al. (1986) measured benzene levels in the evaporative and exhaust emissions. Some evaporative benzene was measured even during evaporative emission tests using benzene-free fuel. The testing with benzene-free fuel had been performed after tests with a fuel containing benzene. Seizinger concluded that canister adsorption and desorption of benzene was a slow process for abrupt changes in benzene fuel composition. The testing showed that evaporative benzene emissions were directly affected by the composition of prior test fuels for as many as three tests. However, no attempt was made to determine whether the charcoal had a stronger affinity for benzene than for other hydrocarbons.

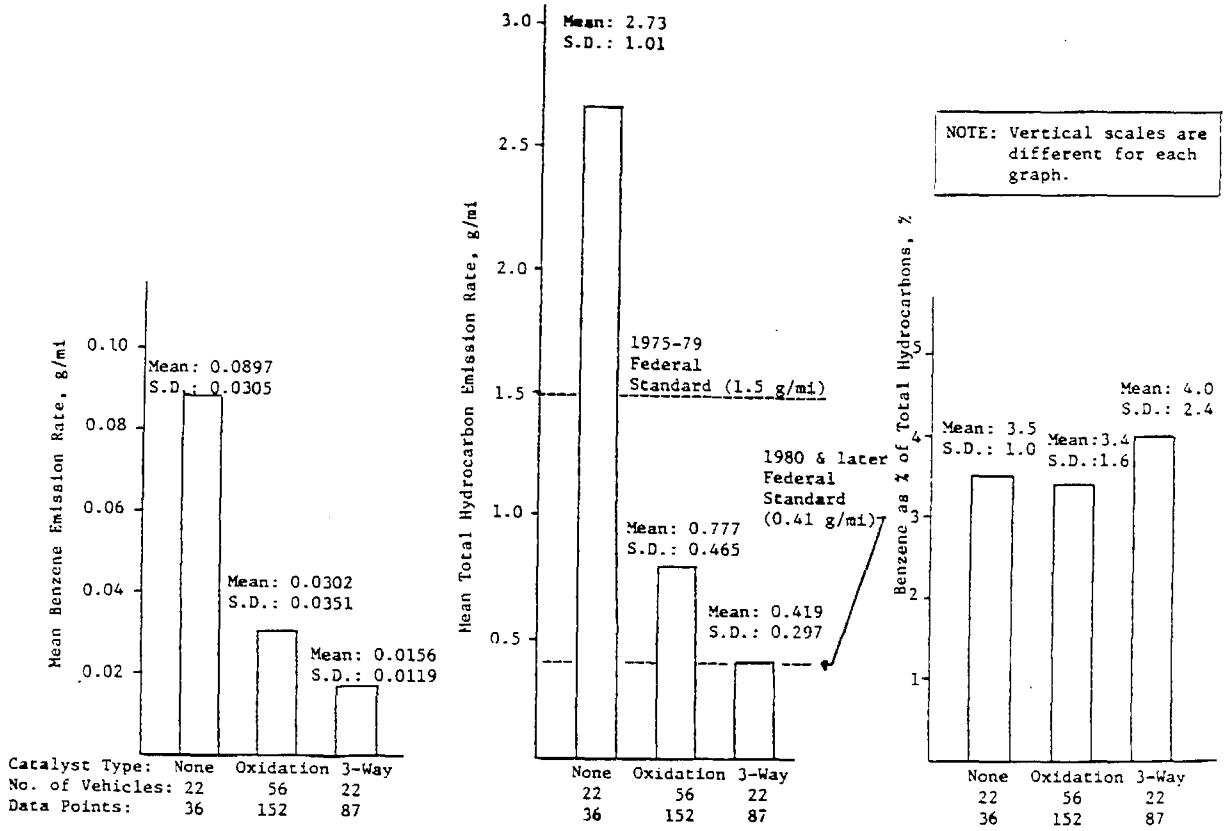
6.2 Exhaust Benzene Emissions

A number of studies have measured tailpipe benzene emissions from gasoline vehicles. These studies have analyzed benzene emissions based on vehicle emission control system type and fuel aromatic content.

6.2.1 Effect of the Emission Control System on Benzene Emissions

Raley et al. (1984) analyzed the test results from previous benzene emission studies to determine the average benzene fraction of the exhaust HC emissions. Vehicles were grouped into classes based on the type of exhaust catalyst used. Three classes were studied: non-catalyst vehicles, oxidizing catalyst vehicles, and three-way catalyst vehicles. Results from previous studies were used only if: the emissions data were reported from FTP tests conducted at the proper ambient temperatures, and typical commercial-grade fuels or indolene were used without being spiked with benzene. Benzene emissions data from a total of 244 tests on 100 test vehicles were analyzed.

Figure 6-1 summarizes the results of the statistical analysis performed by Raley et al. The mean hydrocarbon emission rate was greatest for the non-catalyst vehicles, 2.73 gm/mi. Three-way catalysts emitted the least amount of hydrocarbons, at a mean value of 0.419 gm/mi, while oxidation catalysts were in between, at a hydrocarbon emission rate of 0.777 gm/mi. The same trend was observed with benzene emissions. Non-catalyst vehicles emitted the greatest quantity of benzene, 89.7 mg; oxidizing catalyst vehicles emitted 30.2 mg; and three-way catalyst vehicles emitted 15.6 mg. The mean ratio of benzene to total exhaust hydrocarbons varied little between the different technologies, ranging from 3.4 to 4.0 percent. Thus, the benzene fraction did not appear to differ significantly between the different emission control technologies, even though the absolute emissions of benzene and total HC varied greatly.



Source: Raley et al., 1984

Figure 6-1. Benzene and Hydrocarbon Exhaust Emissions

Seizinger et al. (1986) studied the effectiveness of catalytic converters for oxidizing benzene and other hydrocarbons. Samples of the engines' exhaust gas were taken before it reached the catalytic converter. This allowed a comparison of the benzene fraction in the exhaust before and after the converter. The vehicles used in the test program had either a three-way catalyst or a dual-bed catalyst (dual-bed catalysts consist of a three-way catalyst followed by an oxidizing catalyst). Table 6-2 summarizes the conversion efficiency for all vehicles studied. This summary provides an average of nine tests using different fuels with varying benzene and aromatic contents.

As Table 6-2 indicates, the two three-way catalysts tested exhibited benzene conversion efficiencies greater than 70 percent; for the dual-bed catalysts, benzene conversion efficiencies were greater than 90 percent (Seizinger et al., 1986). Overall, the catalyst conversion efficiency was approximately the same for benzene as for total exhaust HC. Dual-bed catalysts achieved slightly higher conversion efficiencies for both total exhaust HC and for benzene than three-way catalysts.

TABLE 6-2. BENZENE AND HYDROCARBON CATALYTIC CONVERTER EFFICIENCIES

Vehicle	Catalyst	Benzene Conversion Efficiency	Hydrocarbon Conversion Efficiency
1	TWC	74	82
2	TWC	89	88
3	TWC+COC	95	91
4	TWC+COC	92	88
5	TWC+COC	94	88

Source: Seizinger et al., 1986

ARB recently completed an analysis of benzene emissions from in-use, light-duty vehicles (Lyons, 1987). This study concluded that catalyst type is the most important technological factor affecting benzene emissions. At a given HC emission level and for a given fuel system, dual-bed catalysts consistently emitted less benzene than vehicles with single-bed catalysts. The ARB regressions also suggest that, at very low HC exhaust emission levels, benzene emissions may be reduced more than proportionally. At HC emission levels less than 0.1 gm/mile, the benzene weight percentage of total exhaust hydrocarbons appears to drop off rapidly. Thus, the observation that benzene tends to make up a constant weight percent of total HC appears to be incorrect at extremely low HC levels.

6.2.2 The Effect of Fuel Composition on Exhaust Benzene Emissions

Exhaust benzene emissions are closely related to the benzene and other aromatic content of the fuel. However, some benzene is also formed by combustion even in an aromatic-free fuel. The extent of this contribution appears to vary somewhat, but it may be quite significant.

In the statistical analysis of benzene emissions (Raley et al., 1984), a study of the impact of low benzene and aromatic content fuel was located. In this study, a fuel containing 0.3 percent benzene was tested in various vehicles and the exhaust benzene content was measured. The fuel also was a low aromatic fuel, containing only 15 percent aromatics by volume. The data from this study were included in the combined analysis; however, the mean and standard deviation for this fleet also were calculated separately. Table 6-3 summarizes the statistical analysis of this fleet.

In the low benzene content study, the vehicles again were classified by catalyst type. The low benzene fuel did not appear to deviate significantly from the combined analysis. No significant difference in any of the three vehicle classes was observed when compared to the combined analysis. This suggests that benzene formed during the combustion process from other

TABLE 6-3. COMPARISON OF LOW BENZENE FUEL EMISSIONS TO AVERAGE FUEL

	Combined Analysis				0.3 Vol% Fuel Analysis			
			Benzene Emissions				Benzene Emissions	
Catalyst Group	Test Data		g/mi	mg/km			g/mi	mg/km
3-Way Catalyst Vehicles	22 Vehicles	Mean:	0.0156	9.75	4 Vehicles	Mean:	0.0187	11.7
	87 Data Points	S.D.:	0.0119	7.44	22 Data Points	S.D.:	0.0068	4.25
Oxidation Catalyst Vehicles	56 Vehicles	Mean:	0.0302	18.9	6 Vehicles	Mean:	0.0411	25.7
	152 Data Points	S.D.:	0.0351	21.9	33 Data Points	S.D.:	0.0374	23.4
Non-Catalyst	22 Vehicles	Mean:	0.0897	56.1	2 Vehicles	Mean:	0.0795	49.7
	36 Data Points	S.D.:	0.0305	19.1	10 Data Points	S.D.:	0.0146	9.13

Source: Raley et al., 1984

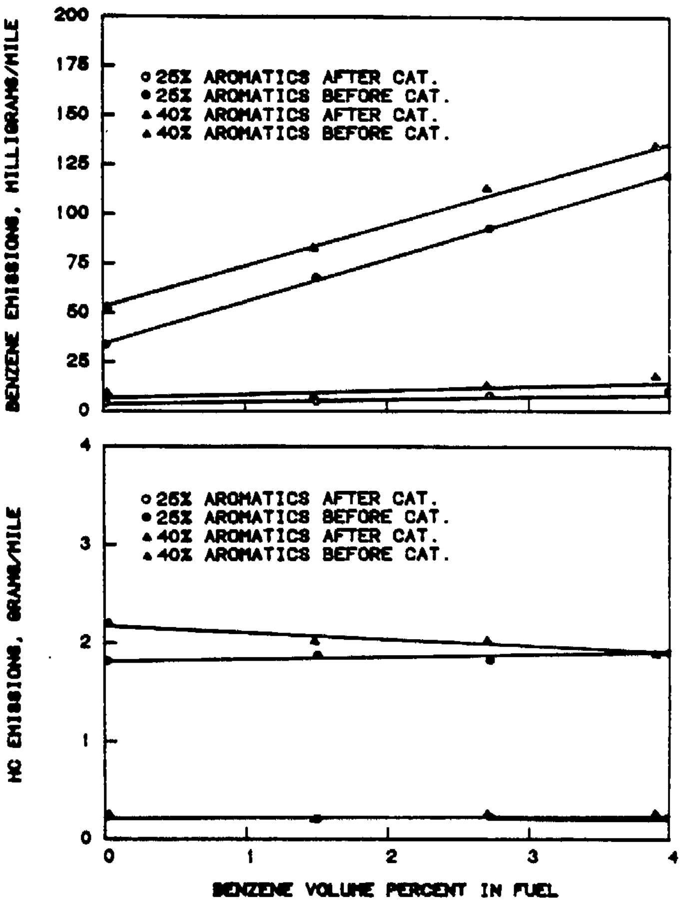
hydrocarbon compounds. Therefore, completely removing aromatics from gasoline, while reducing benzene emissions, may not result in complete removal of exhaust benzene emissions (Raley et al., 1984).

Seizinger et al. (1986) also studied the effect of benzene and aromatic composition on exhaust benzene emissions. Two aromatic contents were studied, 25 and 40 percent. In addition, the fuel's benzene content was varied; it contained 0, 1.5, 2.7, and 4.0 percent benzene by volume. The benzene exhaust emissions were measured during FTP testing. The benzene and hydrocarbon emissions before and after the catalytic converter are plotted in Figure 6-2.

Figure 6-2 illustrates a number of significant points. First, the benzene content of gasoline does not significantly affect total engine-out HC emissions. Increasing benzene content does increase benzene exhaust emissions, however. The increase in exhaust benzene emissions is approximately 2 mg for each volume percent of benzene. Exhaust benzene emissions also increase with additional aromatic content. For an increase of 15 volume percent fuel aromatic content, an increase in exhaust benzene emissions of 4 mg occurred (Seizinger et al., 1986).

Currently, the National Institute for Petroleum and Energy Research (NIPER) is under contract to the ARB to study the fate of benzene precursors in gasoline. The study's objective is to identify specific aromatic compounds that are converted in the engine, or the catalytic converter, to benzene, and to quantify the effects of the concentration of these compounds upon the formation of benzene in the exhaust.

Phase I of the testing has been completed. The project is scheduled to be completed in early 1988. During the Phase I testing, varying quantities of aromatics were added to an alkylate-based fuel. Exhaust emissions tests were performed to measure the exhaust benzene emissions. A regression equation was developed correlating the fuel's aromatic content to exhaust benzene emissions.



Source: Seizinger et al., 1986

Figure 6-2. Benzene and Hydrocarbon Emissions Before and After Catalytic Converter

The results of this phase of testing cannot be directly correlated to "production" gasoline due to the use of the alkylate fuel. However, it appears that fuel benzene is the major source of benzene in the exhaust when using an alkylate-based fuel. Until the final testing with "production" gasoline is completed, the benzene precursors will not be known (NIPER, 1987).

6.3 Benzene Control Measures

As the discussion above has indicated, Benzene emissions could conceivably be reduced either by reducing the benzene and aromatic content of gasoline or by reducing total HC emissions while keeping gasoline composition the same. The latter approach would be much more cost-effective, however, since it would have the advantage of reducing total HC (and possibly other pollutants) as well as benzene.

To illustrate the differences in cost, Radian estimated the cost-effectiveness of removing benzene emissions by modifying the fuel composition. Benzene emissions from gasoline marketing and mobile sources were obtained from the ARB "Proposed Benzene Control Plan." Gasoline use was estimated from data presented by Chevron Research Company. The costs for modifying the fuel composition were estimated to range from \$0.01/gal up to \$0.25/gal. In order to simulate the maximum impact from these modifications, the fuel modifications were assumed to eliminate all benzene emissions due to gasoline marketing and mobile sources.

Even assuming this unrealistic level of benzene control, and even assuming that the necessary modifications could be performed at the unrealistically low cost of \$0.01/gal, the cost-effectiveness of these modifications for benzene control would be of \$65,700/ton of benzene removed. The calculations can be found in Appendix C. Of course, this figure reflects absurdly optimistic assumptions. Making more realistic assumptions as to costs and effectiveness would result in a much larger cost per ton.

ARB staff is already studying a number of HC emissions control measures for mobile sources, including an HC standard of 0.25 gm/mi for light-duty vehicles, more stringent regulation of heavy-duty gasoline vehicles, and regulation of emissions from off-highway motor vehicles. Each of these measures is likely to prove cost-effective for HC control alone. In addition, however, each ton of HC eliminated will carry as an added benefit the elimination of roughly 65-80 pounds of benzene as well.

6.4 Summary, Conclusions, and Recommendations

Benzene can be found in the exhaust and evaporative emissions from gasoline-fueled vehicles. Evaporative benzene emissions appear to be linearly related to the benzene content of the fuel. Exhaust benzene emissions are produced during the combustion process. Benzene and other aromatics in the fuel affect the quantity of benzene in the exhaust.

Benzene exhaust emissions are reduced by the same measures which reduce other hydrocarbon emissions, especially catalytic converters. Dual-bed catalysts, which have marginally better hydrocarbon conversion efficiencies than three-way catalysts, also achieve greater benzene reductions.

Reducing the benzene and aromatic content of unleaded gasoline would reduce benzene evaporative and exhaust emissions. Under current regulations of unleaded gasoline composition, aromatics are one of the main components used to enhance the octane rating of the fuel. Another octane-enhancing constituent would have to be used to improve the octane rating if aromatics were removed. Removing benzene alone (leaving the other aromatics) might be a feasible method for reducing exhaust benzene emissions. However, removing benzene emissions by modifying the fuel composition may not be cost-effective. Rough calculations show that, even if the costs of fuel modification were as low as $0.01 per gallon, the cost-effectiveness of reducing benzene emissions by this means would be about $65,700 per ton.

Another approach to reducing the benzene emissions from motor vehicles would be to reduce the overall hydrocarbon emissions from the vehicle fleet. ARB staff is studying a reduction in the hydrocarbon standard for passenger cars from the present 0.41 gm/mi to 0.25 gm/mi, as well as other mobile-source HC control strategies. These would result in benzene emission reductions as well. Additional measures to reduce evaporative emissions from vehicles would probably also help in reducing benzene emissions.

7.0 THE EFFECTS OF OXYGENATED COMPOUNDS ON VEHICLE EMISSIONS

From a gasoline marketer's perspective, there are several possible advantages to the use of oxygenated fuels. In the case of ethanol-gasoline blends, significant tax subsidies are provided by both state and federal statutes for these blends. These tax benefits can reduce the net cost of each gallon of this fuel sold, even though the cost of ethanol may be substantially higher than the cost of the gasoline it replaces. It is also possible to market this blend as a "premium" product because alcohol addition increases the octane rating of the fuel.

Methanol-gasoline blends have experienced some acceptance in the market, although tax subsidies are not provided for these blends. Methanol also offers the same advantage as ethanol in terms of octane rating. More importantly, the per-gallon cost of methanol, in the current worldwide glut situation, is about half that of gasoline. As a result, a gallon of a methanol-gasoline blend can be produced for at a lower cost than a gallon of straight gasoline. Since customers who purchase such blends are generally unaware of the lower energy content of these blends, there is an economic advantage to methanol-gasoline blend use for gasoline marketers.

Other oxygenated compounds used in gasoline include methyl tertiary-butyl ether (MTBE), which is used as a blendstock by refiners to increase octane quality, and higher carbon alcohols, which are used as "cosolvents" in methanol-gasoline blends to reduce corrosive effects on the fuel system.

With respect to emissions, the principal concern with oxygenated fuel use is the higher volatility of blends caused by the addition of ethanol or methanol. Higher volatility causes increased evaporative emissions. In addition, there is evidence that use of alcohol in gasoline leads to increased NO_x emissions in three-way catalyst equipped vehicles. Finally, there are advantages and disadvantages to the enleanment effect of oxygenated fuels. At least initially, the enleanment effect of oxygenated fuels reduces CO emissions. However, enleanment clearly degrades vehicle driveability, thereby increasing the potential for tampering and maladjustment. This can lead to significant emissions increases for all pollutants.

This section reviews the use of oxygenated compounds as blending agents in unleaded gasoline. The physical and chemical properties of oxygenates, as well as the effects that oxygenated compounds have on the blended gasoline's chemical and physical properties, are described. The impacts of gasoline/oxygenate blends on evaporative and exhaust hydrocarbon emissions are reviewed.

7.1 Properties of Oxygenated Compounds and Their Effect on Blend Properties

Six different oxygenated compounds are used today as blending agents in unleaded gasoline: methanol, ethanol, isopropanol, tertiary butyl alcohol (TBA), methyl tertiary-butyl ether (MTBE), and Oxinol-50® (50/50 blend of methanol and TBA). According to the U.S. Environmental Protection Agency's (EPA's) "substantially similar" rule, these oxygenates can be blended in fuel up to the following maximum levels:

Oxygenated Compound	Percent by Volume
Methanol	0.3
Ethanol	5.4
Isopropanol	7.1
Tertiary Butyl Alcohol (TBA)	8.7
Methyl Tertiary Butyl Ether (MTBE)	11.0
Oxinol-50®	5.5

These blending agents cannot be combined in a single fuel. In addition, the EPA has granted individual waivers for the use of up to 10 volume percent ethanol (Gasohol), up to 15.7 volume percent TBA, and up to 9.5 volume percent methanol/TBA, provided the methanol/TBA ratio does not exceed 1. These waivers do not allow for the addition of other blending agents to a single fuel. All of the blends receiving waivers (except for Gasohol) must meet ASTM D439 volatility specifications (Dorn and Mourao, 1984).

7.1.1 Physical Properties of Oxygenated Compounds

Table 7-1 lists the physical properties of the various oxygenated compounds that are used as blending agents in unleaded gasoline. As shown, the properties of MTBE more closely resemble unleaded gasoline than do the C1 through C4 alcohols. MTBE use in gasoline generally has not been a concern with respect to air pollution control.

7.1.2 Effect of Oxygenated Compounds on Blend RVP

The presence of the hydroxyl group and the ability to form azeotropes cause alcohol-blended fuels to have different properties and to behave differently than their individual components. As Table 7-1 shows, the RVP of all of the alcohols in pure form is less than 5 psi. When blended with hydrocarbons, however, the effect of alcohol on the blend's RVP is much greater than would be predicted from the RVP in pure form. The RVP of pure alcohols is less due to hydrogen bonding.

When mixed in small volumes in gasoline, the bonding forces between alcohol molecules are weakened significantly. This results in a vapor pressure for the mixture that is much greater than that of either component. This effect is most pronounced when methanol and ethanol are mixed with unleaded gasoline. This effect is also seen with isopropanol and tertiary butyl alcohol, as shown in Figure 7-1.

TABLE 7-1. PHYSICAL PROPERTIES OF OXYGENATED COMPOUNDS

Property	Methanol	Ethanol	Isopropyl Alcohol	Tertiary Butyl Alcohol	Methyl Tertiary Butyl Ether	Gasoline
Chemical Formula	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH	$C_4H_9OCH_3$	Various C_4-C_{12} Hydrocarbons
Molecular Weight	32	46	60	74	88	113
Oxygen Content, Mass %	50	35	27	22	18	0
B.P., °F	149	173	180	181	131	80-437
Stoichiometric, A/F	6.4	9.0	10.3	11.1	11.7	14.7
Latent Heat of Vaporization, BTU/Gal[a]	3,300	2,600	2,100	1,700	900	
Reid Vapor Pressure psi at 100°F (kpa)	4.7(32)	2.8[b](19)	1.3[b](9.0)	2.7[b](19)	7.8(54)	9.0(63)
Net Heat of Combustion, BTU/Gal (MJ/kg)	57,000(21)	76,000(28)	86,000(32)	93,000(35)	94,000(35)	115,400(42)
Solubility in H_2O, g/100g H_2O					4.8	
Octane Number[c]						
Research	107	108	112	113	116	91
Motor	---	---	---	---	101	83

[a] 1 BTU/Gal = 279 J/L

[b] Approximate values.

[c] for pure component. Blending octane numbers in gasoline may be different. Motor octane numbers are difficult to obtain on pure alcohols by conventional ASTM method.

Reference: Dorn and Mourao, 1984.

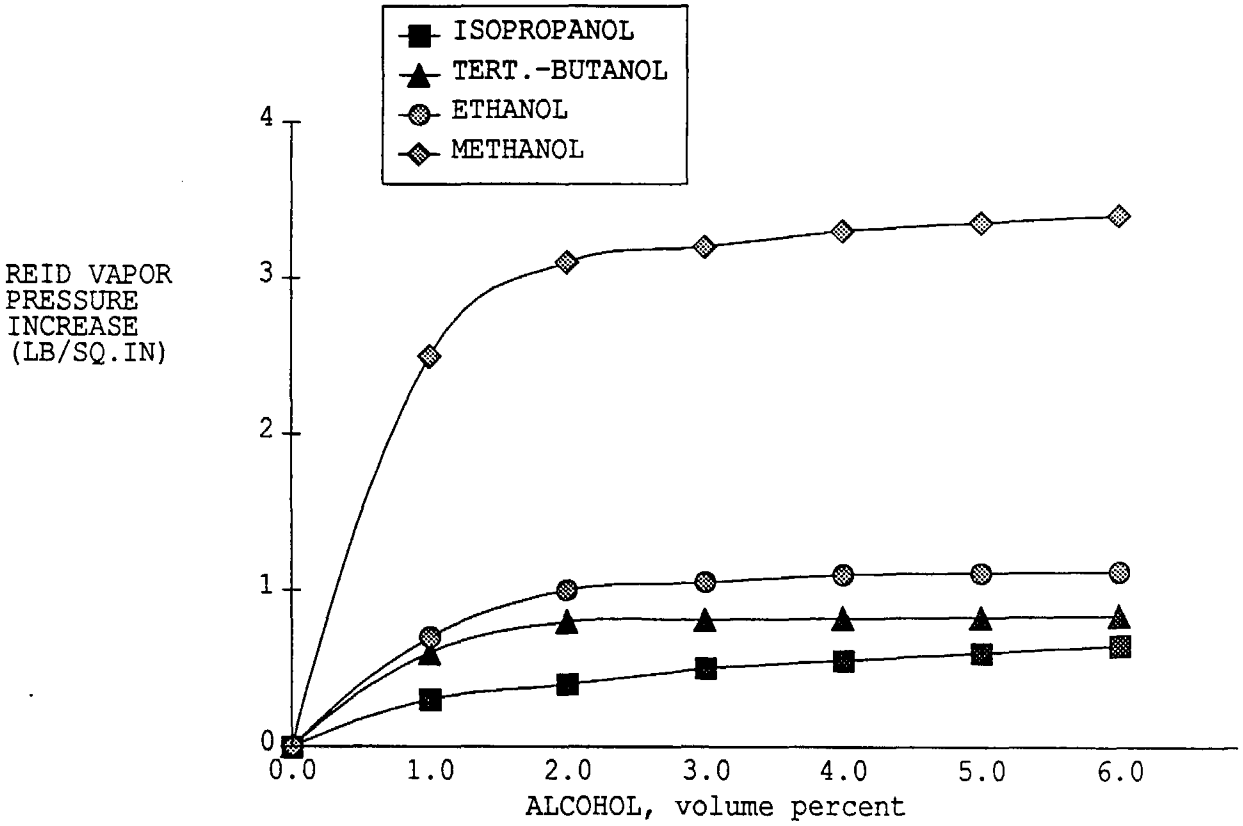


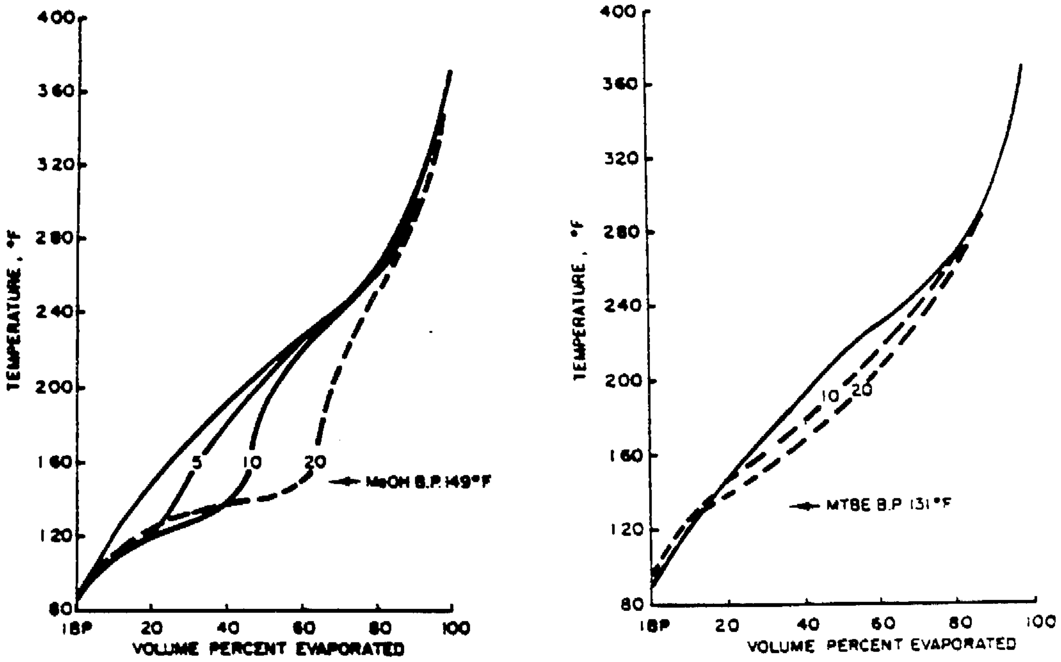
Figure 7-1. Effect of Oxygenated Compounds on Reid Vapor Pressure

7.1.3 Effect of Oxygenated Compounds on Boiling Curve

The blending agents also have a pronounced effect on the boiling or distillation curve for unleaded gasoline. Alcohols significantly lower, or depress, the distillation curve. Figure 7-2 shows the effects of methanol and MTBE, in different volumes, on the distillation curve of an unleaded gasoline. In general, the effect of alcohols on the boiling curve of the blended fuel is significantly greater than MTBE.

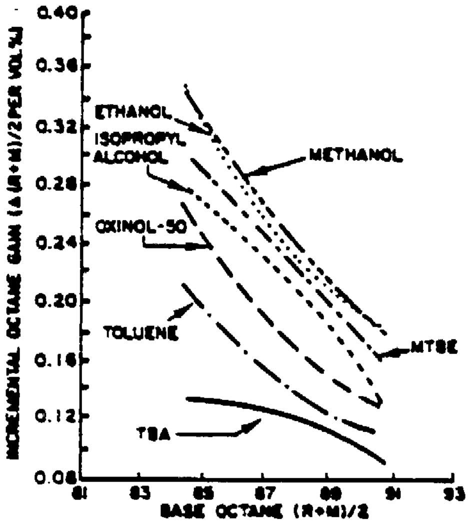
7.1.4 Effect of Oxygenated Compounds on Octane Rating

When used in unleaded gasoline, alcohols and ethers increase the octane rating of the blended fuel. The increase in octane rating depends on the octane rating of the base gasoline. Figure 7-3 shows the incremental gain



Source: Dorn and Mourao, 1984

Figure 7-2. Effect of Oxygenated Compounds on the Distillation Curve



Source: Dorn and Mourao, 1984

Figure 7-3. Effect of Toluene and Oxygenated Compounds on Octane Rating in octane per volume percent of oxygenated compound added. As can be seen, except for TBA, all of the blending agents are better octane enhancers than toluene, a typical refinery product that is used for blending.

7.2 Effect of Oxygenated Compounds on Evaporative Emissions

The use of gasoline/alcohol blends increases evaporative emissions from the gasoline vehicle fleet. Gasoline/alcohol blends can produce greater quantities of evaporative emissions than a straight gasoline, even when the blends are controlled to the same RVP or Front End Volatility Index (FEVI). Use of gasoline/alcohol blends can also cause increased degradation of a vehicle's evaporative emission control system. In addition, intermittent blend use in California can cause the volatility of tank fuel to be greater than the maximum legal RVP, which is 9 psi.

7.2.1 Effect of Gasoline/Alcohol Blends on Evaporative Emissions

Increased evaporative emissions have been observed when testing vehicles using gasoline/alcohol blends. These emissions increases occurred when the blended fuels were volatility adjusted to have the same or lower RVP or FEVI. (The FEVI is defined as the RVP plus 13 percent of the fuel distilled at 158°F.)

The Coordinating Research Council (CRC) conducted a study to determine the effect of oxygenate content on evaporative emissions. In this study, the CRC blended methanol and isobutanol with gasoline. Five different test fuels were studied containing 0 to 15 percent alcohol. The properties of the test blended fuels are presented in Table 7-2. All of these fuels were volatility adjusted to have an RVP and FEVI equal to or lower than the base gasoline.

TABLE 7-2. CRC TEST FUEL PROPERTIES

	Straight Gasoline	Blend MG-1	Blend MG-2	Blend MG-3	Blend MG-4	Blend MG-5
Methanol %	0.0	3.31	3.54	8.83	9.75	13.35
Isobutanol %	0.0	1.21	0.05	2.66	0.0	1.80
Total Alcohol %	0.0	4.52	3.59	11.49	9.75	15.15
RVP, psi	9.7	8.0	8.7	7.6	8.7	8.4
FEVI	12.8	10.9	11.5	11.6	13.2	13.8
% Oxygen Content (calculated)	0.0	1.9	1.8	5.0	4.9	7.1

Evaporative emissions tests were performed on 10 cars having both closed-loop and open-loop fuel control systems. All the vehicles used carburetors. The increase in evaporative emissions compared to the straight gasoline ranged from 46.4 percent up to 146 percent. These test results can be found in Table 7-3. The increase in hot soak emissions was 170 percent and the increase in diurnal emissions was 30 percent compared to the base gasoline (Systems Control, Inc. 1982a). Another CRC testing program evaluating ethanol-gasoline blends, indicated a 65 percent increase in evaporative emissions for 10 cars tested with blends of 10 percent ethanol and 90 percent gasoline (Systems Control, Inc., 1982b).

TABLE 7-3. CRC EVAPORATIVE EMISSION TEST RESULTS (GRAMS PER TEST)

Car Number	Straight Gasoline	Blend MG-1	Blend MG-2	Blend MG-3	Blend MG-4	Blend MG-5
04-1	1.47	1.83	2.58	3.18	2.75	2.82
04-2	1.70	1.88	2.22	2.12	2.15	2.34
04-1	3.17	6.82	6.38	9.52	11.80	9.55
04-2	2.34	4.26	4.77	5.17	4.62	8.15
06-1	2.32	2.68	3.59	3.73	4.14	4.26
06-1	3.29	4.13	6.04	4.18	5.63	4.81
04-3	3.46	5.79	4.07	5.83	8.57	6.88
04-4	3.51	4.02	4.18	4.63	4.25	7.56
04-3	4.07	6.38	6.84	13.15	18.75	19.64
04-4	3.79	4.81	4.83	5.24	6.62	5.62
10 Car Average	2.91	4.26	4.55	5.67	6.93	7.16
Change from Base Gasoline	0.0%	+46.4%	+56.4%	+94.8%	+138.1%	+146.0%

The blended fuels with the most significant deviation in the distillation curve compared to the base gasoline had the greatest increase in evaporative emissions. Although these fuels were volatility modified to have RVPs lower than the base gasoline, significant deviations in the distillation curve are still present. The distillation curves for the methanol/isobutanol test fuels are plotted in Figure 7-4.

The depression of the distillation curve explains the increase in evaporative hydrocarbon emissions for blended gasolines having the same RVP as compared to straight gasoline. RVP measures the volatility of the fuel up to a temperature of 37.8°C (100°F). As can be seen Figure 7-4, the volume evaporated up to a temperature 37.8°C (100°F) is minimal for both gasoline and alcohol/gasoline blends. At temperatures above 37.8°C, however, a significant

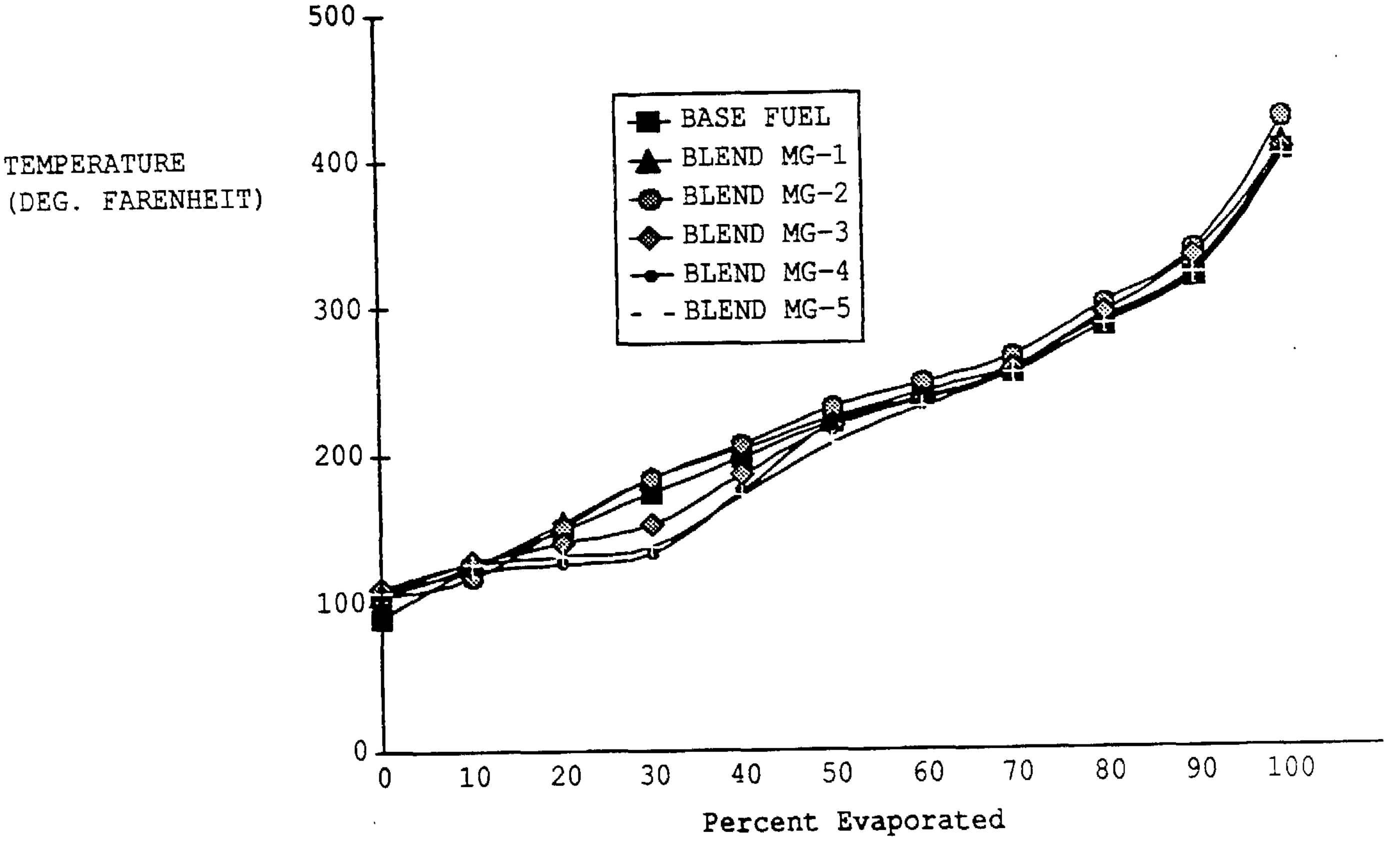


Figure 7-4. Distillation Curves for CRC Methanol/Gasoline Test Fuels

deviation in the distillation curve occurs. Evaporative emissions are affected by a vehicle's underhood and underbody temperatures. These temperatures are typically above 37.8°C, especially during the summer and the hot soak portion of the evaporative emissions test. Therefore, even at a given RVP, significant increases in evaporative emissions should occur with blended fuels due to the depression of the boiling curve.

General Motors has tested three vehicles using gasoline and a methanol/gasoline blend. The blended fuels were volatility adjusted so the distillation curves were approximately the same. The distillation curves and for one of the base fuels and a blended fuel containing 9.3 percent alcohol can be found in Figure 7-5. As shown in the figure, the distillation curves for these two fuels are practically the same.

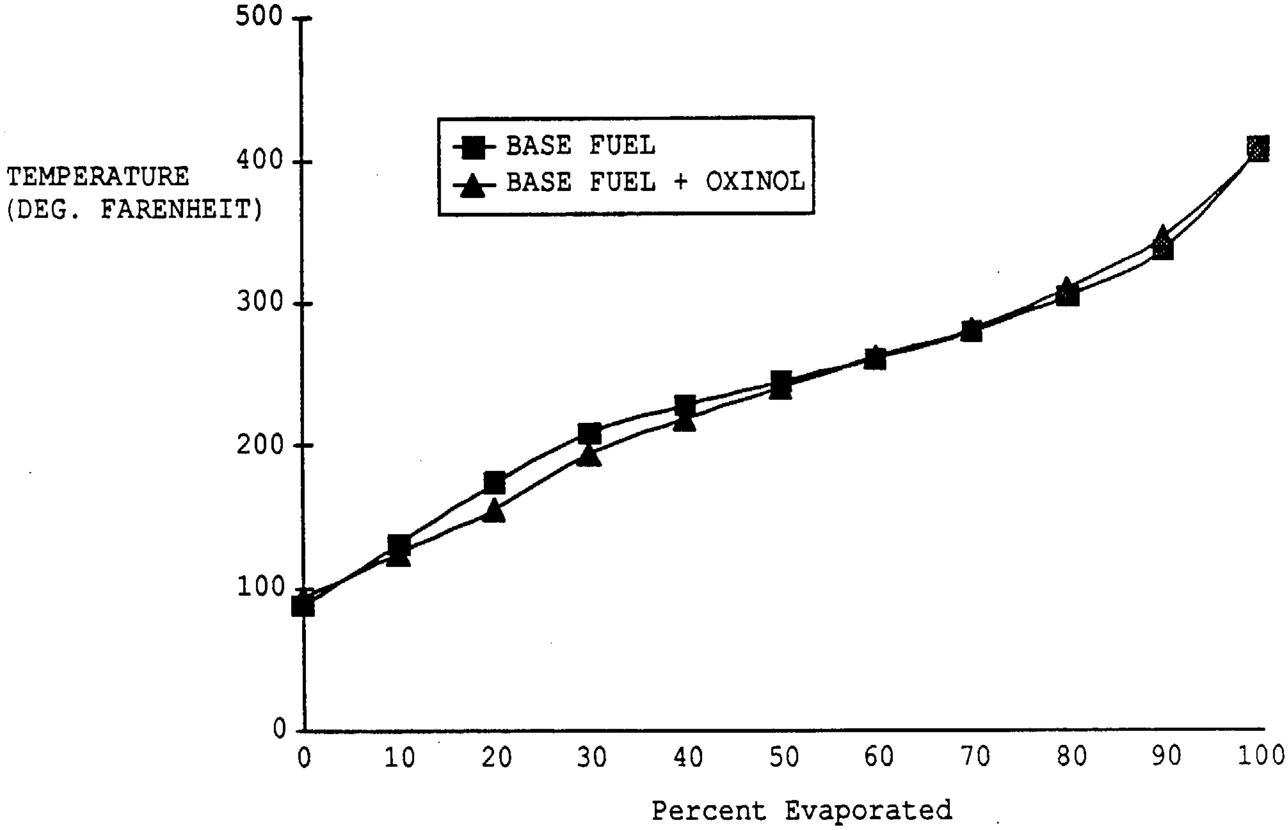


Figure 7-5. Distillation Curves for Fuels with Matched Volatility

Evaporative emission tests were performed using the two fuels in three different vehicles. Charcoal canister weight was measured before and after the diurnal and hot soak portions of the evaporative emissions test. The total quantity of vapor generated during the test was determined by adding the canister weight change to the evaporative emissions measured during the test. Table 7-4 lists the total vapor generated during the emissions tests for all three vehicles. The quantity of vapor generated by the blended fuel in some cases was lower than the quantity of vapor generated by the base fuel (Reddy, 1986).

TABLE 7-4. HYDROCARBON VAPOR GENERATION FOR BASE FUEL, BLENDED FUEL, AND INDOLENE

Vehicle	Fuel	Hydrocarbon Vapor Generated (gm)
Carburetted	Base Fuel	23.8
	Base Fuel + Oxinol	24.8
	Indolene	24.4
TBI	Base Fuel	18.3
	Base Fuel + Oxinol	15.2
	Indolene	16.4
PFI	Base Fuel	21.6
	Base Fuel + Oxinol	19.6
	Indolene	18.2

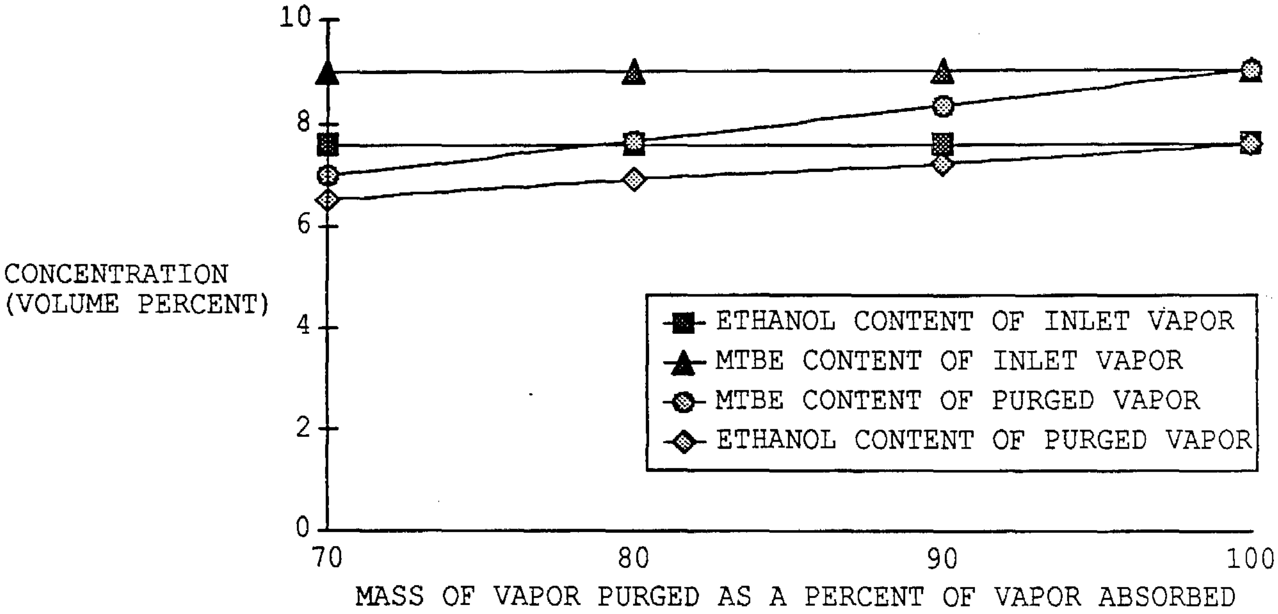
The results of this study indicate that the quantity of vapor generated by a blended fuel may be controllable by matching the distillation curve of the blended fuel with the base fuel. By minimizing the variation between the base fuel's and the blended fuel's distillation curves, the difference in hydrocarbon vapor generation may be reduced or eliminated. Without distillation curve matching, blended fuels with similar RVPs and FEVIs may produce significant evaporative hydrocarbon emissions.

7.2.2 The Effect of Blend Use on Canister Degradation

Significant reductions in evaporative emission control system performance are expected due to the increased use of gasoline/alcohol blends. Alcohol and water are expected to become adsorbed by the active sites in the charcoal canister. These molecules are unlikely to be stripped from the charcoal at the temperatures and pressures present in typical evaporative emission systems.

The high-mileage data used to evaluate the effect of gasoline/alcohol blend usage on evaporative emission control systems have not shown the reductions described above. The discrepancy arises from the test procedure. The evaporative emission control system deteriorates as it stores and purges hydrocarbon vapors. The load/purge cycles are related to the diurnal and hot soak cycles that a vehicle undergoes. Assuming that 50,000 miles of durability testing is completed in three months and a vehicle undergoes one diurnal and three hot soaks per day, the total number of purge/load cycles is 360. In comparison, if a vehicle accumulates 50,000 miles in routine customer service during a period of three years, and it experiences the same number of hot soak and diurnal cycles per day, it will experience 4,320 purge/load cycles.

The charcoal canister has a greater affinity for the oxygenate compounds than hydrocarbons. This effect can be seen in Figure 7-6. This figure plots the concentration of MTBE and ethanol in the purged canister vapor. The oxygenate concentration of the purged vapor is plotted as a function of the ratio of purged vapor to absorbed vapor. The concentration of the oxygenate content entering the canister is also shown. The figure indicates that the charcoal canister preferentially retains the oxygenates. If the canister did not have a stronger affinity for the oxygenates, the oxygenate concentration of the purged vapor would be the same as the inlet concentration at all ratios (Furey and King, 1980).



Source: Furey and King, 1980

Figure 7-6. Charcoal Canister Inlet and Purge Vapor Oxygenate Concentration

The use of alcohol in fuel also tends to cause higher molecular weight hydrocarbons to be present in the vapor. These higher molecular weight molecules are adsorbed by the charcoal and are more difficult to remove from the charcoal under typical purge conditions. As the capacity of a canister is decreased by the adsorption of substances that are more difficult to purge, the performance of the evaporative emission control system will degrade (Crawford et al., 1984).

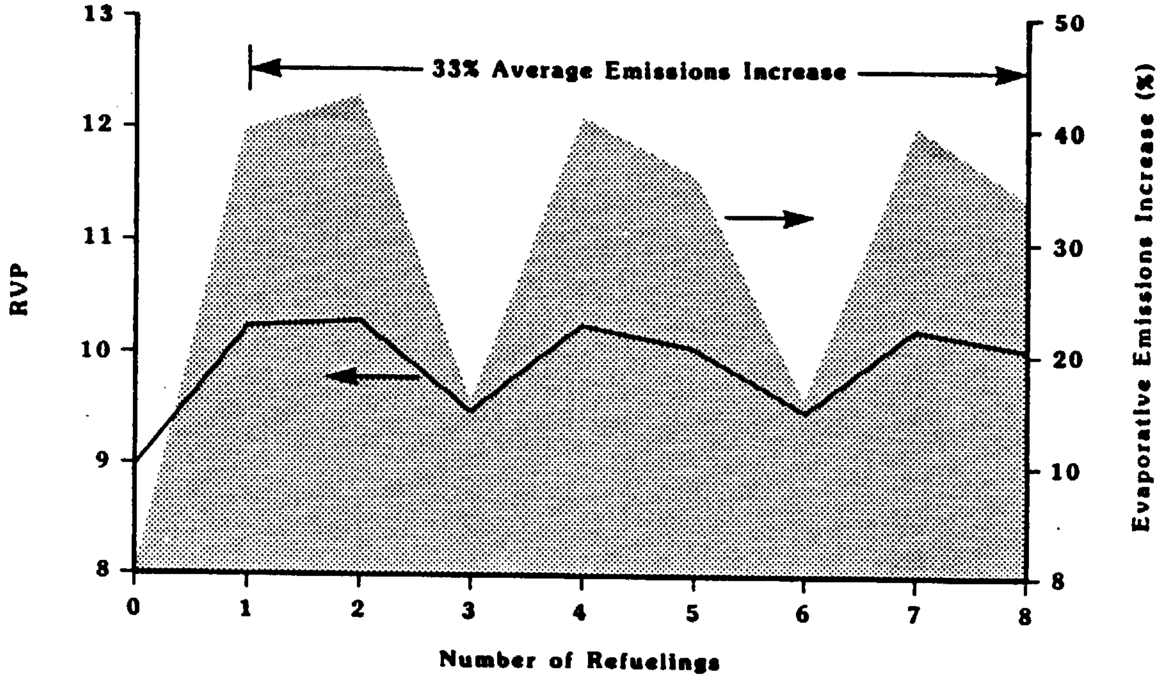
Recent developments in evaporative emission control systems could result in improved evaporative emission control system durability when blended fuels are used. Charcoal canisters are being developed that have integral purge air heaters. These canisters can control the temperature of the purge air, thereby resulting in higher purge air temperatures and the ability to purge higher molecular weight hydrocarbons.

The chemical composition of evaporative hydrocarbons is different when blended fuel is used compared to a straight gasoline. More hydrocarbons in the C5 through C7 class are present in the evaporative emissions. It is believed that these classes of hydrocarbons have a much greater photochemical reactivity (Crawford et al., 1985).

7.2.3 Impact of Intermittent Blend Usage on Evaporative Emissions

In California, the RVP of unleaded gasoline is controlled to a maximum of 9 psi during the "smog" season. This is done to minimize the evaporative hydrocarbon emissions from the gasoline vehicle fleet.

Because of volatility constraints, refueling intermittently with gasoline and with a gasoline/alcohol blend can result in a tank RVP greater than the volatility limit. An analysis performed by Crawford et al. (1984) estimated the increase in RVP due to intermittent fueling of alcohol/gasoline blends. Initially the fuel tank was assumed to be filled with a mixture of 10 percent Oxinol and 90 percent gasoline. The tank was refilled once it became two-thirds empty. Every third refill was with the Oxinol/gasoline blend. All other refills were with 9 psi RVP gasoline without oxygenates. After eight refueling cycles, the average RVP of the tank was 10.01 psi. This increase in average RVP would increase evaporative emissions by an average of 33 percent. The effect of each refueling on RVP and evaporative emissions is shown in Figure 7.7.



Source: Crawford et al., 1985.

Figure 7-7. Effect of Intermittent Use of Volatility Controlled Oxinol

The cause of the volatility increase due to intermittent refueling is related to the effect of oxygenate addition shown in Figure 7-1. A small volume of alcohol added to gasoline causes a significant increase in the blend RVP. The blending RVPs of Oxinol®, ethanol, and TBA are presented in Figure 7-8. If the blend contains 15.7 percent TBA, the TBA will increase the RVP of the blend as if the TBA had an RVP of 12.8 psi. However, when the blend contains only 1 percent TBA, the TBA will increase the RVP of the blend as if the TBA had an RVP of 69 psi. As shown in Figure 7-8, Oxinol® has the greatest blending RVP.

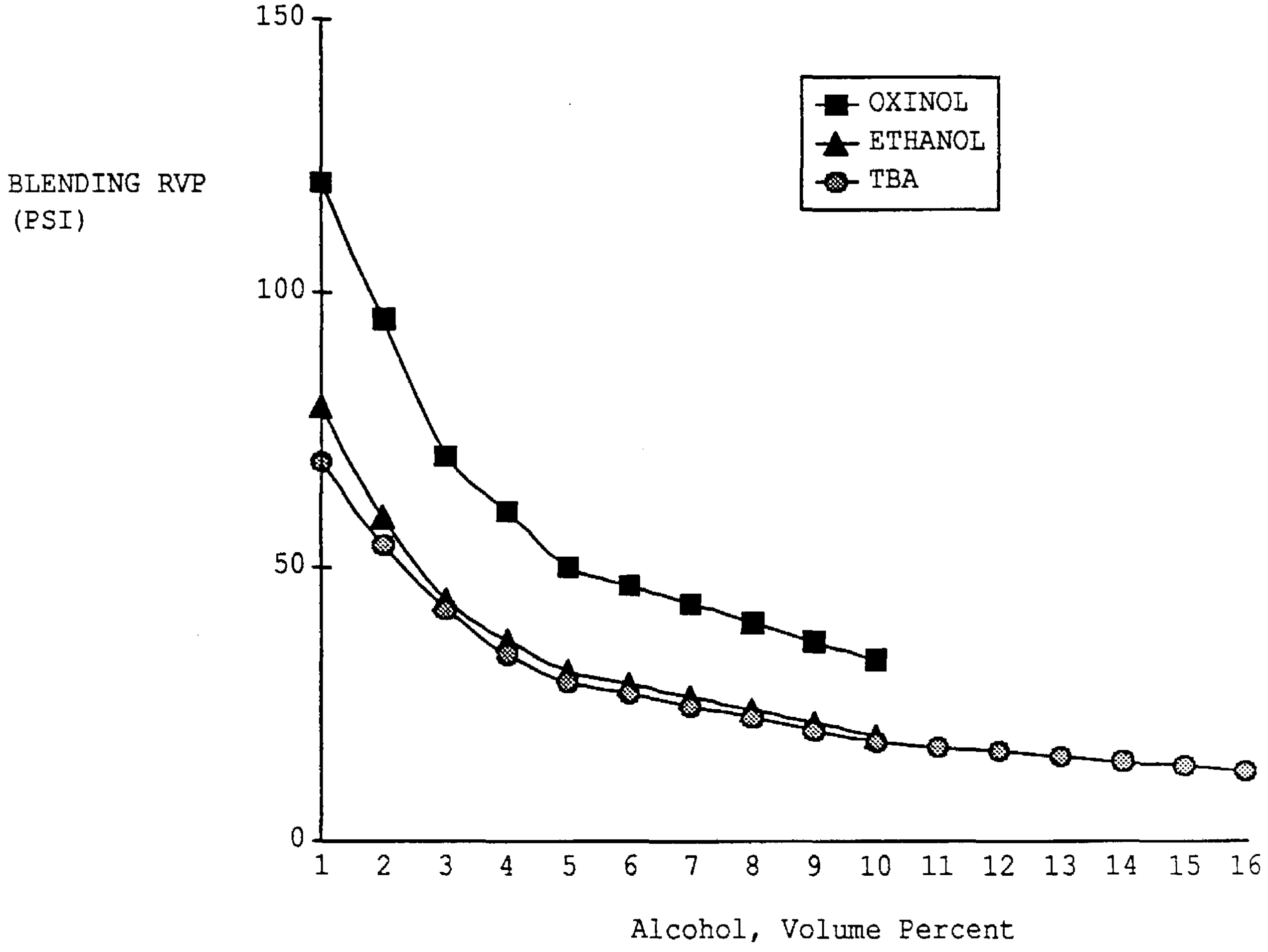


Figure 7-8. Blending RVPs for Different Oxygenates

The RVP increase associated with intermittent refueling could be reduced by requiring blended fuels to have an RVP lower than 9.0 psi. The tank RVPs could be maintained at or near 9.0 psi by requiring blended fuels to have RVPs lower than 9.0 psi. Radian has estimated the maximum blended fuel volatility in order to maintain the tank RVP at or below 9 psi. The refueling scenario studied consisted of refueling with straight gasoline when the tank was one-third full with the blended gasoline. The maximum RVP for the different blends required to maintain the tank RVP at 9.0 psi is listed in Table 7-5. The maximum RVP for the straight gasoline used in the blended fuel is also listed. The maximum RVP for the Oxinol® gasoline blend would be 5.5 psi. The straight gasoline used in the Oxinol® blend would be required to have a maximum volatility of only 2.6 psi RVP. The maximum RVPs for the ethanol/gasoline blend and TBA/gasoline blend are both 6.5 psi. The calculations used to arrive at these estimates can be found in Appendix D.

Requiring the blended fuels to have volatilities lower than the maximum volatility for straight gasoline would reduce evaporative emissions. The maximum RVPs for the blended fuels would be in the 5.0 to 7.0 psi range. When intermittent refueling occurred, the maximum tank RVP would be at or near 9.0 psi. However, a vehicle operating on the blended fuel would probably encounter driveability problems due to the RVP limits. Driveability problems could be so severe that exhaust hydrocarbon emissions could be increased due to misfire, stalls, and restarts.

Table 7-5. MAXIMUM BLEND VOLATILITIES

Blending Agent	Maximum Blended Fuel RVP (psi)	Maximum Gasoline RVP Used with the Oxygenate
Oxinol®	5.5	2.6
Ethanol	6.5	5.1
TBA	6.5	5.3

7.3 Exhaust Emissions Effects

As shown in Table 7-1, one significant difference between oxygenates and gasoline is that the oxygenates contain oxygen and gasoline does not. As discussed below, it is the oxygen content of oxygenates that effects exhaust emissions.

The stoichiometric air/fuel ratio is the mass of air needed to completely burn one pound of fuel. As indicated in Table 7-1, using ethanol as an example, it takes 9 pounds of air to burn 1 pound of ethanol, and 14.7 pounds of air to burn 1 pound of gasoline. It takes less air to burn one pound of ethanol because the ethanol contains oxygen. When ethanol and gasoline are blended together, a blend containing 10 percent ethanol will have a stoichiometric air/fuel ratio of 14.1:1, which is 4.1 percent lower than straight gasoline.

Unless operating under "closed-loop" control, carburetors and fuel injection systems do not automatically compensate for changes in the stoichiometric air/fuel ratio of the fuel being used. Fuel metering systems generally supply a fixed volume of fuel per unit of engine air flow. Because the density of ethanol is greater than gasoline, the density of a 10 percent ethanol/90 percent gasoline blend ("Gasohol") would be 6.24 pounds per gallon. However, this is only a 0.6 percent greater density than straight gasoline, and is not a sufficient density increase to offset the 4.1 percent change in stoichiometric air/fuel ratio caused by blending the ethanol into the gasoline. The net effect is that an engine running on the alcohol-gasoline blend will have 3.5 percent more air relative to the stoichiometric air/fuel ratio than if it were running on straight gasoline. The amount of air being used by the engine does not change, but the amount of air needed to completely burn all of the fuel is reduced. As a result, there is relatively more air available for complete combustion and the engine, therefore, is running "leaner" on the alcohol-gasoline blend than on straight gasoline.

The effect of leaner operation depends on the initial air/fuel ratio. For engines that are operating with fuel rich mixtures (less than the necessary amount of air for complete combustion), leaner operation greatly reduces hydrocarbon and carbon monoxide emissions while increasing NO_x. Fuel rich mixtures are routinely used during cold-start and warmup operation of gasoline-fueled vehicles of all ages. Rich mixtures are necessary to achieve smooth combustion during warmup because gasoline does not fully vaporize and mix with the air in a cold engine. Extra fuel is added to insure that an adequate amount of fuel is vaporized to achieve a combustible mixture. Complete vaporization occurs in the cylinder as the result of the high temperatures created by combustion. However, the excess fuel that was needed to ensure adequate vaporization to start the combustion process cannot be completely burned due to a lack of sufficient oxygen in the cylinder. The result is that partially burned fuel (carbon monoxide) and unburned fuel (hydrocarbons) are emitted in relatively high concentrations.

When alcohol-gasoline blends are substituted for gasoline, slightly leaner operation occurs during the cold-start and warmup period. Therefore, CO and HC emissions are reduced. Usually, there is still adequate mixture enrichment to ensure sufficient fuel vaporization. However, driveability problems may occur in some vehicles. NO_x emissions are increased due to the lean shift; however, NO_x tends to be low during rich operation of a cold engine so the NO_x increase is relatively small.

During warmed-up operation, the expected effects of alcohol-gasoline blends depends on the type of fuel metering system used. Most 1981 and later model passenger cars use three-way catalysts designed to simultaneously reduce HC, CO, and NO_x emissions when the air/fuel ratio is kept very close to the stoichiometric ratio. Maintenance of a precisely stoichiometric ratio cannot be accomplished without the use of an exhaust oxygen sensor (O_2 sensor) and a feedback control system. With the use of oxygen sensors and feedback control, there should be automatic compensation for the enleanment effect of alcohol addition. CO emissions would be expected to remain essentially the same as with straight gasoline.

Between 1968 and 1980, light duty vehicles were required to meet exhaust emission standards, but feedback control of air/fuel ratio was seldom used (and never used until the 1977 model year). Alcohol blending would, therefore, cause leaner air/fuel ratios under both warmup and warmed-up operation. During warmup, these vehicles still used rich mixtures, so alcohol would be expected to reduce HC and CO emissions. However, during warmed-up operation, most vehicles produced during this period utilized leaner than stoichiometric air/fuel ratios to control HC and CO emissions. The effects of enleanment during warmed-up operation depend on the initial air/fuel ratio. Some vehicles would experience emission increases due to misfire caused by excessively lean operation. Other vehicles would experience slight reductions in HC emissions. If the vehicle was running only slightly leaner than stoichiometric, HC emissions would be expected to decrease and NO_x may increase. No significant change in CO emissions would occur once the engine is already running leaner than stoichiometric.

Most vehicles produced prior to 1968 used relatively rich air/fuel ratios even during warmed-up operation. During both warmup and warmed-up operation, such vehicles would be expected to experience significantly lower HC and CO emissions and higher NO_x emissions due to oxygenated fuel use.

Table 7-6 summarizes the expected effects of oxygenated fuel use for vehicles of various ages. As the table shows, all ages of vehicles are expected to experience reductions in HC and CO emissions during cold start and warmup operation. After the vehicle is warmed up, the expected effect on emissions depends on the initial air/fuel ratio and whether feedback control over the air/fuel ratio is employed.

Based on laboratory test results, (Gurney et al., 1980; Systems Control, Inc., 1982; Allsup and Eccleston, 1979; Naman and Allsup, 1980; and U.S. EPA, 1978), carbon monoxide emission reductions are typically about 25-30 percent for blends containing about 3 percent oxygen (equivalent to a blend of 10 percent ethanol and 90 percent gasoline). As might be expected with the use of feedback controls on fuel metering (closed-loop), CO emission reductions appear to be lower for the newer, feedback models.

Table 7-6. EXPECTED EFFECTS OF OXYGENATED FUELS ON EXHAUST EMISSIONS

Age of Vehicle	Operating Mode	Exhaust Emissions HC	CO	NO_x
1981 and newer models	start & warmup	lower	lower	slightly higher
	warmed-up	same	same	same
1968 to 1980 models	start & warmup	lower	lower	slightly higher
	warmed-up	lower or higher	little change	lower or higher
Pre-1968 models	start & warmup	lower	lower	slightly higher
	warmed-up	lower	lower	higher

The effect of the blended fuel use on CO emissions for different model year vehicles is summarized in Table 7-7. The table shows the CO emission decrease expected by vehicle model year category when converting from gasoline to a 10 percent ethanol blend. Late model vehicles with electronic fuel control display the smallest decrease in CO emissions.

TABLE 7-7. CARBON MONOXIDE EMISSION DECREASE WHEN USING GASOHOL

Model Year	CO Decrease (gm/mi)
1973-74	17.4
1975-79	9.4
1980-83	2.8
1984	0.08

Source: Ragazzi, 1985

The effect of oxygenated fuel use on HC and NO_x exhaust emissions is less consistent. When a large sample of tests is averaged, the change in HC and NO_x emissions for blends containing 3 percent oxygen is generally less than 15 percent (lower for HC, higher for NO_x). As shown in Table 7-8, Coordinating Research Council test results (Systems Control, Inc., 1982b), on 14 1980 model cars are representative of the emissions effects that 10 percent ethanol blending can be expected from late model vehicles.

TABLE 7-8. CRC EMISSION TEST RESULTS FROM 14 1980 MODEL CARS USING GASOHOL

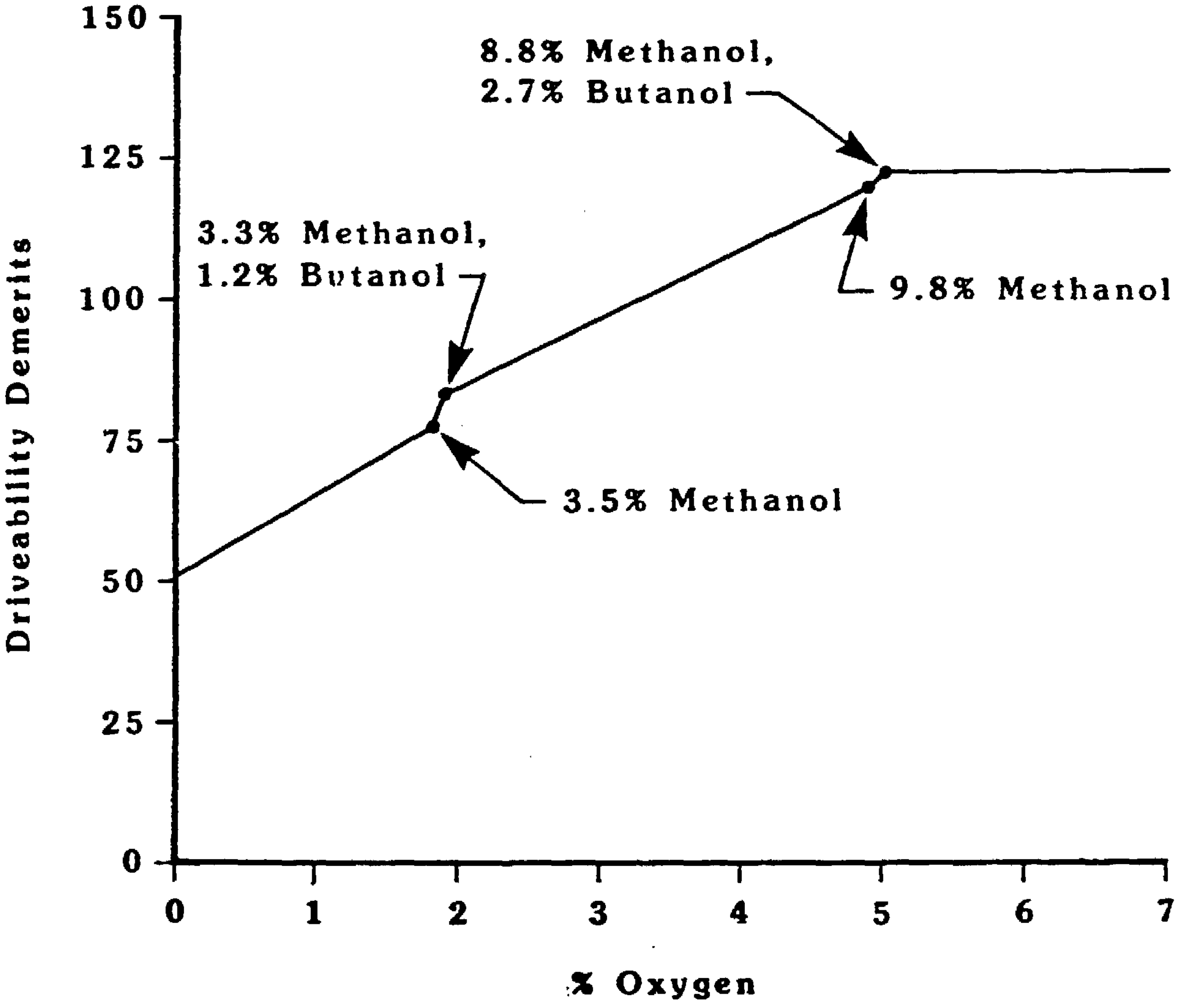
Exhaust HC	Carbon Monoxide	Oxides of Nitrogen
not significant	- 26%	+ 15%

Increases in tailpipe aldehyde emissions would be expected to occur when using oxygenate/gasoline blends. Aldehyde exhaust emission increases of approximately 4 mg/mi have been measured when using 10 percent ethanol gasoline blends compared to straight gasoline. The aldeyhyde exhaust emission factor for the base gasoline was 8.6 mg/mi compared to 12.6 mg/mi for the ethanol/gasoline blend (Systems Control Inc., 1982b).

7.4 Driveability

In addition to the impact on emissions, the driveability of the vehicle also is affected. Depending on the type of alcohol used, a significant leaning of the air/fuel ratio occurs when gasoline/alcohol mixtures are used on vehicles designed to use gasoline. Vehicles that do not have a "feedback" mechanism cannot enrich the mixture, so the vehicle operates at a leaner-than-designed air/fuel ratio. These cars tend to exhibit driveability problems that require the vehicle to be serviced. Modifications that solve the driveability problem also reduce the emissions improvement. Typically, the service performed enriches the operating air/fuel ratio, thereby returning the vehicle to its prior emission performance. In a significant number of cases, the repair actually caused the emissions performance to be worse than when the vehicle was using only straight gasoline (Crawford et al., 1984).

The driveability of the vehicles using methanol and ethanol blended fuels was measured during tests conducted under a CRC study (System Control, Inc., 1982a and 1982b). As the oxygen content of the fuel increased, the driveability of the vehicles decreased. With 10 percent ethanol the average driveability decreased by 47 percent, the total number of demerits increased from an average of 24.4 to 39.5 (Systems Control Inc., 1982b). Similar results were obtained during the driveability testing of the methanol blended fuel. In the methanol study, driveability demerits increased from approximately 50 to 120 when 8.8 percent methanol and 2.7 percent butanol were added to the base fuel (Systems Control Inc., 1982a). Figure 7-9 shows the relationship between fuel oxygen content and driveability based on the CRC study of methanol-gasoline blends.



Source: Crawford et al., 1985.

Figure 7-9. Effect of Fuel Oxygen Content on Driveability

The limited data on carburetted vehicles indicates that significant emission increases occur as driveability problems are corrected by emission control system modifications. A 50 percent increase in exhaust HC emissions and a 138 percent increase in CO emissions occurred after carburetted vehicles were modified for improved driveability when using a 15 percent methanol blend. The same vehicles were tested with straight gasoline after the driveability was improved. Emission increases of 138 percent and 360 percent occurred for HC and CO, respectively. Therefore, it appears that CO emission increases will occur when carburetted vehicles are restored for driveability after conversion to blended fuels (Crawford et al., 1984).

7.5 Materials Compatibility

Alcohol fuels have been shown to corrode various metallic components that are found, or have been found, in the fuel distribution system. The metals, which are encountered during distribution or in the vehicle's fuel delivery system, include steel, copper, brass (copper/zinc alloy), carburetor metal (zinc alloy), magnesium, aluminum, terne plate (lead/tin alloy), and solder (lead/tin alloy).

The presence of water in the fuel system would tend to increase the corrosive activity of the blended fuels due to the potential for phase separation. Corrosion concerns have been addressed by many automobile manufacturers. They are reducing the number of components that can be corroded by blended fuels. To date, the field tests using Gasohol and up to 5 percent methanol have shown a variety of problems. As discussed below, materials compatibility does not appear to be a serious problem with ethanol-gasoline blends or low-level methanol gasoline blends in which cosolvent alcohols are also used.

Ethanol. Late model vehicles are generally compatible with Gasohol, so changes in maintenance frequency are not associated with the use of ethanol-gasoline blends. However, older vehicles may require some increased maintenance. Increased maintenance requirements may occur due to two different factors. First, ethanol causes more rapid deterioration of certain fuel system components than gasoline. Second, ethanol acts as a detergent, removing accumulated fuel system deposits that can plug fuel filters.

Joseph and Grogan (1980) reported on the maintenance experience with a fleet of 900 cars and trucks operated on ethanol-gasoline blends by DuPont. Based on the use of the blends for about one year, the authors concluded that there were "no significant unanticipated maintenance problems". However, increased maintenance frequency was required on some cars.

In the DuPont fleet test, plugged fuel filters were reported to be the most frequent problem. Some older vehicles in the fleet experienced fuel filter plugging on two or more occasions. Two of the vehicles in the fleet required fuel tank cleaning to prevent repeated fuel filter plugging.

Certain vehicles also experienced driveability problems caused by deterioration of the rubber seals used in the carburetor accelerator pump. When these seals failed, there was inadequate mixture enrichment during acceleration, and misfire and stumbling was noticed. Driveability was restored when the accelerator pumps were replaced.

Carburetor jets on several vehicles became plugged with resin particles from the electric fuel pump. Ethanol deteriorated the resin that was used to seal the fuel pump, causing small particles to be sloughed off and plugging the carburetor jets. Carburetor cleaning and rebuilding was required to restore driveability.

Finally, 25 of the 900 vehicles (2.8 percent) used in the DuPont fleet experienced carburetor flooding associated with the absorbtion of Gasohol by carburetor floats that were made of a phenolic resin. This problem was most prevalent when a 20 percent blend of ethanol and gasoline was being used. The investigators speculated that float deterioration may be a function of ethanol concentration and time. The carburetor float problems observed would be expected to eventually lead to I/M program failures for some vehicles. Proper identification of the problem would be uncertain.

In another fleet test conducted by Contra Costa County, California, Gibbs and Gilbert (1981) observed significant wear of Viton fuel inlet needle tips after 16,499 miles of operation on Gasohol. The needle tip wear was thought to be caused by the lead hydroxychloride particles formed from the corrosive effect of ethanol on the fuel tank coatings (a lead-tin alloy). Continued deterioration of the needle tips would lead to excessive mixture richness and increased emissions. This would cause a vehicle to fail I/M. If properly diagnosed, replacement of the needles would correct the problem.

In a fleet test of about 100 cars and trucks by Southwestern Bell Telephone Company, fuel filter plugging during the initial phases of the program were the only problem noted (Gurney et al., 1980). According to the report on the fleet test, "with the exception of the fuel filters that were used and the two carburetors that received the extremely fine sediment, no fuel system failures could be attributed to the Gasohol."

The available data on maintenance impacts are fairly consistent in that increased maintenance frequency seems to be restricted to older vehicles. For older vehicles that have not been using Gasohol, some vehicles can be expected to experience fuel filter plugging. This will be manifested as obvious hesitation and power loss during acceleration or surging during higher speed cruise conditions. Once accumulated deposits are removed, filter plugging will cease and normal fuel filter maintenance will generally be adequate.

Based on fleet test experience, maintenance problems other than fuel filter plugging appear to be fairly rare. Individual vehicle models may experience problems with abnormal deterioration of miscellaneous fuel system components. Emissions may be increased over time, as these maintenance problems increase in frequency. Detection and correction of such defects would be facilitated by I/M programs, but not ensured.

Methanol. Field test experience with methanol-gasoline blends indicates similar materials compatibility problems to those observed with ethanol-gasoline blends. When used in concentrations of greater than 10 percent total alcohol, customer complaints associated with materials compatibility problems appear to be substantial. One California marketer of high level methanol-gasoline blends reported accelerator pump failures in many vehicles (personal communication with Henry Seal, 1987). Tests of similar high-level methanol-gasoline blends by the EPA also have resulted in accelerator pump failures.

7.6 Conclusions and Recommendations

Increases in hydrocarbon evaporative and exhaust emissions may occur from the use of alcohol/gasoline blends. Intermittent refueling with blended gasolines will cause the tank RVP to increase above the volatility limit of 9 psi. Long-term use of alcohol/gasoline blends may reduce the capacity of the evaporative emission control system and further increase hydrocarbon emissions. Short-term increases in tailpipe NO_x may occur due to the use of alcohol/gasoline blends. If driveability problems associated with blend use are repaired in carburetted vehicles, the NO_x increase could give way to increases in HC and CO emissions.

Increased evaporative emissions may occur from using alcohol/gasoline blends due to volatility differences, evaporative emission control system degradation, and intermittent use. Because of the potential for evaporative hydrocarbon emission increases ARB should consider additional volatility constraints for blended fuels. One possibility for reducing evaporative emissions due to blend use may be to specify a distillation curve for blended gasolines. General Motors has shown that the total quantity of vapor generated by blends is less than or equal to straight gasoline when the distillation curves are approximately the same. However, this approach does not deal with the problem of intermittent use.

The evaporative emissions increase due to intermittent use could be reduced by requiring blended fuels to have a maximum RVP below 9 psi. Maximum RVPs for blends of Oxinol®, ethanol, and TBA have been calculated. The maximum RVP varies from 5.5 for Oxinol® to 6.5 for ethanol and TBA blends. The reduced volatility would most likely result in decreased vehicle driveability when regularly using the blended fuel. However, when intermittently used, the tank RVP would not be expected to exceed 9.0 psi. The possibility of increased exhaust emissions associated with lower volatility blends should be evaluated before any regulatory action is proposed.

Another issue that needs further evaluation is the apparent reduction in evaporative emission control system performance due to blend use. Oxygenated compounds are preferentially absorbed by the charcoal canisters. The higher weight alcohol compounds are also more difficult to purge from the canister once they have been absorbed. Increasing the size of the charcoal canister may be one way to mitigate the decreased system performance. Adoption of the on-board vapor control regulation will most likely not mitigate additional evaporative emissions due to decreased system performance. The certification fuel will not contain oxygenates; therefore, the canister will not be sized to compensate for the additional evaporative emissions and system degradation due to oxygenate blends. This degradation needs to be better qualified.

8.0 AFTERMARKET FUEL ADDITIVES

Aftermarket fuel additives have been marketed and used for many years. Originally, these additives included water emulsifiers, fuel system cleaners, and octane boosters. These and other types of additives are still common in auto parts stores in California. Water emulsifiers are expected to have little impact on emissions, while fuel system cleaners probably have a beneficial effect. Some chemicals which might be used as octane boosters could be cause for concern if used in catalyst-equipped vehicles, however.

Two relatively new classes of additives, also common in auto parts stores, are lead substitutes and "pollution control" additives. Lead substitutes are marketed with the claim that they prevent valve seat recession due to the use of current reduced lead-content leaded gasoline in older engines. At least one such additive actually claims to contain tetra-ethyl lead (TEL). "Pollution control" additives are being marketed that they can clean catalytic converters and/or reduce HC and CO emissions to assist in passing the Smog Check. The claims made for both additive classes are cause for serious concern regarding the potential emissions impacts of these products.

The composition of aftermarket additives is considered proprietary, and is not stated on the product label. Although additives must be registered with EPA, emissions testing or even proof of efficacy is not required in most cases. Thus, the potential emissions impact from any given product may be difficult to assess. Although Radian was able to obtain some limited information from additive manufacturers on a confidential basis, considerable uncertainty remains.

8.1 Types of Aftermarket Fuel Additives

Most aftermarket fuel additives can be classed into one of five categories:

- Water Emulsifiers;
- Fuel System/Intake Manifold Cleaners;
- Octane Boosters/Anti-Knock Additives;
- Lead Substitutes; and
- "Pollution Control" Additives.

Each of these categories is discussed below.

8.1.1 Water Emulsifiers

Water emulsifiers are used to emulsify water in a vehicle's fuel tank. These products remove water from the fuel tank to prevent fuel line freeze-up, corrosion and fuel filter plugging. These products have been on the market for a number of years and consist primarily of alcohols. Their concentration when added to the fuel tank is not expected to cause significant emissions impacts.

8.1.2 Fuel System/Intake Manifold Cleaners

Fuel system and intake manifold cleaners have also been available for a number of years. These products are concentrated formulations of the gasoline detergents/polymeric dispersants and fluidizer oils marketed by a number of additive manufacturers and refiners. These products are becoming more popular due to the publicity surrounding fuel-injector deposit problems. A number of oil companies and aftermarket additive manufacturers currently retail fuel-injector and carburetor cleaners, e.g. Chevron Techroline (tm). These products should reduce the emissions from vehicles with injector deposits, and thus produce a net reduction in emissions. Refer to Section Four for a more detailed description of the effects of detergents and polymeric dispersants.

8.1.3 Octane Boosters/Anti-Knock Additives

Information on the active ingredients in octane-boosting aftermarket additives is not generally available. However, a refiner provided confidential information on the constituents found in some octane boosters/anti-knock additives. According to the refiner, products in this group can contain aniline, MMT, MTBE, and other alcohols. Aniline is a high octane benzene derivative which can produce significant intake system and combustion chamber deposits.

Some other octane boosters which could conceivably be included in these products include lead compounds such as TEL and TML, or other high-octane crude oil-based compounds such as isooctane, toluene, benzene, and other aromatics. The major concern here is with the possible metallic components. Sale of lead products for use in motor vehicles is illegal in California, but this law is difficult to enforce, since the product composition is not shown on the label. While TEL producers attempt to keep their product out of the hands of the aftermarket vendors, they are not always successful. The effect of lead on emission control system components is documented in Section Three. Use of these products in vehicles with catalytic converters will result in significant emission increases.

As discussed in Section Three, manganese is much less damaging than lead to catalytic converters, but it increases engine-out HC emissions. MMT may legally be sold for use in vehicles without catalytic converters, but this is no guarantee that it will be used only in those vehicles. Use of large amounts of MMT in catalytic converter-equipped vehicles could plug the catalyst or otherwise impact the emission control system.

The use of oxygenated compounds as octane enhancers could result in increased fuel tank RVP and possibly increased evaporative emissions. Slight increases in exhaust hydrocarbon emissions would also be expected. Refer to Section Seven for a discussion of the effect of oxygenated compounds on vehicle emissions. With aromatic-based octane enhancers, there is a potential for increased benzene emissions.

8.1.4 Lead Substitutes

Lead substitutes have become popular due to the EPA-mandated reduction in the lead content of leaded gasoline. These products claim to act as valve-seat lubricants, thereby reducing the possibility for valve seat recession due to inadequate lead in the gasoline. Additives, other than lead, which are known to act as valve seat lubricants include phosphorus, manganese, sodium, and potassium. Other proprietary additives have demonstrated effectiveness comparable to that of lead (Weaver, 1986).

In a survey of the fuel additives available at local automotive parts stores, a number of lead substitutes were found. One lead substitute, which is marketed by Bardahl as "Instead O' Lead Gold," advised the purchaser this product was intended for use in pre-1974 vehicles. It also stated it was not for use in any vehicle that had a catalytic converter.

Another product marketed by Octane Boost Corporation, "Real Lead," claimed to contain tetraethyl lead (TEL). Industry sources have indicated that this product is essentially high-lead leaded gasoline. Sale or use of this product in motor vehicles is prohibited in California (Cackette, 1987). The front of the Real Lead package included a warning (in very small type) informing the purchaser that this product was not for use in motor vehicles in California, but only for boat engines. The product container also listed the following benefit claims:

- Lowers exhaust emissions;
- Promotes smoother engine operation;
- Inhibits rust and corrosion; and
- Protects against icing stall in cold weather.

This product was offered for sale in an auto parts store, which appeared to offer no significant marine equipment or accessories, and was stocked on the shelf with numerous other additives clearly intended for use in motor vehicles. It is doubtful, therefore, whether marine customers constituted the primary market for this product.

8.1.5 "Pollution Control" Additives

Another group of fuel additives found on the shelves today are "pollution control" additives. The claims for these types of additives range from "cleaning" catalytic converters to a guarantee that the user will pass the Smog Check HC and CO tests, or the purchaser's money is returned.

"Catalytic converter cleaners" are being marketed by a number of different companies. One of the additives marketed by Unival Corporation was briefly described in the July 13, 1987, edition of the automotive publication Autoweek. According to Autoweek, Unival's product will remove sulfurous odors from your converter, extend the life of the catalyst, and lengthen the interval between tune-ups.

A "catalytic converter cleaner" marketed by Mechanics was found at a local auto parts store. The information on the container stated the product would help eliminate sulfur odor, could help pass emissions control tests, extends the life of catalytic converter, deodorizes, and helps keep the engine from overheating.

A product marketed by Wynn's is the "Smog Check Pollutant Controller." If used as directed, the Wynn's product guarantees passage of a required test of CO and HC or the purchaser's money will be refunded. Wynn's suggests using its product every 3,000 miles for continued reduction in emissions of carbon monoxide and hydrocarbons. Additional advantages of using Wynn's product are that it "cleans catalytic converters", and it helps eliminate "rotten egg" odor. No ingredients are listed on the product container.

An aftermarket additive company supplied confidential composition information for its "pollutant control" additive. This company made claims about its product similar to those previously listed. The company's product is EPA-registered and patented. The ingredients include an oxygenated compound and an ashless detergent. The oxygenated compound leans the mixture, thereby reducing HC and CO emissions. In addition, H_2S emissions would be reduced slightly due to the formation of SO_2 during lean operating conditions. Constant use of this product in closed-loop vehicles would not be expected to cause lean operation because the fuel control system would adjust to compensate for the excess oxygen.

8.2 Regulation of Aftermarket Additives

Current regulatory oversight of aftermarket additives does not appear to be sufficient. Cans of tetraethyl lead can be purchased over the counter at auto parts stores in California. Other products currently marketed claim to clean catalytic converters, or to ensure that a vehicle passes the tailpipe HC and CO test. In general, the ingredients in these products are unknown. Without knowing their composition, the impact of these additives on emission control system components, or the environment, cannot be determined.

There appears to be no effective surveillance or regulation of these products. Additive and fuel manufacturers are required to register their products with the EPA, but no emissions testing or even proof of effectiveness is required. EPA testing of fuels and additives is performed only when the manufacturer requests a test, or when a complaint is received (Michael Lesh, EPA Fuels Registrar, personal communication, 1987). There is apparently no mechanism for confirming on any routine basis that additives actually on the shelves have been registered with EPA, or that the additive contents disclosed to EPA are in fact those included in the product. In addition, product labels do not disclose product compositions, making it difficult for consumers to make an informed choice.

8.3 Summary, Conclusions, and Recommendations

Aftermarket fuel additives are currently marketed with claims that they remove water from fuel tanks, clean fuel systems and intake manifolds, enhance the octane rating of gasoline, act as lead substitutes to protect valve seats, and improve the performance of pollution control devices. The potential exists for some of these products to impair the performance of emission control devices and to increase emissions. However, since the ingredients of the majority of these components are unknown, no conclusion regarding their effect on vehicle emissions performance can be made. The additives with the greatest potential for detrimental effects are the octane boosters, lead substitutes, and catalytic converter cleaners. Of special concern is the fact that additives claiming to contain tetra-ethyl lead are readily available over-the-counter in auto parts stores.

It is recommended that ARB act in conjunction with EPA to re-evaluate their regulation and oversight of the aftermarket additive industry. Some demonstration of effectiveness, and of an absence of adverse emission control impacts, should be required in order for additives to be registered. Public access to additives containing lead and other substances that are known to cause significant detrimental impacts to emission control systems should be minimized. Products not intended for vehicles that use unleaded gasoline should have spouts that are too large to be inserted into the fillpipe restrictor. Products containing lead should not be sold in automotive parts stores, since it is illegal to use these products in motor vehicles in California.

Aftermarket additive manufacturers should be required to include EPA registration information on their labels. If a labeling requirement was developed, aftermarket additives not registered with EPA could be easily identified. In addition, it is recommended that random surveys of aftermarket additives be performed. Products should be tested to verify the registration information provided to EPA.

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APPENDIX A

Calculations Estimating Excess Emissions Due to Fuel Injector Deposits

BY DAW DATE 12/9/87 SUBJECT Estimate of Number of MPFI Passenger Cars in California SHEET NO. 1 OF
CHKD. BY CB DATE 12/15/87 JOB NO. 245-050-05-00

References: Lyons and Kenny, 1987

Heavenrich, et al., 1986

California Department of Transportation, Nov. 1986

Estimated Total Number of Gasoline Powered Automobiles on the Road in California in 1986 (CalTrans, 1986)

12,841,000

California Automobile Sales for 1983 - 1986 (Estimated from Lyons and Kenny, 1987)

1986	1,250,000
1985	1,200,000
1984	1,115,000
1983	850,000

Nationwide Automobile Sales for 1975 through 1986 (Heavenrich, et al 1986)

Model Year	National Sales	California Sales		Est. Calif Sales*
		Total	% of Natl.	
1986	11,076,000	1,250,000	11.3%	
1985	10,891,000	1,200,000	11.0%	
1984	10,675,000	1,115,000	10.4%	
1983	8,002,000	850,000	10.6%	
1982	7,819,000			844,000
1981	8,733,000	Avg	10.8%	943,000
1980	9,443,000			1,020,000
1979	10,794,000			1,165,000
1978	11,175,000			1,207,000
1977	11,300,000			1,220,000
1976	9,722,000			1,050,000
1975	8,237,000			890,000

1975 - 1986 Est. Total California Vehicle Sales 12,754,000

* Estimated California Sales = Natl Sales x .108

BY DAW DATE 12/9/97 SUBJECT Estimate of Number of MPFI Passenger Cars in California SHEET NO. 2 OF
CHKD. BY CB DATE 12/15/97 JOB NO. 245-050-05-00

Fraction of California Passenger Car Vehicles using Fuel-Injection (Estimated from Lyons and Kenny, 1986)

Model Year	Percentage
1986	65%
1985	60%
1984	48%
1983	36%

Because Fuel Injector Deposits are a concern for MPFI vehicles and not Throttle Body Fuel-Injected Vehicles, the percentage needs to be segregated into TBI and MPFI.

Assume the California Sales Fractions for TBI and MPFI are the same as the National Sales Fraction

National Fuel Injection Sales Fraction (from Heavenrich et al.)

Model Year	Total F.I.	TBI	MPFI	MPFI % of Total F.I.
1986	65%	30%	35%	54%
1985	55%	30%	25"	45%
1984	40%	25%	15%	38%
1983	30%	20%	10%	33%
1982	18%	10%	8%	44%
1981	9%	2%	7%	78%
1980	7%	0%	↓	100%
1979	↓	↓	↓	↓
1978	↓	↓	↓	↓
1977	↓	↓	↓	↓
1976	↓	↓	↓	↓
1975	↓	↓	↓	↓

BY DAW **DATE** 12/9/87	**SUBJECT** Estimate of Number of MPFI Passenger Vehicles in California	**SHEET NO.** 3 **OF**
CHKD. BY CB **DATE** 12/15/87		**JOB NO.** 245-050-05-00

RADIAN CORPORATION

Estimated Number of MPFI Passenger Cars in California in 1986

Assumptions - Use Lyons and Kenny data for 1983 - 1986

- Assume Total F.I. use in California decreases by 6%/year from 1983 until 1979
- Assume constant minimum F.I. sales in California of 12%.
- Assume California MPFI fraction is the same as the National fraction

Model Year	California F.I.	MPFI % of Total	Est. Calif MPFI %
1986	65%	54%	35.1%
1985	60%	45%	27%
1984	48%	38%	18%
1983	36%	33%	12%
1982	30%	44%	12%
1981	24%	78%	19%
1980	18%	100%	18%
1979	12%	↓	12%
1978	↓		↓
1977			
1976			
1975			

Estimated Total Number of MPFI Vehicles on the Road in California (Assume Vehicle Sales equals Vehicles on the Road)

Model Year	Total Vehicles	MPFI Vehicles	MPFI Fraction
1986	1,250,000	438,750	35.1%
1985	1,200,000	324,000	27%
1984	1,115,000	200,700	18%
1983	850,000	102,000	12%
1982	844,000	101,280	12%
1981	943,000	179,170	19%
1980	1,020,000	183,600	18%
1979	1,165,000	139,800	12%
1978	1,207,000	144,840	↓
1977	1,220,000	146,400	
1976	1,050,000	126,000	
1975	890,000	106,800	
Total	12,754,000	2,193,340	17.2%

BY DAW DATE 12/9/87 SUBJECT Estimated Emissions Increase Due to MPFI Injector Deposit SHEET NO. 4 OF

CHKD. BY CB DATE 12/15/87 JOB NO. 245-050-05-00

Methodology: – Assume EMFAC7C Emission Factors Apply to MPFI Vehicles without Injector Deposits

– Assume 5% of the MPFI Vehicles Have Injector Deposits that cause:

200% Increase in Tailpipe HC emissions

200% Increase in Tailpipe CO emissions

– Calculate the Increase in Emissions Due to Injector Deposits

Model Year	Vehicle Mileage ①	Annual VMT ①	Emission Factors ② (gm/mi) HC	CO
1986	13,000	15,900	.4228	4.693
1985	27,200	15,000	.6043	7.041
1984	38,700	14,000	.7911	9.298
1983	48,500	13,100	.8007	10.817
1982	56,800	12,200	1.009	12.258
1981	64,800	11,300	1.094	13.528
1980	71,200	10,300	1.970	18.227
1979	76,300	9,400	2.089	21.259
1978	80,800	8,500	2.194	22.258
1977	84,500	7,600	2.280	23.079
1976	87,800	6,700	3.939	32.138
1975	90,500	6,600	4.043	32.889

① Data obtained from EMFAC7C

② Calculated Using EMFAC7C Data

BY DAW DATE 12/9/87 SUBJECT Estimated Emissions Increase Due to MPFI Injector Deposits

CHKD. BY CB DATE 12/15/87

SHEET NO. 5 OF

JOB NO. 245-050-05-00

RADIAN CORPORATION

Estimated Emissions Increase Due to Injector Deposits =

Emissions Factor × 2.0.

Estimated Increase Due to Injector Deposits

	Increase in Emissions (gm/mi)	
Model Year	ΔHC	ΔCO
1986	.8456	9.306
1985	1.2086	14.082
1984	1.5822	18.596
1983	1.7614	21.634
1982	2.018	24.516
1981	2.188	27.056
1980	3.940	36.454
1979	4.178	42.518
1978	4.388	44.516
1977	4.560	46.158
1976	7.878	64.276
1975	8.086	65.778

BY DAW DATE 12/9/87 SUBJECT Estimated Emission Increase Due to MPFI Injector Deposits
CHKD. BY CB DATE 12/15/87
SHEET NO. 5A OF
JOB NO. 245-050-05-a

Estimated Total Annual Emissions Increase Due to Injector Deposit

Model Year	Number of Vehicles w/ Deposits*	Annual VMT (1×10^6)	ΔHC (gm) (1×10^6)	ΔCO (gm) (1×10^6)
1986	21,935	348.8	294.9	3273.8
1985	16,200	243.0	293.7	3421.9
1984	10,035	140.5	222.3	2612.7
1983	5,100	66.8	117.7	1445.2
1982	5,064	61.8	124.7	1515.1
1981	8,960	101.2	221.4	2738.1
1980	9,180	94.6	372.7	3448.5
1979	6,990	65.7	274.5	2793.4
1978	7,242	61.6	270.3	2742.2
1977	7,320	55.6	253.5	2566.4
1976	6,300	42.2	332.5	2712.4
1975	5,340	35.2	234.6	2315.4
Total	109,666	1317.0	3062.8	31585.1

Estimated HC Increase $= 3{,}062{,}800\,\text{kg} \times \frac{2.2\,\text{lb}}{\text{kg}} \times \frac{1\,\text{ton}}{2000\,\text{lb}} = 3369.1$ tons

Estimated CO Increase $= 31{,}585{,}100\,\text{kg} \times \frac{2.2\,\text{lb}}{\text{kg}} \times \frac{1\,\text{t}}{2000\,\text{lb}} = 34{,}743.6$ tons

COST-EFFECTIVENESS CALCULATION

- ESTIMATE UNLEADED GASOLINE CONSUMPTION
- CALCULATE UNLEADED GASOLINE CONSUMPTION BY DETERGENT TYPE
- CALCULATE ADDITIONAL COST IF ALL UNLEADED GASOLINE WAS REQUIRED TO USE DEPOSIT CONTROL ADDITIVES

1986 Estimated California Gasoline Consumption (from Chevron Research Company)
12.5×10^9 gallons

1986 Unleaded Gasoline Consumption (from California Energy Commission)
$.75 \times 12.5 \times 10^9$ gallons $= 9.375 \times 10^9$ gallons

BY DAW DATE 12/9/87 SUBJECT Cost-Effectiveness SHEET NO. 6 OF

CHKD. BY CB DATE 12/15/87 Calculation JOB NO. 245-050-05-00

Estimated California Unleaded Gasoline Detergent Use

No Detergents = .05 (9.375×10^9) = 468×10^6 gallons

Carb/Injector Detergents = .50 (9.375×10^9) = 4680×10^6 gallons

Detergent/Dispersants = .15 (9.375×10^9) = 1406×10^6 gallons

Deposit Control Additives = .30 (9.375×10^9) = 2813×10^6 gallons

Estimated Detergent Costs

Carburetor/Injector Detergents = $.001/gal

Detergent/Dispersants = $.001/gal

Deposit Control Additives = $.01/gal

Cost Increase to Use Deposit Control Additives

Increased Cost = (Current Detergent Cost) x (Gallons Using Detergent)

Increased Cost/No Detergent = (.01 - .00) (468×10^6) = 4,680,000

Increased Cost/Carb/Inj. Detergent = (.01 - .001) (4680×10^6) = 42,120,000

Increased Cost/Detergent-Disp. = (.01 - .001) (1406×10^6) = 12,654,000

Total Cost Increase $59,454,000

Cost-Effectiveness

HC Removal = ($59,500,000/2)/(3,400 tons) = $8,750/ton

CO Removal = ($59,500,000/2)(34,700 tons) = $875/ton

APPENDIX B

Calculations Estimating the Change in Exhaust and Evaporative Hydrocarbon Emissions Due to Changes in Fuel Volatility

BY DAW DATE 12/14/87 SUBJECT Estimated Evaporative Emissions SHEET NO. 1 OF
CHKD. BY DATE JOB NO. 245-050-05-00

RADIAN CORPORATION

Equations Obtained from Kishan et al. 1987

FUEL INJECTED VEHICLES

Malfunctioning Evap. Systems

$$\text{Diurnal HC emissions} = e^{-14.75 + .527(RVP) + .130(ITT) + .164(\Delta T)}$$

where RVP = Fuel RVP in psi
ITT = Initial Temperature of the Tank Fuel, °F
ΔT = Diurnal Temperature Rise, °F

In this case $ITT = 60°F$
$\Delta T = 24°F$

RVP(psi)	6	7	8	9	10
Diurnal HC Emissions (gm)	1.16	1.96	3.33	5.64	9.55

$$\text{Hot Soak HC emissions} = e^{-4.68 + .271(RVP) + .041(Amb.T)}$$

where RVP = Fuel RVP in psi
Amb. T = Ambient Temperature, °F

For Ambient T = 82°F

RVP(psi)	6	7	8	9	10
Hot Soak HC Emissions (gm)	1.36	1.78	2.34	3.07	4.02

For Ambient T = 95°F

RVP (psi)	6	7	8	9	10
Hot Soak HC Emissions (gm)	2.32	3.04	3.99	5.23	6.96

BY DAW DATE 12/14/87 SUBJECT Estimated Evaporative Emission SHEET NO. 2 OF

CHKD. BY DATE JOB NO. 245-020-05-00

Equations Obtained from Kishan et. al, 1987

FUEL INJECTED VEHICLES

Problem Free Evap Systems

Diurnal HC Emissions = $e^{-14.69 + .611(RVP) + .094(ITT) + .150(\Delta T)}$

where RVP = Fuel RVP in psi
ITT = Initial Temperature of the Tank Fuel °F
ΔT = Diurnal Temp. Rise, °F

In this case ITT = 60°F
ΔT = 24°F

RVP (psi)	6	7	8	9	10
Diurnal HC Emissions (gm)	.176	.325	.599	1.104	2.034

Hot Soak HC Emissions = $e^{-4.32 + 1.95(RVP) + .027(Amb.T)}$

where RVP = Fuel RVP in psi
AmbT = Ambient Temperature, °F

For Ambient T = 82°F

RVP (psi)	6	7	8	9	10
Hot Soak HC Emissions (gm)	.392	.477	.579	.704	.856

For Ambient T = 95°F

RVP (psi)	6	7	8	9	10
Hot Soak HC Emissions (gm)	.557	.677	.823	1.0	1.215

BY DAW DATE 12/14/87 SUBJECT Estimated Evaporative Emissions SHEET NO. 3 OF
CHKD. BY DATE JOB NO. 245-050-05-00

RADIAN CORPORATION

Equations Obtained from Kishan et al, 1987

CARBURETTED VEHICLES

Malfunctioning Evap Systems

Diurnal HC Emissions = $e^{-13.54+.559(RVP)+.102(ITT)+.156(\Delta T)}$

where RVP = Fuel RVP in psi
ITT = Initial Tank Temperature °F
ΔT = Ambient Temperature Rise °F

In this case ITT = 60°F
ΔT = 24°F

RVP (psi)	6	7	8	9	10
Diurnal HC Emissions (gm)	.73	1.27	2.22	3.88	6.78

Hot Soak HC Emissions = $e^{-2.42+.108(RVP)+.037(Amb.T)}$

where RVP = Fuel RVP in psi
Amb.T = Ambient Temperature °F

For Ambient T = 82°F

RVP (psi)	6	7	8	9	10
Hot Soak HC Emissions (gm)	3.53	3.94	4.38	4.89	5.44

For Ambient T = 95°F

RVP (psi)	6	7	8	9	10
Hot Soak HC Emissions (gm)	5.71	6.37	7.09	7.90	8.80

BY DAW DATE 12/14/87 SUBJECT Estimated Evaporative Emissions SHEET NO. 4 OF ___
CHKD. BY ___ DATE ___ JOB NO. 245-050-05-00

Equations Obtained from Kishan et. al. 1987

CARBURETTED VEHICLES

Problem Free Evap. Systems

Diurnal HC Emissions = $e^{-14.66 + .664(RVP) + .088(ITT) + .14}$

Where RVP = Fuel RVP in psi
ITT = Initial Tank Temperature °F
ΔT = Ambient Temperature Rise, °F

In this Case ITT = 60°F
ΔT = 24°F

RVP (psi)	6	7	8	9	10
Diurnal HC Emissions (gm)	.158	.307	.570	1.160	2.25

Hot Soak Emissions = $e^{-4.13 + .26(RVP) + .026(AmbT)}$

Where RVP = Fuel RVP in psi
AmbT = Ambient Temperature in °F

For Ambient T = 82°F

RVP (psi)	6	7	8	9	10
Hot Soak HC Emissions (gm)	.645	.837	1.085	1.408	1.826

For Ambient T = 95°F

RVP (psi)	6	7	8	9	10
Hot Soak HC Emissions (gm)	.905	1.174	1.522	1.974	2.560

BY DAW DATE 12/14/87 SUBJECT Estimated Evaporative Emissions SHEET NO. 5 OF

CHKD. BY DATE JOB NO. 245-050-05-00

Calculate Evaporative Hydrocarbon Emissions Factor

From MOBILE3

$$\text{Evap. HC gm/mi} = \frac{(\text{Hot Soak (gm)})(3.05) + \text{Diurnal (gm)}}{31.1 \text{ mi/day}}$$

Fuel-Injected Problem Free Vehicles

Evap. HC (gm/mi)

RVP	82°F Hot Soak	95°F Hot Soak
6.0	.044	.061
7.0	.058	.077
8.0	.076	.100
9.0	.104	.133

Fuel-Injected Malfunctioning Vehicles

RVP	82°F Hot Soak	95°F Hot Soak
6.0	.171	.265
7.0	.238	.361
8.0	.333	.495
9.0	.482	.694

Carburetted Problem-Free Vehicles

RVP	82°F Hot Soak	95°F Hot Soak
6.0	.069	.094
7.0	.092	.125
8.0	.125	.167
9.0	.176	.230

Carburetted Malfunctioning Vehicles

RVP	82°F Hot Soak	95°F Hot Soak
6.0	.370	.583
7.0	.427	.666
8.0	.501	.767
9.0	.603	.900

BY DAW	DATE 2/14/87	SUBJECT Evap. Emissions/Exhaust Emissions Comparison	SHEET NO. 6 OF
CHKD. BY	DATE		JOB NO. 24, 050-05-00

EMFAC 7C Emission Factors

Vehicle Model Year	Vehicle Mileage	Annual VMT	HC gm/mi	CO gm/mi
1986	13,000	15,900	.4229	4.693
1985	27,200	15,000	.6043	7.041
1984	38,700	14,000	.7911	9.298
1983	48,500	13,100	.8807	10.817
1982	56,800	12,200	1.009	12.258
1981	64,800	11,300	1.094	13.528
1980	71,200	10,300	1.970	18.227
1979	76,300	9400	2.089	21.259
1978	80,900	8,500	2.194	22.258
1977	84,500	7,600	2.230	23.079
1976	87,800	6,700	3.939	32.138
1975	90,500	6,600	4.043	32.899

Estimated California Sales Fraction*

Vehicle Model Year	Fuel-Injection Sales Fraction	Total Vehicle Sales	Fuel-Injected Vehicles
1986	65%	1,250,000	812,500
1985	60%	1,200,000	720,000
1984	48%	1,115,000	535,200
1983	36%	850,000	306,000
1982	30%	844,000	253,200
1981	24%	943,000	226,300
1980	18%	1,020,000	183,600
1979	12%	1,165,000	139,800
1978	↓	1,207,000	144,800
1977		1,220,000	146,400
1976		1,050,000	126,000
1975		890,000	106,800
		12,754,000	3,700,600

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* Obtained from Calculations performed for Section 4.0 analysis in Appendix A

BY DAW DATE 12/14/87 SUBJECT Estimated Evaporative Emission SHEET NO. 7 OF
CHKD. BY DATE JOB NO. 245-050 05-00

CALCULATE FLEET COMPOSITE EMISSION FACTOR

Assume - 25% of all carbureted vehicles have malfunctioning evaporative emission control systems (US EPA Estimate)

10% of all fuel-injected vehicles have malfunctioning evaporative emission control systems (US EPA Estimate)

Evaporative Emission Factor = (Frac. Malf.) x (Malf. E.F.) + (Frac. Prob-Free) x (Prob. Free E.F.)

32°F Hot Soak
(gm/mi)

RVP	CARB.	F.I.	Composite*
9.0	.283	.142	.242
8.0	.219	.102	.185
7.0	.176	.076	.147
6.0	.144	.061	.120

95°F Hot Soak
(gm/mi)

RVP	CARB.	F.I.	Composite*
9.0	.398	.189	.337
8.0	.317	.140	.266
7.0	.260	.105	.215
6.0	.216	.081	.177

* Composite = Sales Fraction F.I (E.F.) + Sales Fraction Carb. (E.F)
= .29 (F.I.) + .71 (Carb)

Sales Fraction Obtained From Sheet 6

BY DAW DATE 12/14/87 SUBJECT Evap Emissions/Exhaust Emissions Comparison SHEET NO. 8 OF
CHKD. BY DATE JOB NO. 245-050-05-00

Calculate Fleet Aggregate Exhaust HC Emission Factor

$$EF = \sum_{MY=1975}^{1986} \frac{VMT_{MY} \times S.F._{MY}}{\Sigma\, VMT \times S.F.} \times \text{Model Year Emission Factor}$$

Annual VMT, Sales Fraction, and HC Emission Factors were obtained from page 6.

Model Year	Annual VMT	Vehicle Sales	HC Emission Fact	MY Σ
1986	15,900	1,250,000	.4228	.0603
1985	15,000	1,200,000	.6043	.0790
1984	14,000	1,115,000	.7911	.0885
1983	13,100	850,000	.8007	.0703
1982	12,200	944,000	1.009	.0745
1981	11,300	943,000	1.094	.0836
1980	10,300	1,020,000	1.970	.1484
1979	9,400	1,165,000	2.089	.1640
1978	8,500	1,207,000	2.144	.1614
1977	7,600	1,220,000	2.280	.1516
1976	6,700	1,050,000	3.939	.1987
1975	6,600	890,000	4.043	.1703

Note: $\Sigma\, VMT \times SF = 1.394702 \times 10^{11}$ Fleet Composite = 1.450

From Chevron Research Company (1987) Exhaust HC Increase Due to RVP Decrease from 8.4 psi to 6.1 psi = 10%

$\therefore$ The Exhaust Emissions Increase = (.1)(1.45) = .145 gm/mi

Calculate Evap HC Emissions Reduction due to Reducing RVP

82°F Hot Soak	Evap. HC E.F.	RVP (psi)
	.214 gm/mi	8.5 *
	.120 gm/mi	6.0

Δ HC = .09 gm/mi

* Evap HC EF at 8.5 psi was linearly interpolated using 9.0 and 8.0 RVP data

BY DAW DATE 12/14/87 SUBJECT Evap / Exhaust Emissions Comparison SHEET NO. 9 OF

CHKD. BY DATE JOB NO. 245-050-05-00

Calculate Evap. HC Emission Reduction due to Reducing RVP

95°F Hot Soak	Evap HC E.F.	RVP (psi)
	.302 gm/mi	8.5*
	.177 gm/mi	6.0

Δ HC = .125 gm/mi

* Evap. HC E.F. at 8.5 psi was linearly interpolated using 9.0 and 8.0 RVP data

APPENDIX C

Calculations Estimating the Cost-Effectiveness of Removing Benzene from Gasoline

BY DAW DATE 12/10/87 SUBJECT Benzene Emissions SHEET NO. 1 OF

CHKD. BY CB DATE 12/15/87 JOB NO. 245-050-05-00

RADIAN CORPORATION

Estimate Cost-Effectiveness of Removing all Benzene and Benzene Pre-cursors from Gasoline

Tons / Year

	1984	2000
Gasoline Marketing	300	420
Mobile Sources	1,600	2,100

Source: Ames et al., 1986, State of California Air Resources Board, Staff Report, Proposed Benzene Control Plan

Assume Benzene Emissions Will Increase Linearly Between 1984 and 2000

∴ Estimated 1988 Benzene Emissions

Gasoline Marketing $120\left(\frac{4}{16}\right) + 300 = 330$

Mobile Sources $500\left(\frac{4}{16}\right) + 1,600) = 1725$

Also Assume Gasoline Sales Increase Linearly from 1984 through 1988 at a rate of .5 billion gallons/year

California Gasoline Market

1985 Estimate ①	1987 Estimate ①	1988 Estimate
12×10^9 gal	13×10^9 gal	13.5×10^9 gallon

Assume fuel Modification Cost \$.01/gal, \$.10/gal \$.25/gal

And that the fuel modifications remove all gasoline marketing and mobile source benzene emissions

① Provided by Chevron Research Corp

BY DAW DATE 12/10/87 SUBJECT Benzene Emission SHEET NO. 2 OF

CHKD. BY CB DATE 12/15/87 JOB NO.

Cost-Effectiveness Calculations

Assumed Fuel Modification Cost (¢/gal)	Gasoline Sales	Annual Cost for Benzene Removal
.01	13.5×10^9	\$$135 \times 10^6$
.10	13.5×10^9	\$$1350 \times 10^6$
.25	13.5×10^9	\$$3375 \times 10^6$

Assumed Fuel Modification Cost (¢/gal)	Annual Cost (\$/yr)	Benzene Reduction (tons/yr)	Cost-Effectiveness \$/ton
.01	\$$135 \times 10^6$	2055	\$65,700
.10	\$$1350 \times 10^6$	2055	\$660,000
.25	\$$3375 \times 10^6$	2055	\$1,600,000

APPENDIX D

Calculations Estimating Maximum Blended Fuel RVP Values

BY DAW	DATE 12/11/87	SUBJECT Calculate/Estimate	SHEET NO. 1 OF
CHKD. BY CB	DATE 12/15/87	Blending RVP Values	JOB NO. 245-050-05-00

Blending RVP Values for Oxinol - 50 (from Crawford et al., 1985)

Volume % Oxinol	Blending RVP (psi)
1	120
2	95
3	70
4	60
5	50
10	33

Calculate the Blending RVP Values for Ethanol and TBA

Assume - Gasoline RVP = 9.0 psi

Blended Fuel RVP = (Vol % Gasoline) (Gasoline RVP) + (Vol % Oxygenate)(Oxygenate Blending RVP)

① ∴ Blending RVP =

$$\frac{\text{Blended Fuel RVP} - (\text{Vol \% Gasoline})(\text{Gasoline RVP})}{(\text{Vol \% Oxygenate})}$$

Blended Fuel RVP Values are from: American Petroleum Institute, 1976,
Furey and King, 1980,

Volume % Ethanol	Blended Fuel RVP (psi)	(Reference)
1	9.7	(API, 1976)
2	10.0	
3	10.05	
4	10.1	
5	10.1	
10	10.0	(Furey and King)

Volume % Ethanol	Blending RVP (psi)*
1	79.0
2	59.0
3	44.0
4	36.5
5	31.0
10	19.0

* Calculated Using Equation ①

BY DAW DATE 12/11/97 SUBJECT Calculate/Estimate SHEET NO. 2 OF
CHKD. BY EB DATE 12/15/97 Blending RVP Values JOB NO. 245-050-05-00

Volume % TBA	Blended Fuel RVP (psi)	
1	9.6	reference (API, 1976)
2	9.9	
3	10.0	
4	10.0	
5	10.0	
10	9.9	Estimated
15.7	9.6	Estimated

Volume % TBA	Blending RVP (psi) *
1	69.0
2	54.0
3	42.3
4	34.0
5	29.0
10	18.0
15.7	12.8

Calculate Blending Gasoline's RVP required to ensure the blends RVP is at 9.0 psi

Maximum Legal Volumes in Unleaded Gasoline

Oxinol	9.5 %
Ethanol	10.0%
TBA	15.7%

Blend RVP = (Vol. % Gas) (Gas RVP) + (Vol % Oxygenate) (Oxygenate Blending RVP)

② $\therefore$ Gas RVP = $\dfrac{\text{Blend RVP} - (\text{Vol \% Oxygenate})(\text{Oxygenate Blending RVP})}{(\text{Vol \% Gasoline})}$

Maximum Gasoline RVP When Blended with

Gasoline RVP (psi)	Blending Agent + Volume
6.41	9.5% Oxinol
7.89	10.0% Ethanol
8.29	15.7% TBA

* Calculated Using Equation ①, page 1

Assume the tank is refilled when its 1/3 full with straight gasoline of 9.0 psi, Calculate the tank RVP after refilling

Oxinol

$$\text{Tank RVP} = (2/3) \times (\text{RVP of straight gas.}) + \overbrace{1/3(.905(\text{RVP } 6.41)) + 1/3(.095(\text{Blending RVP of Oxinol}))}^{\text{Oxinol Blend Composition}}$$

$$\text{Tank RVP} = 66.\bar{6}\%(9.0) + 30.2\%(6.41) + 3.16\%(\text{Blending RVP for Oxinol})$$

Blending RVP for Oxinol in a concentration of 3.16% is approximately 70

$$\text{Tank RVP} = .66\bar{6}(9.0) + .302(6.41) + .0316(70)$$

$$\text{Tank RVP} = 10.15 \text{ psi}$$

Calculate the RVP of the gasoline/oxinol mixture required to keep the tank at an RVP of 9.0 psi.

$$\text{Tank RVP} = 9.0 \text{ psi} = 66.6\%(9.0) + 30.2\%(\text{Blend}) + 3.16\%(70)$$

$$\text{Gasoline RVP} = \frac{9.0 - 66.\bar{6}\%(9.0) - 3.16\%(70)}{.302}$$

$$= 2.6 \text{ RVP}$$

Therefore, in order to keep the tank RVP when refueling after using a mixture of oxinol/gasoline, the oxinol/gasoline volatility would have to be limited to:

$$\text{Oxinol/Gasoline Blend RVP} = .905(2.6) + .095(33)$$

$$= 5.5 \text{ psi}$$

In addition the maximum RVP of the gasoline being blended with oxinol would have to be limited to 2.6 psi.

BY DAW DATE 12/11/87 SUBJECT Estimate Tank RVP at the next refueling with straight gasoline SHEET NO. 4 OF
CHKD. BY CB DATE 12/15/87 JOB NO. 245-050-05-00

Assume the tank is refilled when its 1/3 full with straight gasoline of 9.0 psi, Calculate the RVP after refilling

Ethanol

$$\text{Tank RVP} = (2/3) \times (\text{RVP of straight gas}) + \overbrace{1/3(.9)(7.89) + 1/3(.1)(\text{Blending RVP of Ethanol})}^{\text{Gasohol Composition}}$$

$$\text{Tank RVP} = 66.\bar{6}\%(9.0) + 30\%(7.89) + 3.\bar{3}\%(\text{Blending RVP for Ethanol})$$

Blending RVP for Ethanol in a concentration of 3.3% is approx. 44.0

$$\text{Tank RVP} = .6\bar{6}(9.0) + .3(7.89) + .03\bar{3}(44)$$

$$\text{Tank RVP} = 9.83 \text{ psi}$$

Calculate the RVP of the gasoline/ethanol mixture required to keep the tank at a RVP of 9.0 psi

$$\text{Tank RVP} = 9.0 \text{ psi} = 66.6\%(9.0) + 30\%(\text{Gas}) + 3.\bar{3}\%(44)$$

$$\text{Gasoline RVP} = \frac{9 - .6\bar{6}(9) - .03\bar{3}(44)}{.3}$$

Maximum Gasoline Blending RVP = 5.1 psi

Therefore, in order to keep the tank RVP at 9.0 psi when refueling with straight gasoline after using a mixture of ethanol/gasoline, the gasohol volatility would have to be limited to:

$$\text{Ethanol/Gasoline Blend RVP} = .9(5.1) + (.1)(19)$$
$$= 6.49 \text{ psi}$$

In addition, the maximum RVP of the gasoline being blended with ethanol would have to be limited to 5.1 psi.

BY DAW DATE 12/11/87 SUBJECT Estimate Tank RVP at the next refueling with straight gasoline SHEET NO. 5 OF

CHKD. BY CB DATE 12/15/87 JOB NO. 245-050-05-00

RADIAN
CORPORATION

TBA

$$\text{Tank RVP} = 2/3(\text{RVP of straight gasoline}) + \overbrace{1/3(.843)(8.29) + 1/3(.157)(\text{Blending RVP of TBA})}^{\text{TBA Blend Composition}}$$

$$\text{Tank RVP} = 2/3(9) + .281(8.29) + .052(\text{Blending RVP of TBA})$$

Blending RVP for TBA at a 5.2 vol % concentration is 29

$$\text{Tank RVP} = 6 + 2.33 + .052(29)$$

$$\text{Tank RVP} = 9.84 \text{ psi}$$

Calculate the RVP of the gasoline/TBA mixture required to keep the tank RVP at 9.0 psi.

$$\text{Tank RVP} = 9.0 = 6 + .281(\text{Gas RVP}) + .052(29)$$

$$\text{Gasoline RVP} = \frac{9 - 6 - .052(29)}{.281}$$

$$\text{Gasoline RVP} = 5.31 \text{ psi}$$

Therefore, in order to keep the tank RVP at 9.0 psi when refueling with straight gasoline after using a mixture of gasoline/TBA, the gasoline/TBA volatility would have to be limited to:

$$\text{Gasoline/TBA Blend RVP} = .843(5.31) + .157(12.8)$$

$$= 6.49 \text{ psi}$$

sierra research

A Study of Excess Motor Vehicle Emissions - Causes and Control

Section VII

Proposed Test Procedure and Emission Standard Revisions for Medium- and Light-Heavy-Duty Trucks

Technical Support Document

prepared for:

State of California
Air Resources Board

prepared by:

Sierra Research, Inc.
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Sacramento, California 95814
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SECTION VII

A STUDY OF EXCESS MOTOR VEHICLE EMISSIONS - CAUSES AND CONTROL

Proposed Test Procedure and Emission Standard Revisions for Medium- and Light-Heavy-Duty Vehicles

prepared for:

California Air Resources Board

December 1988

prepared by:

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1521 I Street
Sacramento, CA 95814
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PROPOSED TEST PROCEDURE
AND EMISSION STANDARD REVISIONS
FOR MEDIUM- AND LIGHT-HEAVY-DUTY VEHICLES

Table of Contents

PROPOSED TEST PROCEDURE
AND EMISSION STANDARD REVISIONS
FOR MEDIUM- AND LIGHT-HEAVY-DUTY VEHICLES

1. SUMMARY

Significant emission reductions can be achieved through changes to test procedures and emission standards for medium-duty vehicles (MDVs) and light-heavy-duty vehicles (LHDVs). The emission standards that apply to these categories do not yet require the same degree of emissions control as is required for passenger cars and light-duty trucks. In addition, the medium-duty vehicle test procedures currently allow vehicles to be tested with essentially no cargo. As a result, emission control systems do not have to be designed to control emissions under operation at higher engine loads. Since trucks are frequently used to carry cargo, the lack of required control at higher loads can cause emissions to increase dramatically.

For gasoline-powered medium-duty vehicles, 6,001-8,500 lbs. gross vehicle weight (GVW), increased use of fuel injection and improved catalyst systems would allow emission standards to be tightened. Increasing the test weight for MDVs would also require emission control systems to be redesigned so that "full time" catalytic control is provided. The emission standard changes proposed by the staff are shown in Table 1.

Table 1

Current and Proposed Standards
for Medium-Duty Vehicles

		----- grams/mile	------	
	Test Weight	NMHC	CO	NOx
Current Standards	0-3,750	0.39	9.0	0.4
	3,751-5,750	0.50	9.0	1.0
	5,751-8,500	0.60	9.0	1.5
Proposed Standards	0-3,750	----- not allowed -----		
	3,751-5,750	----- not allowed -----		
	5,751-8,500	0.39	5.0	1.1

The proposed medium-duty standards reflect a reduction in allowable emission levels ranging from 27% for NOx, to 35% for HC, and 39% for CO. However, the proposed requirement for all vehicles to be tested at their rated GVW would further increase the emission reductions achieved in actual customer service.

For gasoline-powered light-heavy-duty vehicles, 8,501-14,000 lbs. GVW, increased use of fuel injection and three-way catalysts would result in significantly reduced NOx emissions. In addition, testing of these vehicles on chassis dynamometers would more accurately reflect their operation in city traffic and facilitate in-use compliance testing. Testing the whole vehicle instead of just the engine also makes it feasible to specify an evaporative emissions standard based on the Sealed Housing for Evaporative Determinations (SHED) technique. The standards proposed by the staff are shown in Table 2.

Table 2

Current and Proposed Standards
for Light-Heavy-Duty Vehicles

	Test Weight	HC	CO	NOx	Evap
Current Standards	NA	1.1	14.4	6.0	engineering analysis
Estimate of What Current Standards Would Be in Grams/Mi		0.72	11.1	3.9	
Proposed Standards	8,501-10,000	0.50	5.5	1.3	3.0
	10,001-14,000	0.60	7.0	2.0	3.0

Note: Current exhaust emissions standards are in grams/bhp-hr (engine dyno test) with <u>total</u> HC standard.
Proposed standards are in grams/mile (chassis dyno test) with <u>non-methane</u> HC standard.

Since there is a test procedure change involved, the effect of the proposed standards on allowable emissions cannot be computed directly from the value of the current and proposed standards. However, an analysis of what the current standards would be on a "grams/mile" basis indicates that the proposed standards will reduce allowable emissions from gasoline-powered light-heavy-duty vehicles by about 30% for HC, 50% for CO and about 70% for NOx. No significant change in CO emissions is expected.

For Diesel-powered vehicles, no changes to the optional 100,000 mile certification standards for medium-duty vehicle NOx emissions are being proposed at this time. More stringent hydrocarbon standards, proportional to the proposed 50,000 mile standards, are proposed for Diesels. Compliance with the same carbon monoxide standards as recommended for gasoline vehicles is also proposed.

The staff is proposing that Diesel-powered medium duty vehicles also be tested at GVW instead of curb weight plus 300 pounds. Because more vehicles will be tested at the upper end of the test weight categories, a 25% increase in the particulate emissions standard for the heaviest vehicles is also proposed. This adjustment makes the stringency of the standard comparable to the standard that currently applies to the middle test weight range of the medium-duty class. Under the staff's proposal, all medium-duty vehicles will be tested in the 6,001-8,500 pound test weight range and they would be required to meet a particulate standard of 0.10 g/mi. Compliance with the proposed particulate standards will likely require traps on all Diesel-powered vehicles.

The current and proposed standards for the 100,000 mile, Diesel option are shown in Table 3.

Table 3

Current and Proposed
Optional 100,000 Mile Standards
for Diesel-Powered Medium-Duty Vehicles

		grams/mile			
	Test Weight	HC	CO	NOx	PM
Current Standards	0-3,750	0.46	10.6	1.0	0.08*
	3,751-5,750	0.50*	9.0*	1.5	0.08*
	5,751-8,500	0.60*	9.0*	2.0	0.08*
Proposed Standards	0-3,750	not allowed			
	3,751-5,750	not allowed			
	5,751-8,500	0.46	5.0	2.0	0.10*

*Standard applies for 50,000 miles only.

For Diesel-powered light-heavy-duty vehicles, particulate standards of equal stringency to those which apply to medium-duty vehicles are proposed. As shown in Table 4, for vehicles up to 10,000 pounds test weight, the particulate standard would be 0.12 g/mi. For vehicles 10,001-14,000 pounds, the standard would be 0.15 g/mi. These standards will probably require the use of particulate traps on all vehicles.

As with medium-duty vehicles, optional 100,000 mile NOx standards are provided for Diesels. By setting the standards at twice the level of the 50,000 mile standards, the 100,000 mile NOx standards for light-heavy-duty Diesels reflect approximately the same percentage increase in emissions as has historically been provided for medium-duty vehicles certified under the 100,000 mile option. These standards are achievable through the use of EGR and/or pre-chamber engines.

Table 4

Proposed Optional 100,000 Mile Standards
for Diesel-Powered Light-Heavy-Duty Vehicles

		grams/mile			
	Test Weight	HC	CO	NOx	PM
Light-Heavy-Duty Vehicles	8,501-10,000	0.60	5.5	2.6	0.12
	10,001-14,000	0.70	7.0	4.0	0.15

To provide manufacturers with adequate lead time to comply with the proposed standards, the staff is recommending a 1992 model year implementation date for both the medium-duty and light-heavy-duty proposed standards. However, the staff is also proposing a 1995 implementation date for a requirement that all medium-duty and light-heavy-duty vehicles be certified to meet standards that are numerically higher by 25% for a period of 100,000 miles. This requirement would be consistent with the current approach used by EPA under which compliance is required for the expected "full-life" of the these same vehicles. By supplementing the basic 50,000 mile standards with a requirement to meet less stringent standards for 100,000 miles, manufacturers will have the proper incentive for designing emission control systems to last for the expected service life of the vehicle.

Regarding the proposed light-heavy-duty standards, opposition from vehicle manufacturers is expected because the chassis dynamometer testing requirement will increase the possibility that in-use compliance problems will be detected. In addition,. certification testing may be more costly.

Both the medium-duty and light-heavy-duty standards proposed for gasoline-powered vehicles may be opposed because compliance will require 3-way catalysts to be kept in operation under all engine loads. This may require control systems to be designed to protect the catalyst from excessive temperature while achieving the improved cold start performance needed to meet the more stringent HC standards. These simultaneously imposed requirements could require some vehicles to be equipped with by-passable catalysts for cold start and warm up operation. Such systems could increase vehicle costs by about $100-120. Adding 3-way catalyst systems to light-heavy-duty engines could add about another $200 to the cost of vehicles using those engines. However, the staff's analysis indicates that the additional emission control provided would be so large that the cost of meeting the proposed standards would represent a good value, relative to other emission control strategies.

The optional 100,000 mile standards for Diesel-powered medium-duty vehicles are not expected to generate opposition because they do not represent a significant increase in stringency over the current set of standards. However, compliance with the particulate standard may be difficult. Due to the limited demand for Diesel-powered medium-duty vehicles in recent years, manufacturers have devoted limited effort to the development of trap technology for these vehicles.

Opposition is expected to the staff's proposed optional standards for Diesel-powered light-heavy-duty vehicles. These standards would accelerate the requirement for Diesel particulate traps by imposing trap-forcing standards for the 1992 model year. Under the current standards, traps might not be required until the 0.1 g/bhp-hr particulate standard is enforced in 1994.

The proposed optional standards may also be opposed on the grounds that they increase the stringency of the NOx emission standards. The staff would agree that the optional NOx standards may be difficult for Diesel-powered vehicles to meet without heavy reliance on exhaust gas recirculation. This, in turn, will increase the difficulty in meeting the particulate standard.

The combination of NOx and particulate standards proposed for Diesel vehicles could result in a suspension of Diesel sales in the light-heavy-duty category. However, the staff believes it is important to require that emissions be controlled to the same levels that can be met with gasoline-powered vehicles to prevent emissions from this category from increasing. A relaxation of the proposed standards to ensure continued Diesel sales could lead to increased particulate and NOx emissions because Diesel engine sales in the light-heavy-duty vehicle category have been increasing.

By the year 2000, adoption of the standards proposed by the staff is estimated to reduce emissions from gasoline-fueled medium- and light-heavy-duty vehicles by 6% for HC, 11% for CO, and 20% for NOx. This represents reductions in the total emissions from on-road motor vehicles by about 1% for HC, 2% for CO, and 3% for NOx. The cost/effectiveness of the standards has been estimated to be well under $2.00 per pound of HC and NOx emissions control, a much lower cost than for other measures that have been adopted to control emissions in California.

###

2. INTRODUCTION

Over the history of the motor vehicle emissions control program, passenger cars and light-duty trucks have received the greatest amount of attention. Because of their great numbers, cars and light trucks have been major contributors to the state's air pollution problems. However, as controls on cars and light trucks become more effective, other vehicle categories become a more significant fraction of the remaining air pollution problem.

The Significance of MDVs and LHDVs

Figures 1, 2, 3, and 4 show the relative contribution of hydrocarbon, carbon monoxide, oxides of nitrogen, and particulate emissions from each category of on-road motor vehicles. Based on ARB's "official" emissions inventory, the figures show emissions from medium-duty vehicles (6,001-8,500 lbs. GVW), and light-heavy-duty vehicles (8,501-14,000 lbs. GVW) account for 8.5% of the HC emissions, 12.6% of the CO emissions, and 7.9% of the NOx emissions from on-road vehicles.

Figure 1

Hydrocarbon Emissions Distribution for On-Road Vehicles (1987 Estimates)

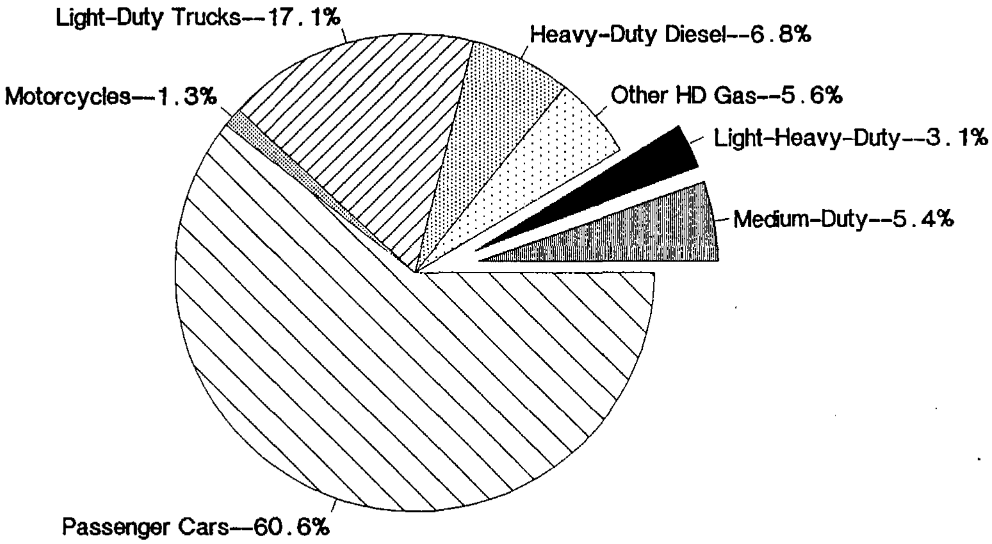


Figure 2

Carbon Monoxide Emissions Distribution for On-Road Vehicles (1987 Estimates)

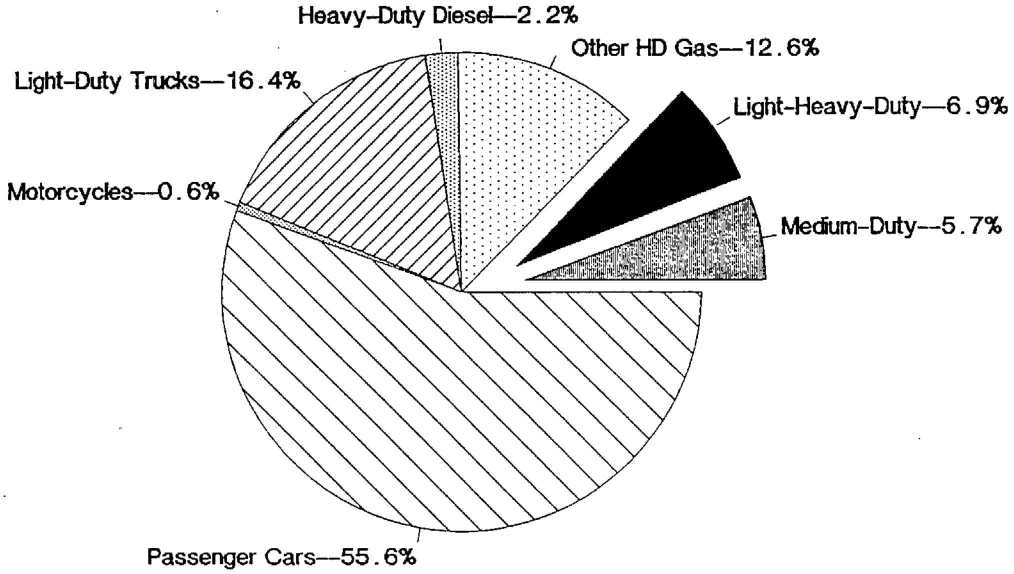


Figure 3

Oxides of Nitrogen Emissions Distribution for On-Road Vehicles (1987 Estimates)

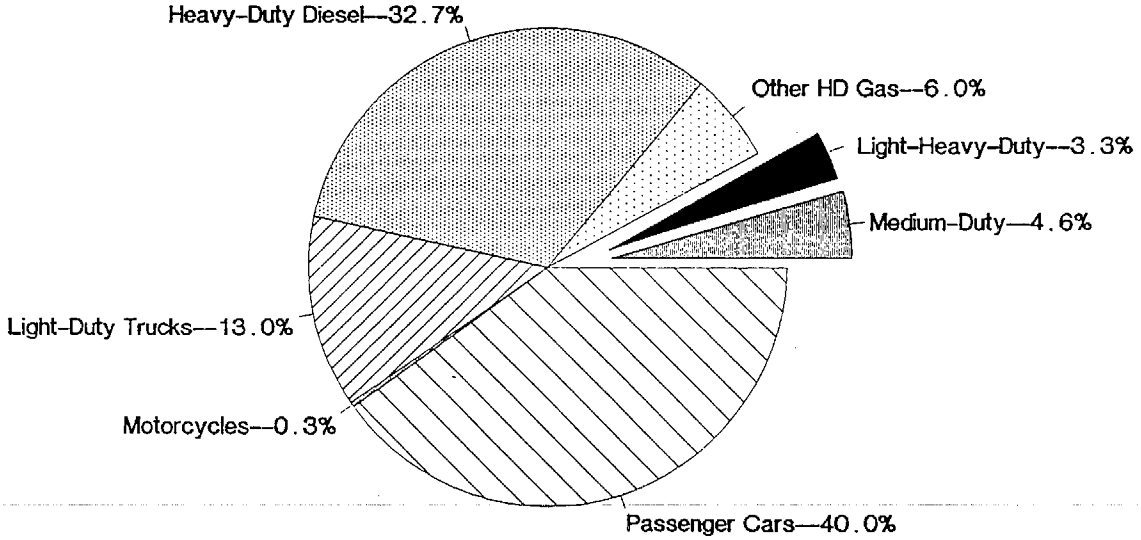
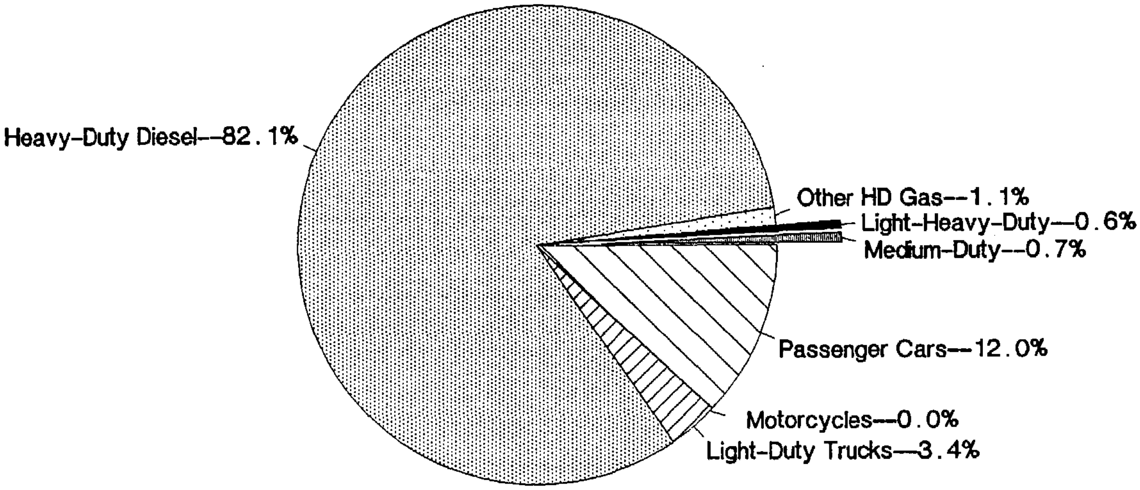


Figure 4

Exhaust Particulate Emissions Distribution for On-Road Vehicles (1987 Estimates)



Because of the currently low sales of Diesel-powered vehicles in these categories, medium- and light-heavy-duty vehicles account for only 1.3% of the particulate emissions.

Test Procedure Concerns

As the above figures illustrate, MDVs and LHDVs represent a significant fraction of the emissions from on-road vehicles. However, a recent analysis indicates that the actual emissions from these vehicle categories are greater. As described in detail in a later section of this report, when MDVs and LHDVs carry cargo, emissions can increase substantially.

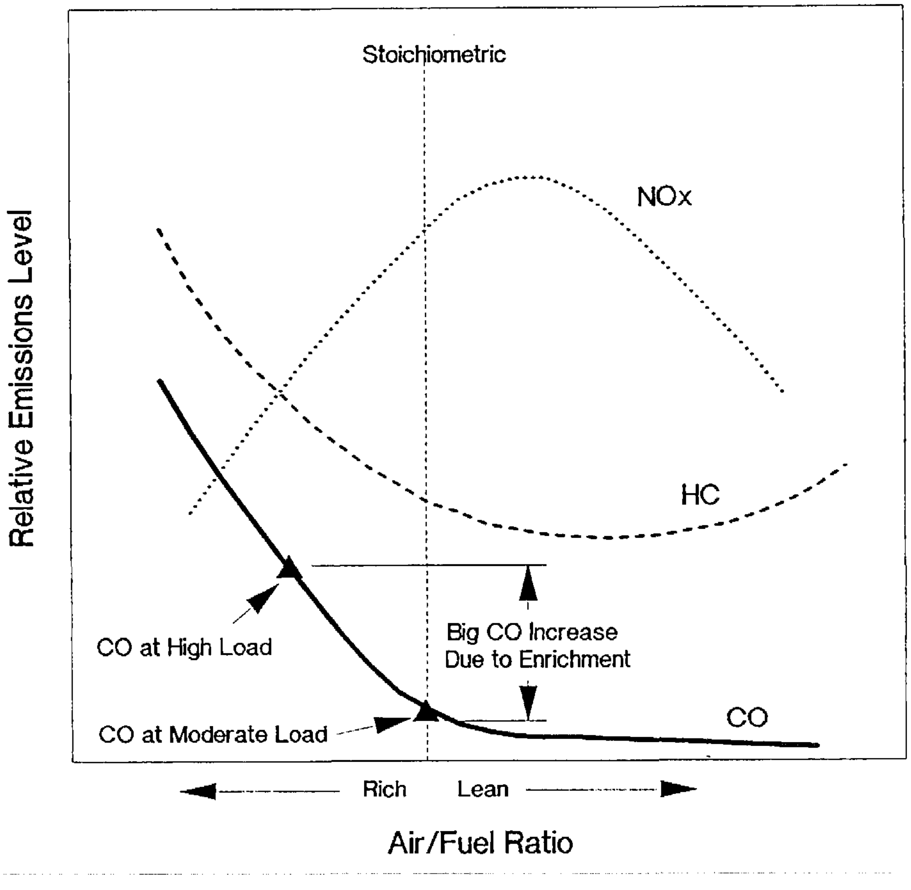
Under current regulations, MDVs are tested on chassis dynamometers with the dynamometer adjusted to simulate the unladen weight ("curb weight") of the vehicle plus 300 pounds to simulate a driver and one passenger or a small amount of cargo. The use of curb weight plus 300 pounds is a carryover from the light-duty vehicle test procedure. While curb weight plus 300 pounds may be reasonable for light-duty vehicles, MDVs and LHDVs frequently carry a significant amount of cargo.

It is well established that emissions are increased by higher vehicle loading, however, the emissions increase associated with higher loading of MDVs and LHDVs appears to be much higher than previously thought. When MDVs and LHDVs carry significant amounts of cargo, engine power demand to keep up with city traffic approaches the maximum available power. Under such high load, the air-fuel ratio is enriched for a slight power benefit and to reduce the potential for valve burning. Under rich conditions, a 3-way catalyst does not control unburned hydrocarbons or carbon monoxide. Although the warmed up catalyst is capable of reducing HC and CO by about 90%, the conversion efficiency drops to near zero as the engine approaches full power output. As a result, HC and CO are ten times higher than they would be if the catalyst were still working. In addition, the enriched operation causes HC and CO emitted by the engine to increase even more. The mechanisms by which the emissions increase occurs is illustrated in Figures 5 and 6.

Figure 5 shows the relationship between engine air/fuel ratio and exhaust emissions. As the figure illustrates, emissions of HC and CO increase substantially at air/fuel ratios richer than the chemically correct stoichiometric ratio (about 14.7:1 for typical gasolines). By enriching the mixture to about 12:1, the horsepower of the engine

Figure 5

Exhaust Emissions vs. Air/Fuel Ratio

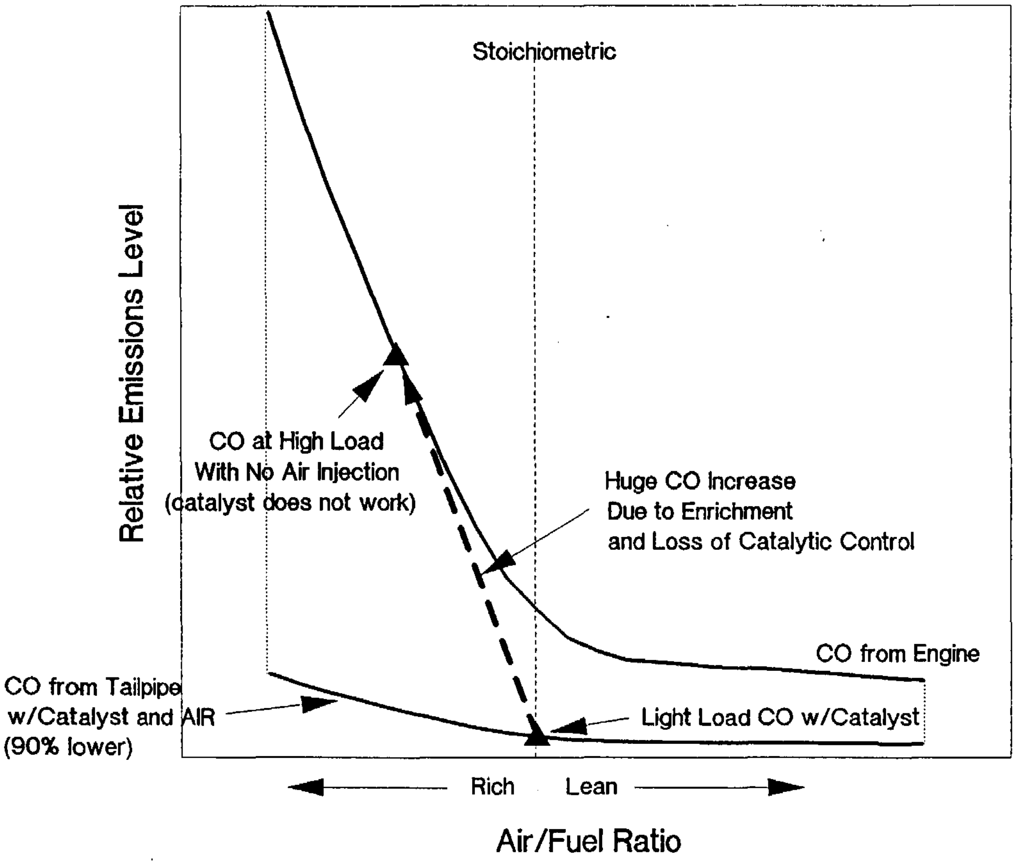


can be increased by about 3-5%.[1,2]* Although the fuel economy of the engine suffers, enrichment at full power is commonly used to increase peak horsepower because gasoline engines normally only operate at or near full-load for limited periods of time and the fuel economy loss during that operation is not considered important. In addition, mixture enrichment at full power reduces the potential for exhaust valve burning by depleting the oxygen in the exhaust gas. In certain applications (primarily aircraft engines), mixture enrichment is carried to extremes in order to actually cool the engine with evaporating fuel. The fuel efficiency penalty is so severe for fuel-cooling that its use is generally restricted to the take-off mode of aircraft engine operation.

Figure 6 illustrates the enrichment effect when the engine is equipped with a catalytic converter. (The scale has been expanded to show the effect of catalytic control more clearly and only CO emissions are shown.) When excess oxygen is present, a warmed up catalyst can reduce CO emissions by approximately 90%. To provide the excess air

Figure 6

Exhaust Emissions vs. Air/Fuel Ratio With and Without Catalytic CO Control



* Superscripts denote references listed at end of text.

needed to catalytically oxidize CO, air injection is required when the air/fuel ratio is adjusted richer than stoichiometric. However, it is standard practice for vehicle manufacturers to design their emission control systems so that no air injection occurs at high engine power levels. Even when the engine is equipped with an air pump, the air flow is diverted during high load conditions so that catalytic oxidation of the carbon monoxide and unburned HC will <u>not</u> occur.

By not providing air injection under fuel-rich, high power conditions, the catalyst is "protected" from the higher temperatures that would occur during the catalytic oxidation of such high levels of carbon monoxide emissions. As a result, catalyst durability is improved and it becomes easier for manufacturers to meet the emission standards for the required 50,000 mile distance. This "catalyst protection" technique is possible because the official emission test procedure does not measure vehicle emissions under very high load conditions. Unfortunately, high power levels frequently occur in actual customer service and the emissions of the vehicles can increase by more than a factor of ten under such conditions.

As described in the body of this report, the latest analysis indicates that MDVs and LHDVs could account for <u>over 20%</u> of the carbon monoxide emissions from all on-road vehicles due to the loss in emissions control that is currently permitted under high load conditions.

Development of the Staff Proposal

In order to achieve further control of vehicular emissions and to address the concerns about the adequacy of the current test procedures, the following tasks have been completed:

1. an analysis has been conducted to determine the relative stringency of the current standards for medium- and light-heavy-duty vehicles and the standards which have been adopted for passenger cars and light trucks;

2. the operational characteristics of medium- and light-heavy-duty vehicles have been investigated to determine the extent to which operation at high power levels may be occurring in customer service;

3. computer simulations of vehicle emissions under varying load conditions have been conducted in order to quantify the impact of high load operation on vehicle emission levels;

4. the technological feasibility, cost, and lead time for more stringent medium- and light-heavy-duty vehicle emission standards has been evaluated; and

5. the costs and feasibility of chassis dynamometer testing for light-heavy-duty vehicles has been investigated.

This report describes the results of the tasks listed above and makes recommendations for more effective emission standards and test procedures.

Organization of the Report

Following the summary and this introduction, Section 3 describes the physical and operational characteristics of medium- and light-heavy-duty vehicles. Information is provided regarding the cargo-carrying patterns for these vehicles obtained from the California Truck Inventory and Use Survey (TIUS).

Section 4 contains an analysis of how the emission standards for medium- and light-heavy-duty vehicles compare to the emission standards for passenger cars and light trucks. The relative stringency of the current standards is evaluated based on the work required for different vehicles to keep up with city traffic.

Section 5 contains an analysis of how vehicle cargo loading affects exhaust emission levels. Load increases are related to fuel consumption (and therefore exhaust volume) through the use of a predictive model developed by EPA. This section also describes a more elaborate computer model, incorporating engine maps of catalyst-equipped vehicles, that was also used to estimate the effect of load increases on exhaust emissions.

Section 6 contains a comparison of the engine dynamometer test procedure currently used to test light-heavy-duty engines and the chassis dynamometer procedure currently used to test medium-duty vehicles. Physical changes to test facilities needed to test all medium- and light-heavy-duty vehicles on chassis dynamometers at their gross vehicle weight (GVW) are described.

Section 7 contains an assessment of the emission control system changes needed to further reduce emissions from medium- and light-heavy-duty vehicles. Concerns manufacturers have raised regarding "full time" catalytic control of exhaust emissions during high power conditions are addressed. System configurations to achieve additional control without catalyst damage are described.

Section 8 contains a discussion of the cost, cost/effectiveness, and lead time associated with the production of emission control systems designed to achieve further control.

Section 9 contains the overall conclusions and recommendations being made by the staff after its consideration of more stringent medium- and light-heavy-duty standards and test procedures. Finally, Section 10 contains a list of references cited in the body of the report.

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