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Methanol Fuel Additive Demonstration

 CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY



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METHANOL FUEL ADDITIVE DEMONSTRATION

**Final Report
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ABSTRACT

One potential strategy for achieving significant reductions in motor vehicle emissions is the replacement of conventional fuels with methanol; however, safety and toxicity problems associated with M100 have prevented its wider acceptance and use as a clean motor fuel. Some of these problems include:

- Poor vehicle cold-starting
- Low fuel lubricity
- Flammability of saturated vapors in storage and fuel tanks
- Low flame luminosity
- Human toxicity by inhalation, absorption through the skin, or ingestion.

Additives to the fuel have been proposed as one means of alleviating these problems by creating desirable properties to nullify or offset the negative effects of the fuel. However, these additives, while improving the properties of the fuel, should not reduce the benefits of neat methanol as a clean motor fuel.

This final report discusses the results of an extensive literature search for additives to address the items listed above; a laboratory test program emphasizing flame luminosity, fuel lubricity, and flammability; a comparison of the generated laboratory data to real world situations; and hydrocarbon speciation of exhaust emissions from a vehicle operating on potential additive packages. The literature search identified potential additive candidates, with suggested concentrations, to improve significantly the safety and reduce the toxicity of the fuel without altering its potential for emissions reduction. These candidate additives were also screened for possible formation of known or suspected toxic combustion products.

In the laboratory test program, the candidates were screened for their effectiveness in improving the fuel properties. The flame luminosity was measured with a system specially designed to monitor the light produced by the flame in terms of foot-candles. Concentrations were originally held below 5 percent by volume, but later in the program results indicated that higher concentrations and multiple component additives were required to achieve a luminous flame throughout the burn. Lubricity was measured with a Ball-on-Cylinder Lubricity Evaluator (BOCLE). For the flammability limits, a device was designed to determine the presence of flammable vapors above the liquid at different concentrations.

This work led to the identification of potential additive packages for M100, with each package being evaluated for synergistic effects using same test procedures. Toluene and a proprietary alcohol-soluble solid material yielded the greatest potential for luminosity improvement in the initial effort (Task 1 - additive package concentrations limited to 5 percent), while fatty acids and organic amine salts were effective at improving the lubricity of the fuel. Butane and butene lowered the flammability limit below 18°C. In the expanded effort (Task 1 Expansion - no limit on the additive package except to cost less than 125 percent of the gasoline portion of M85), potential additives were investigated at higher concentrations. Two blends (4 percent toluene plus 2 percent indan, and 5 percent indan plus 5 percent cyclopentene) were selected for further study and were burned under outdoor conditions and compared to neat methanol, neat ethanol, and M85 under the same conditions. Each burn was performed on five different surfaces: concrete, asphalt, sheet metal, grass, and soil. Speciated hydrocarbon exhaust

emissions from a Volkswagen Jetta fueled with two additive blends were compared to speciated emissions from the same vehicle operating on M100, M85, and an "industry average" gasoline. In this vehicle, the additive blends did not significantly decrease the ozone-forming potential when compared to M85. The cost of these additive packages would increase the price of the fuel by more than 15 percent of the current M85 fuel cost at the pump in California. Lower feedstock costs or cheaper alternative additive components would reduce these costs.

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DISCLAIMER

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

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- Result in no more than 50 percent of the exhaust reactive hydrocarbons compared to M85 (15 percent gasoline and 85 percent methanol) without the additional additives.
- Not exceed 5 percent by volume in neat methanol fuel.

This survey resulted in a diverse list of potential compounds that have either been used or were suggested as additive candidates for fuel methanol.

Before testing, each potential additive was screened in several different ways. First, the compounds were screened for specific properties which would meet the list of criteria above. Each compound was then screened through the general literature for toxic characteristics, compared to the CARB list of known and suspected toxic air contaminants, and intuitively examined for the possibility of forming toxic compounds as combustion products. In addition, compounds containing halogens, phosphorus, and metals were avoided due to possible formation of toxic substances in the combustion chamber and due to the potentially harmful effect on automotive catalysts. Many classes of compounds were avoided using these criteria. For the laboratory screening, each potential compound was examined to determine its effect on flame luminosity, fuel lubricity, and flammability limits utilizing procedures established for the measurement of these parameters. The most promising compounds were then combined to produce additive packages which were found to improve the properties of fuel methanol.

In the initial effort, the total concentration for all compounds in the additive packages was held under 5 volume percent except for ethanol, which was added at a concentration between 15 and 20 volume percent. With these combinations, the flammability and fuel lubricity were improved to a level equivalent to M85. Flame luminosity was improved when compared to M100, but higher concentrations were required to reach the luminosity of ethanol. Cold-starting, warm-up performance, and upper cylinder lubricity, as well as reductions in exhaust reactive hydrocarbons and other emissions, were not verified experimentally in the first part of the program.

A peer review meeting was held to present the data from the initial effort to individuals directly involved with methanol fuel. As a result, the original work was expanded to include a continuation of the laboratory evaluation to improve the test procedures, to investigate additional additives at higher concentrations, to compare outdoor burns to laboratory data, and to conduct hydrocarbon speciation of emissions from two potential additive blends. The 5 volume percent limitation was lifted and replaced by a limit on the total cost of the additive package (not to exceed 125 percent of the gasoline component cost in M85).

The flame luminosity was measured with a system specially designed to monitor the amount of light produced by the flame in foot-candles. Ethanol was chosen as the luminosity standard for these experiments. Each compound was compared to neat ethanol as a standard and M85 as a target. A minimum threshold visibility for the human eye was determined as a result of the preliminary testing and the visual response of the human eye. This threshold was the result of a "subjective consensus" of technical observers at Southwest Research Institute using different lighting situations. Under darkroom conditions, 0.1 foot-candles was easily seen; however, under twilight conditions, a luminosity of 0.2 foot-candles could be detected by many of the observers. Under daylight conditions, an M85 flame at 0.1 - 0.2 foot-candles was difficult to detect during the middle portion of the burn. The subjective nature of estimating a minimum threshold visibility and the variables involved in determining the proper lighting conditions made an absolute lower limit difficult to establish. For the purposes of this program, the minimum threshold visibility as measured by the test apparatus was 0.2 foot candles.

Flame luminosity can be improved for fuel methanol through the addition of compounds which themselves burn with visible flames. The luminosity depends on several factors:

- Type of fire (pool, spill, or container)
- Path length and size of flame
- Surface where burning takes place (porous or non-porous)
- Lighting conditions (dark, twilight, or bright sunshine)
- Background of the flame in relation to the observer
- Concentration, volatility, and luminosity of additives
- Flame color.

Each of these factors affects the visibility of a fire in relation to the observer.

The type of fire has a large effect on the visibility of the flame. Complex liquids burn by the destructive distillation of the mixture. The more volatile components are distilled and become consumed during the first portion of the flame, followed by the less volatile (relative to methanol), higher molecular weight compounds. The container also has an important effect on the luminosity of the flame; glass and metal containers of the same fluid components give different luminosities. Synergistic and material interactions take place between the container and the burning liquid that enhance or diminish the luminosity of the flame. The fire location (a spill on the pavement or in a container) will also affect an observer's ability to see the flame. Flame visibility and recognition distances on porous surfaces are much lower and shorter than on non-porous ones.

The path length and flame size also have an important effect on the flame visibility, because the intensity of the light is dependent on the width and height of the flame. For this reason, a larger fire is much more visible than a smaller fire. Although the path length cannot be readily changed in a fire, the luminosity of the flame can be affected by the components of the burning material.

The lighting conditions and background play a large role in the visibility of a flame. Human eyes are capable of detecting radiation only in a relatively narrow band of the electromagnetic spectrum. Within this narrow band, the eye is more sensitive to light from the middle wavelengths of the visible light spectrum (yellow, green, and orange). Blue and red light are less easily detected by the human eye, so the "apparent" luminosity is lower even though the energy density may be the same. A methanol flame is difficult to see because the flame is blue, and the energy density from combustion is lower than other more luminous materials. This situation produces two negative aspects for methanol flame luminosity: a light background makes the flame difficult to see since there is little contrast between the flame and the background, and the flame color is in a region of the visible spectrum which has low visibility for the eye. With sunlight and twilight conditions, the flame is difficult to see because the ambient lighting conditions approach those of the flame. Conversely, during darkness, the blue flame is easily seen because there is no scattered light to interfere with the detection of the flame. A low energy density flame combined with blue light, which is less readily detected by the eye contribute to low flame visibility for methanol.

The concentration, volatility, and luminosity of additives as well as the flame temperature and formation of soot particles affect the visibility of a flame. Many additives in methanol increase the flame

visibility by forming incandescent soot particles in the flame. These soot particles glow in the flame and produce "gray-body radiation" or colored light (yellow and orange) in the visible region of the spectrum. Methanol typically burns with a very cool flame temperature and produces very few soot particles. This cool flame does not excite any soot particles which may be produced, so no "gray-body radiation" results, and a methanol flame has a low flame luminosity. Compounds dissolved in methanol burn with characteristic luminosity "signatures" (foot-candles versus time) which vary immensely, depending upon the volatility and the soot-forming tendency of the burning components. With complex mixtures such as gasoline blended with methanol, the "signature" was a "U-shaped" trace, likely caused by the destructive distillation of the gasoline components. For example, M85 produced a luminosity equivalent to about 70 to 90 percent of the luminosity of ethanol through the initial and final portions of the burn. During the middle portion of the burn, M85 yielded only a 0.15 foot-candle increase over M100. The luminosity "signature" changed depending on the various components, their tendency to form gray-body radiation, and their volatility. Therefore, the concentration and type of luminosity additives were very important when trying to improve the flame luminosity throughout the entire burn.

Several classes of compounds were identified as potential luminosity improvers. This compounds included:

- Aromatics
- Alcohol-soluble hydrocarbons
- Oxygen-containing compounds (alcohols, ethers, esters, aldehydes, ketones, and acids)
- Organometallics
- Organic alcohol-soluble dyes
- Boron compounds
- Miscellaneous compounds containing nitrogen and sulfur functional groups.

The best combination of compounds for improving flame luminosity were those with unsaturation, cyclization, and aromaticity. Chemicals with unsaturation, cyclization, and aromaticity result in molecules with lower hydrogen/carbon number ratios. These lower hydrogen/carbon number ratios tend to improve the flame luminosity more than compounds with higher hydrogen/carbon number ratios. Carbon chain branching also increases the luminosity; but in combination with methanol, higher concentrations were required. Unsaturated, branched-chain, and cyclic hydrocarbons typically increased the flame luminosity in the initial part of the burn more than straight chain hydrocarbons; however, many of these compounds required concentrations above 10 volume percent to raise the luminosity to the level of the minimum threshold visibility (0.2 foot-candles). Aromatics and certain substituted cyclic hydrocarbons improved the flame luminosity in the latter part of the burn.

Toluene enhanced the luminosity in the initial part of the burn because it forms a methanol azeotrope that has a high volatility and good soot-forming properties. Cyclopentene is also effective in improving the luminosity in the early stages of the burn. Indan added luminosity to the final stages of the burn. When these compounds are combined in methanol, they sustained good flame luminosity throughout the burn above the minimum threshold visibility. Other compounds such as the coded sample MO, methylcyclopentane, mesitylene, trimethyl borate, and benzaldehyde also improve the flame luminosity at relatively low concentrations, but each had problems associated with its use as a viable candidate additive.

For lubricity, the additives identified for methanol addressed both lubrication and corrosion. The mechanism operating with methanol fuel involves the washing away of the lubricant and subsequent corrosion caused by the formation of acids and other oxidizing agents from the fuel. Many different proprietary compounds (mostly fatty acids and organic amine salts) were tested with a device to measure the sliding wear from metal-to-metal contact under a constant load (Ball-on-Cylinder Lubricity Evaluator - BOCLE). Several commercial, proprietary, lubricity/corrosion additives were identified from these experiments, and most were equally effective in improving the lubricity. These additives were equivalent to M85 in the reduction of wear when compared to the wear from M100.

Flammability limits were determined with a device to measure the flammability in the vapor space. A flammability limit below -18°C (0°F) with sufficiently high volatility for good cold-starting was the desired goal. The goal was achieved with either butane or butene at a concentration between 2 and 3 volume percent. Addition of toluene increased the rich flammability limit of the mixture, and 15 volume percent of ethanol decreased the rich flammability limit. When the total additive concentration was held below 5 volume percent, the rich flammability limit was about -20°C . With complex additive package combinations of 20 volume percent ethanol and 5 volume percent of other additives for improving properties, the rich flammability limit was about -25°C . These rich flammability limits were well below normal ambient temperatures and below the typical daily temperatures except in mountainous areas or on extremely cold days. Supplementary tests showed that 2.0 - 2.5 volume percent butane or butene will raise the volatility (Reid Vapor Pressure) to 8.5 psi. Therefore, the flammability limits of saturated fuel vapors in underground and vehicle storage tanks can be lowered below ambient temperatures with sufficient volatility to provide good cold-starting and warm-up performance to -18°C (0°F) by interchanging either butane or butene. Weathering effects were not addressed in this program.

This program led to the identification of several different compounds for improving the properties of fuel methanol based on laboratory testing. These compounds, when combined into additive packages, served to meet many of the criteria listed above. Table 1 lists the additive package nominees and their suggested concentration ranges based on the initial criteria. Additional work revealed two additive combinations equivalent to M85 in duration of a luminous flame above the threshold visibility. These two blends were 5 percent indan plus 5 percent cyclopentene and 4 percent toluene plus 2 percent indan.

Outdoor burns of several combinations were performed to compare the laboratory results with real world situations. These experiments were conducted with larger quantities of fuel (about one liter) on a variety of surfaces to compare the interactions of burning liquids. Five different liquids:

- 100% methanol
- 100% ethanol
- M85
- 4% toluene + 2% indan in methanol
- 5% indan + 5% cyclopentene in methanol

were ignited on each of five surfaces:

TABLE 1. ADDITIVE PACKAGE NOMINEES AND SUGGESTED CONCENTRATION RANGES

Property	Additive	Concentration
Flammability	Butane	2.2-2.5 Vol%
Flammability	Butene	2.2-2.5 Vol%
Luminosity	Toluene	4 Vol%
Luminosity	Cyclopentene	5 Vol%
Luminosity	Indan	2-5 Vol%
Luminosity	MO (coded sample)	0.75-1.0 Wt%
Lubricity*	DCI-4A, OS85798, OS86453, OS86454, OS86455, OS86456, OS86457, OS86458, OS86460, VX3181, VX3182, Metacor 704, Unicor J, IPC 44210	0.12 Wt%
Taste	Bitrex	0.0012 Wt%
Color	Various Alcohol-soluble Dyes	0.00013-0.013 Wt%
Odor	Various	0.007 Wt%
*These corrosion-inhibitor/lubricity improvement additives are considered to be interchangeable as regards their compatibility with other additive package constituents at the nominated low level of concentration.		

- Concrete
- Asphalt
- Sheet metal
- Grass
- Soil.

A panel of eight to nine observers watched the burns, rated the visibility, and answered questions about the lighting conditions, flame color, flame luminosity, flame height, background, and other distinguishing features. All burns were performed during bright sunlight or partly cloudy conditions. In general, the additive blends performed as well as or better than ethanol and M85 on most surfaces, and the additive blends were significantly better than M100 in all cases. These results, while limited to a small number of observers, indicated that the flame visibility of methanol could be improved through the use of selected additives under real world conditions.

Emission testing was performed on two different vehicles with several different additive blends. The measured emissions included a complete hydrocarbon speciation (C₁ - C₃ hydrocarbons plus benzene and toluene, C₄ hydrocarbons including 1,3-butadiene, and C₅ - C₁₀ hydrocarbons), aldehydes, and methanol. All exhaust emissions were measured on a bag by bag basis and compared for their ozone formation potential based on the most current Carter Maximum Incremental Reactivities (MIRS).

A 1986 Toyota Camry (dedicated M85 vehicle) was tested with a Southwest Research Institute (SwRI) methanol blend and with an actual commercial blend of M85 fuel obtained from California. The SwRI methanol blend was made from M100 blended to contain additives for flame luminosity, flammability limit, fuel lubricity, taste deterrent, and odorant. The additives and their respective concentrations were:

- 6 volume percent toluene
- 2.5 volume percent butane
- 0.12 weight percent DCI-4A (Dupont)
- 0.0001 weight percent Bitrex (denatonium benzoate)
- 0.007 weight percent odorant.

No dye was added for these experiments. In a separate set of tests, a 1989 dual-fuel Volkswagen Jetta was tested with five fuels:

- M100
- 4% toluene + 2% indan blended with M100
- 5% indan blended with M100 + 5% cyclopentene
- Auto/Oil industry average gasoline (RF-A)
- M85 blended from RF-A.

This vehicle was unique because a switch allowed the vehicle to operate in either the gasoline or M85 mode. No on-board fuel sensor was employed on this vehicle.

Both vehicles were tested with different additive blends, but the results from these tests were similar in many ways even though the engines and emission control systems were different on each vehicle. In general, the hydrocarbons in the exhaust were analogous to the hydrocarbons in the fuel. Cold-start emissions contributed the majority of the exhaust emissions from both vehicles, and methanol was the major hydrocarbon constituent in the exhaust. Ozone formation potential was lower for the additive blends when compared to M85, but the criterion for no more than 50 percent of the exhaust reactive hydrocarbons was not met. It should also be noted that in these vehicles M100 did not meet this criterion. The toxic emissions (sum of benzene, 1,3-butadiene, three isomers of xylene, formaldehyde, acrolein, and acetaldehyde) from the Jetta with the additive blends were variable compared to M100; the additive with 4 percent toluene plus 2 percent indan had more, and the additive with 5 percent indan plus 5 percent cyclopentene had less toxic emissions than M100. Toxic emissions from the Camry on M100 were significantly less when compared to M85 and slightly higher than M85 with the Jetta. When the

toxic emissions were compared to the industry average gasoline, all four methanol fuels were significantly better in terms of toxic emissions than the industry average gasoline. In general, the additive blends performed well when compared to M85 and M100 with minimal emissions impact observed for the regulated emissions.

One criterion of this program was that the cost of including an additive package in methanol to address the safety and physical properties of the fuel should not increase the cost of the fuel significantly as compared to the cost of M85. For the two additive combinations investigated in the expanded programs, these costs were estimated to be comparable to the current market price for M85 in California. To compute the additive costs, the spot price for toluene was reviewed for calendar year 1991 and compared with gasoline. The price of toluene was about \$0.90 per gallon. Cyclopentene and indan were not available as bulk chemicals, so the approach to developing costs for these compounds was to estimate the cost of production from other available materials. Dicyclopentadiene was available in desired quantities as starting material to make cyclopentene by partial hydrogenation of cyclopentadiene monomer. Cyclopentene can be made in California for between \$1.38 to \$2.58 per gallon depending on purity. A cost of \$1.61 for medium purity with a 20 percent rate of return and a 13 year plant life was used in estimating the additive cost for cyclopentene. Indene was selected as the starting material to produce indan. Economic evaluation indicated that indan could be produced in California for \$7.62 per gallon. The estimated cost increase for the 4 percent toluene plus 2 percent indan was about 19 cents/gal, and the cost for the 5 percent cyclopentene plus 5 percent indan was about 46 cents/gal.

Based on the premium unleaded wholesale rack price for gasoline, the cost increase for the 15 percent concentration of gasoline in M85 was 11.2 cents/gal. For the additive package with 4 percent toluene plus 2 percent indan, the additives yielded a cost increase of about 18.8 cents/gal. This increase was about 68 percent greater than the cost for the gasoline portion of M85. The added cost for the 5 percent indan plus 5 percent cyclopentene was about 46 cents/gal, which equates to over a 400 percent of the cost of added gasoline. Thus, both additives exceeded the 125 percent criterion for this program. The average spot market price for M85 over the last five months was about 37 cents/gal, and the average pump price for M85 was about 80 cents/gal. If the cost increase for the flame luminosity additives, transportation, and blending were included in the cost, then the pump cost of the 4 percent toluene plus 4 percent indan would be about 91 cents/gal, and the cost for 5 percent indan plus 5 percent cyclopentene would be about \$1.17/gal. These costs were an increase of 14 and 46 percent more than the average pump price for M85. If the additives for flame luminosity, fuel lubricity, taste deterrent, odor, and color were included, then the cost would increase by an additional 3 cents/gal. When the total cost increase of the fuel with the lower priced additive package was compared to the price of M85 at the pump, the price increase was less than projected 125 percent. The main cause for the higher additive costs with respect to gasoline were due to the indan in the additive package. If a substitute for indan could be found or the feedstock price was reduced, then the additive costs would decrease significantly.

In conclusion, flame luminosity was found to be the most difficult fuel property to control. The other properties were improved with less than 5 volume percent of selected additives, but flame luminosity needed a combination of additives for early and late in the burn and total concentrations greater than 6 percent by volume. Improvement in flame luminosity must be weighed with respect to the other property improvements and the lower exhaust emissions from a clean fuel. Table 2 ranks the two flame luminosity additives selected from the Task 1 Expansion. On this basis, the best overall flame luminosity additive for luminosity and emissions is 5 percent indan plus 5 percent cyclopentene, but the best additive in terms of cost is 4 percent toluene plus 2 percent indan.

TABLE 2. SUMMARY OF ADDITIVES FOR FLAME LUMINOSITY

	M85	M100	4% Toluene + 2% Indan	5% Indan + 5% Cyclopentene
Average Luminosity	0.8/0.15/0.25	0.001	0.15/0.5/1.3	2.2/0.15/2
% Luminous Flame	74	0	81	78
Outdoor Burns				
Concrete	Visible	Poor	Better than M85	Visible throughout burn
Asphalt	Visible	Poor	Better than M85	Visible throughout burn
Sheet Metal	Visible	Poor	Better than M85, bad smell	Visible throughout burn
Grass	Visible	Poor	Occasionally visible	Visible throughout burn
Soil	Visible	Smoke	Occasionally visible	Visible throughout burn
Emission Testing on Volkswagen Jetta				
HC	0.16	0.22	0.19	0.16
CO	0.95	0.46	0.80	0.77
NO _x	0.08	0.06	0.06	0.07
NMOG, g/mi	0.16	0.21	0.22	0.20
Ozone, g/mi	0.22	0.26	0.26	0.27
Specific Reactivity	1.35	0.90	1.16	1.36
Total Toxics, mg/mi	12.5	13.8	15.4	13.2
Cost Increase, \$/gal	0.112	NA	0.188	0.462

This report summarizes the results from a comprehensive program to investigate additives that will improve many of the properties of concern with methanol fuel. Table 3 gives subjective levels of achievement for the different criteria in the original program. The levels of achievement include:

- Not determined - not examined as part of the literature search or laboratory effort in this program
- No change - additives are not expected to change the properties of the fuel or no improvement
- Some improvement - improvement over M100, but not as good as neat ethanol or M85
- Good improvement - achieved sufficient improvement to meet or exceed performance of neat ethanol or M85.

Most of the achievements met or exceeded the requirements for "some improvement" over M100. Specific testing for cold-starting, upper cylinder lubrication, materials compatibility, and light- and heavy-duty vehicle compatibility was beyond the scope of this program and was not conducted. Additional testing will be required to resolve these issues.

TABLE 3. LEVEL OF ACHIEVEMENT OF PROGRAM OBJECTIVES

	Not Determined	No Change	Some Improvement	Good Improvement
Flammability				X
Lubricity				X
Flame Luminosity			X	
Safety				X
<5 Volume Percent			X	
Cold-Starting	X			
Upper Cylinder Lubricity	X			
Regulated Emissions Impact Compared to M100		X		
Toxic Emissions Impact Compared to M100			X	
<50 Percent of Reactive Hydrocarbons Compared to M85			X	
Cost		X		
Materials Compatibility	X			
Light- and Heavy-Duty Vehicle Compatibility	X			

RECOMMENDATIONS FOR FURTHER WORK

The principal objectives of this program were to conduct a literature search of potential additives and then to perform laboratory evaluations on these additives. This testing was designed to determine the effectiveness of these additives for improving the safety properties of methanol fuel. All data generated in the initial stages in this program resulted from extensive laboratory evaluations (no engine work). The work was later expanded to include higher additive concentrations, outdoor (real world) burns, and vehicle emissions testing. As a result, many of the original objectives were achieved, but additional work is still needed to complete the efforts started in this program.

Since no one additive is capable of achieving all desired fuel properties, combinations of additives are necessary. Synergistic effects are possible when additives are combined into a package, so additional testing will be necessary to evaluate these effects. Testing should include but not be limited to flame luminosity, flammability, lubricity, and volatility.

The selected additive packages should provide at least the following:

- Provide front-end volatility to maintain good cold-starting and warm-up at temperatures down to -20°C . Actual volatility needs will be impacted by the cold-start technology employed by the vehicle manufacturer.
- Safety properties to reduce the potential for inadvertent misuse
- Flame luminosity through the majority of the burn
- Flammability of saturated fuel vapors within defined upper and lower limits
- Emission improvement of reactive hydrocarbons compared to M85
- Lubricity equivalent to M85.

Potential additives selected to meet the above criteria include:

- | | |
|-----------------------|---|
| • Butane | • Butene |
| • Toluene | • Cyclopentene |
| • Indan | • Mesitylene |
| • Benzaldehyde | • Methylcyclopentane |
| • Trimethyl borate | • Methanol soluble dye (possibly blue?) |
| • Bitrex | • Vilex |
| • Organic amine salts | • Fatty acids. |

Additional testing should include a laboratory evaluation of selected additive packages for lubricity/corrosion inhibitor effectiveness and elastomer compatibility. Many individuals from the peer review meeting suggested this type of testing. Corrosion inhibitor effectiveness is measured by visual and gravimetric evaluation of conventional ASTM coupons for all automotive, fuel-wetted metals and alloys per ASTM G31-79 and G46-76. Elastomer hardness and shrink/swell are determined according to ASTM D471-79 and 02240-81 using ASTM O-ring coupons.

An important property for continued evaluation of methanol additives involves vehicle cold-starting at low ambient temperatures (-18°C or 0°F). Cold-start testing could be conducted in several ways. One method of testing could utilize a cold-start procedure developed in a congressionally-mandated methanol fuel demonstration program at Southwest Research Institute (SwRI). In this procedure, vehicles are placed in a cold box (located in the Belvoir Fuels and Lubricants Research Facility at SwRI) and started at temperatures as low as -18°C (0°F). A second method could utilize a cold cell in the Engine and Vehicle Research Division at SwRI and includes cold-starting with an engine only. Cold-starting and driveability could also be determined with a dynamometer in a cold box to 45°F in the Department of Automotive Fuels and Fluids Research at SwRI. The Department of Emissions Research also has a low temperature emissions test facility. This facility is capable of performing emission tests at subambient temperatures to 20°F and cold-start testing as low as 0°F.

Fuel weathering was not addressed in this program. Butane and butene were proposed as two components to improve the rich flammability limit of the fuel. Many individuals at the peer review meeting expressed some concern about fuel weathering with these components. Experiments should be performed to investigate fuel weathering and steps to prevent it.

Other evaluations needed are demonstrations in both light- and heavy-duty vehicles to determine the effects of the additive packages in actual vehicles. Evaluations should include vehicle performance, driveability, catalyst deterioration, engine durability, and safety-related features. Catalyst deterioration could be monitored through upstream and downstream sampling of the gaseous emissions during steady-state operation on a chassis dynamometer.

Vehicle emissions testing should be conducted with each additive package. Screening tests for light-duty vehicles would involve the Federal Test Procedure, which utilizes the Urban Dynamometer Driving Schedule. Heavy-duty testing could be performed on a heavy-duty chassis dynamometer or an engine test stand. Emission measurements should include quantification of regulated and possibly toxic substances. Procedures are available at SwRI to monitor toxic substances in exhaust emissions. Sampling techniques may include: Tedlar bags; impingers and special absorbing reagents; traps with Thermosorb/N, Carbosieve/Tenax, or polyurethane foam for the collection media; or filters. Specific toxic substances monitored will depend upon the selected additives. In all cases, methanol, speciated hydrocarbons, and aldehydes should be monitored to determine the reactive hydrocarbons in the exhaust. These steps will demonstrate the effectiveness of the additive package for improving the properties of methanol fuel and its effect on the vehicle, engine, and emission control systems.

Another criterion for the evaluation of potential methanol additives is the effect on upper cylinder lubricity. A procedure is available for comparing engine wear rates using a 2.3 L Ford engine running on methanol fuel. The objective of this proposed test is to determine the upper cylinder wear control characteristics of the methanol fuel additives tested in this program. The test consists of an engine mounted on a test stand, which is configured to conduct Sequence V-D tests with a specially modified carburetor to accommodate methanol fuels. These modifications include main jet and air bleed changes to provide near-stoichiometric air/fuel ratios. Engine wear is measured by the wear metals in the engine oil over a 24 hour test period.

Fuel injector wear is another area that was not addressed in this program. Some concern was expressed about the usefulness of the Ball-on-Cylinder Lubricity Evaluator (BOCLE) measurements for lubricity in determining injector and fuel pump wear. An alternative procedure for evaluating the effectiveness of potential additives would be useful. A device called a Port Fuel Injector (PFI) Deposit Tester has been designed by SwRI and is available for testing injector fouling. This device can be adapted for use in evaluating injector wear prevention of lubricity additives by replacing the standard injectors with

commercially available methanol injectors. Injector wear could be measured by the weep rate after several hours of operation. In addition, fuel pump wear could be evaluated with a standard methanol fuel pump. A correlation between measurements from the BOCLE and the PFI tester would then be attempted. The correlation should be performed with additives that yield both acceptable and unacceptable lubricity with the BOCLE. This device may provide a bench test to prove fuel lubricity in injectors without performing expensive, long-term injector wear tests in an actual engine.

For flame luminosity, a substitute for indan which provides luminosity in the latter part of the burn would be useful. Indan has a high cost relative to the other additives because it is derived from coal tar and is difficult to purify. Substitute compounds should be similar to indan molecular weight, boiling point, hydrogen/carbon number ratio, etc. Some possible candidates which are produced in commercial quantities, at reasonably high purity, and at somewhat lower price include the polymethyl benzenes such as 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene.

All of the recommendations listed above have varying levels of effort. Some recommendations may be easy to achieve while others may be more difficult. To define specific programs would require a knowledge of the areas and level of effort desired for each task. No effort was made to propose costs for each recommendation.

I. INTRODUCTION

A. Background

One of the potential strategies for achieving significant reductions in vehicle emissions is the replacement of conventional motor fuels with methanol fuels. Neat methanol (M100) has many potential advantages for achieving low exhaust emission levels, but there are several areas of concern that require attention before this fuel can replace conventional fuels. These concerns include:

- Difficult vehicle cold-starting, especially at low ambient temperatures
- Poor fuel lubricity
- Flammability of saturated vapors in storage tanks
- Low flame luminosity
- Toxicity by inhalation, absorption through the skin, or ingestion.

Fuel additives have been proposed as one means of alleviating these problems. This program addresses the ability of additives to improve fuel properties without increasing engine wear or the exhaust emissions from an engine designed for M100.

The program originally included three tasks:

- Task 1 - a literature search and laboratory screening of additive candidates
- Task 2 - short-term vehicle demonstration
- Task 3 - long-term vehicle demonstration.

The initial laboratory testing phase of this project began in June, 1988 and ended in January, 1990. An interim report was prepared and submitted to fulfill the reporting requirements for Task 1 - Literature Search and Additive Evaluation. A peer review meeting was held at the South Coast Air Quality Management District (SCAQMD) office in El Monte, California on August 23, 1990. Much information was presented by the representatives from all interests involved with methanol fuel, including:

- Engine and vehicle manufacturers
- Fuel and additive suppliers
- Individuals/companies working in other safety-related areas of methanol fuel
- Government officials.

This meeting was an open forum for the presentation and exchange of ideas on the topic of additives for methanol fuel property improvement and safety. Comments solicited from participants at the meeting resulted in a change in the scope of work for the remainder of the program. The scope of work for the second and third tasks was reorganized at the request of the California Air Resources Board (CARB), the

California Energy Commission (CEC), and SCAQMD into a Task 1 Expansion which included a continuation of the laboratory evaluation to improve the test procedures, an investigation of additional additives at higher concentrations, a comparison of outdoor burns to laboratory data, and a hydrocarbon speciation of emissions from several potential additive blends. The Task 1 Expansion was completed in May, 1992.

B. Objectives

The overall objective of this research project was to develop methanol fuel additive packages which minimized or alleviated air quality concerns, while addressing other safety and operational concerns for methanol fuel. Specifically, the Task 1 - Literature Search and Additive Evaluation objectives were to:

- Perform a literature search identifying generic chemical compound classes which have or might show promise as methanol additives
- Discuss commercially available materials, formulations, and other related technologies with representatives of the additive manufacturing industry
- Acquire samples and screen these materials in a physical testing program for flame luminosity, flammability limit, and fuel lubricity.

Experiments were designed to result in a slate of candidate additives for in-vehicle testing with a current technology engine in Tasks 2 and 3. As a result of the peer review meeting, Tasks 2 and 3 were reorganized into an expansion of the original Task 1. The objectives of this task expansion were to:

- Make improvements in the test procedures for determining luminosity
- Continue investigation of additional additives at higher concentrations with the cost to not exceed 125 percent of the gasoline component cost in M85
- Make the results more useful to the diverse groups needing information on safety of methanol fuel
- Provide a set of standard procedures based on others' work for the comparison of the different properties
- Make recommendations for additional work
- Provide more real world information which would be applicable to the diverse group of companies and individuals involved with methanol fuel.
- Conduct hydrocarbon emissions speciation on fuel-additive packages.

C. Approach

1. Task 1 - Literature Search and Additive Evaluation

Task 1 - Literature Search and Additive Evaluation was designed to investigate the literature for potential candidates to be used as additives for improving the flame luminosity, flammability

limits, and fuel lubricity. A literature search was initiated in parallel with setting up laboratory equipment, contacting key members of the technical community, and acquiring chemicals and commercial additives. Candidate additives were screened with three laboratory techniques which demonstrated their properties in combination with methanol. An optometer with a photometric filter and a cosine diffuser was set up to monitor the flame luminosity of various compounds as they were burned in combination with methanol. Fuel lubricity was measured with the Ball-on-Cylinder Lubricity Evaluator (BOCLE) apparatus. A specially designed apparatus was used to determine the flammability limit as a function of temperature. A slate of additive package constituents was developed for consideration in carrying forward this work to the vehicle test activities in Tasks 2 and 3. The overall approach to the Task 1 program is illustrated in Figure 1. Emission testing was also performed in Task 1 on a 1986 Toyota Camry (dedicated M85 vehicle) fueled with an SwRI methanol blend and with an actual commercial blend of M85 fuel obtained from California. In these tests, the M85 served as the baseline. The SwRI methanol blend was made from an M100 methanol fuel (EM-850-F) and was blended to contain the following additives:

- 6 volume percent toluene
- 2.5 volume percent butane
- 0.12 weight percent DCI-4A (Dupont)
- 0.0001 weight percent Bitrex (denatonium benzoate)
- 0.007 weight percent odorant.

The purpose for the emissions testing in Task 1 was to provide preliminary information on effect of the additive package on the exhaust emissions.

2. Peer Review Meeting

A peer review meeting was held in El Monte, California in August, 1990; and several concerns were expressed regarding the procedures used to evaluate flame luminosity, flammability limit, and fuel lubricity. The individuals who attended this meeting voiced their opinions that some changes should be made to improve the information obtained from the analytical procedures. As a result, the following steps were taken:

- Individuals present at the peer review meeting were contacted for their ideas to improve the methods and for details of their in-house methods for flame luminosity, flammability limit, and fuel lubricity
- Comments and recommendations for improving the methods were evaluated and combined
- EPA was contacted for information on real world flammability problems associated with fuel tank explosions
- Outside burns performed with larger quantities of methanol (approximately one liter on five surfaces) as a comparison between real world and laboratory conditions.

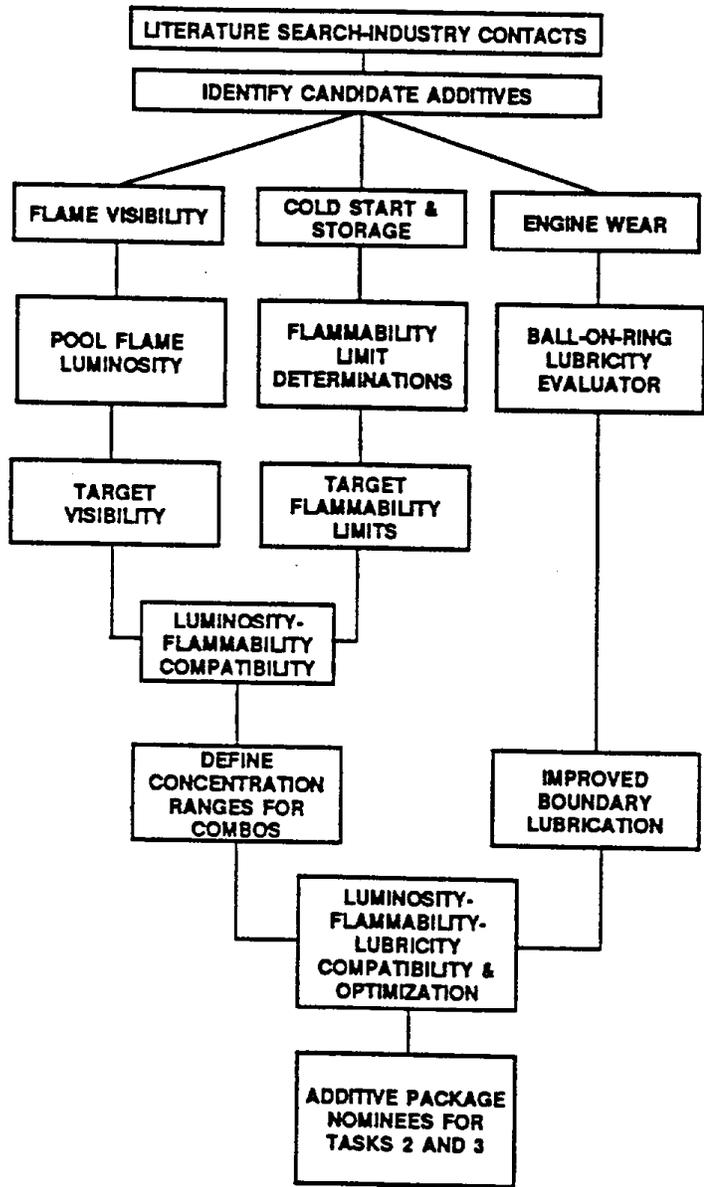


FIGURE 1. TASK 1 METHODOLOGY

Rather than continue the program with Tasks 2 and 3, a decision was made to review the efforts in Task 1 and expand the objectives and original scope of work for Task 1.

3. Task 1 Expansion

In the original program, total additive concentrations were to be held below 5 volume percent. While concentrations below 5 volume percent were successful in improving many properties of the fuel, this concentration constraint severely limited the additives which could be used to improve the flame luminosity. As a result of the peer review meeting, the 5 volume percent limitation was lifted and replaced by a limit on the total cost of the additive package not to exceed 125 percent of the gasoline component cost in M85. Only additives with a low potential of forming exhaust components from the CARB toxic and air contaminant list were considered.

Outdoor burns were performed on several surfaces including concrete, asphalt, sheet metal, grass, and soil. Burns were videotaped and compared by subjective consensus with ethanol, methanol, gasoline, and M85. The most important considerations were a flame:

- Visible in daylight
- Luminous as M85
- Continuously luminous throughout the entire burn.

Based on the results of the investigation for flame luminosity, two additive packages were prepared and tested in a Volkswagen Jetta. Hydrocarbon speciation emission tests were performed with duplicate tests on each additive package. Emission measurements included C₁ to C₃ hydrocarbons plus benzene and toluene, C₄ hydrocarbons, C₅ to C₁₀ hydrocarbons, and aldehydes and ketones. Exhaust emission results were compared to M100, M85, and an Auto/Oil industry average gasoline (RF-A).

II. LITERATURE SEARCH

A. Sources

Two computer search services were used to survey the literature for compounds which could be used as additives to methanol. The computer search services used were Dialog Information Services, Inc. and ORBIT IV (System Development Corporation). Several different databases were available within each service. The file search selected from ORBIT IV (System Development Corporation) was the Society of Automotive Engineers (SAE). Those databases selected from Dialog Information Services, Inc., were:

- Chemical Abstracts
- National Technical Information Service (NTIS)
- Compendex
- EI Engineering Meetings.

Chemical Abstracts contains the basic bibliographic information from the various chemical and chemistry-related journals. The NTIS database consists of the unclassified, publicly-available, unlimited-distribution reports of government-sponsored research, development, and engineering, plus analyses prepared by federal agencies, their contractors, or grantees. The agencies include the National Aeronautics and Space Administration, Department of Defense, Department of Energy, Housing and Urban Development, Department of Transportation, Environmental Protection Agency (EPA), Department of Commerce, and others. Compendex is a database produced by Engineering Information, Inc., which provides coverage of the world's significant engineering and technological literature. It includes publications from approximately 4500 journals and 2000 conferences, publications of engineering societies and organizations, technical reports, and monographs. The EI Engineering Meetings database covers publications of proceedings from engineering and technical conferences, symposia, meetings, and colloquia. The SAE database is entitled "SAE Global Mobility," and includes all publications of the SAE.

The literature was searched back to 1970 for SAE, Compendex, and EI Engineering Meetings. Chemical Abstracts was checked to 1967 and NTIS was searched to 1964. A listing of titles was then compared to the key survey made in 1984 by Fanick, et al,^(1,2) on safety-related additives for methanol fuel. This work provided a comprehensive review and analysis of all important publications through 1984. Therefore, the material described in later sections includes principally post-1984 publications. Further, Sections II. G. through II. I. were excerpted directly from "Survey of Safety Related Additive for Methanol Fuel" by Fanick and Smith⁽¹⁾ for completeness of this literature search, since few other publications were found on these subjects which added to available data.

B. General

The literature search entailed the identification of potential candidate additives to meet the following criteria:

- Reduce the flammability of saturated fuel vapors in underground and vehicle storage tanks by lowering the flammability limit below ambient temperature.
- Provide sufficient front-end volatility to maintain good cold-startability and warm-up performance at 0°F.

- Alleviate safety concerns about flame luminosity by defining minimum perceptible luminosity limits.
- Prevent inadvertent misuse through acceptable standards for proper identification and detection of methanol as a harmful substance; these standards include the use of dyes, odorants, and denaturants for identification and detection.
- Have sufficient upper cylinder lubricity, particularly in heavy-duty engines, if manufacturers identify this as a need.
- Provide minimal emissions impact from toxic substances and regulated emissions compared to M100.
- Be relatively inexpensive and commercially available.
- Be compatible with the best available light- and heavy-duty methanol engine technology and fuel system materials.
- Be compatible with both light - and heavy-duty vehicles.
- Result in no more than 50 percent of the exhaust reactive hydrocarbons compared to M85 without the additional additives.
- Not exceed 5 percent by volume in neat methanol fuel.

This last limitation was changed in the Task 1 Expansion to include higher concentrations, but not to exceed 125 percent of the cost for the gasoline component in M85.

The American Petroleum Institute (API) recently published what is probably the most comprehensive exposition on oxygenates since the work of Keller et al.⁽³⁾ in the 1970's. The report covers chemical and physical properties of alcohols and ethers, oxygenate production technology, gasoline blends, neat alcohol fueling in automotive applications, non-automotive applications (marine, aircraft, etc), distribution and storage, safety, and toxicity.⁽⁴⁾ This report contains some 275 references on these subjects, and is one of the definitive general works on the subject. Technical material and discussions are necessarily rather broad in nature, but the following items are paraphrased as directly applicable to this present study:

- M100 causes a several fold increase in the wear rates when compared with unleaded gasoline. Start-up wear is caused by metal-to-metal contact resulting from the washing away of the normal oil film by liquid alcohol during starting. Start-up wear occurs when very long cranking times are required to start the engine, emphasizing the relationship between cold-start properties and wear. M100 wear during warmed-up engine operation has been identified as a type of corrosive wear which was theorized to result from formic or performic acid formation during combustion and the direct attack of the acid on the iron. Thus, corrosion inhibitors and lubricating oil additives might provide effective protection against this corrosive aspect as well as improving mechanical wear properties.
- Inadequate cold-starting characteristics and misfiring during warm-up are clearly identified as the most important unresolved engineering problems which remain for vehicles designed for M100 operation. Figure 2 illustrates the effectiveness of butane in methanol in improving cold-start characteristics.

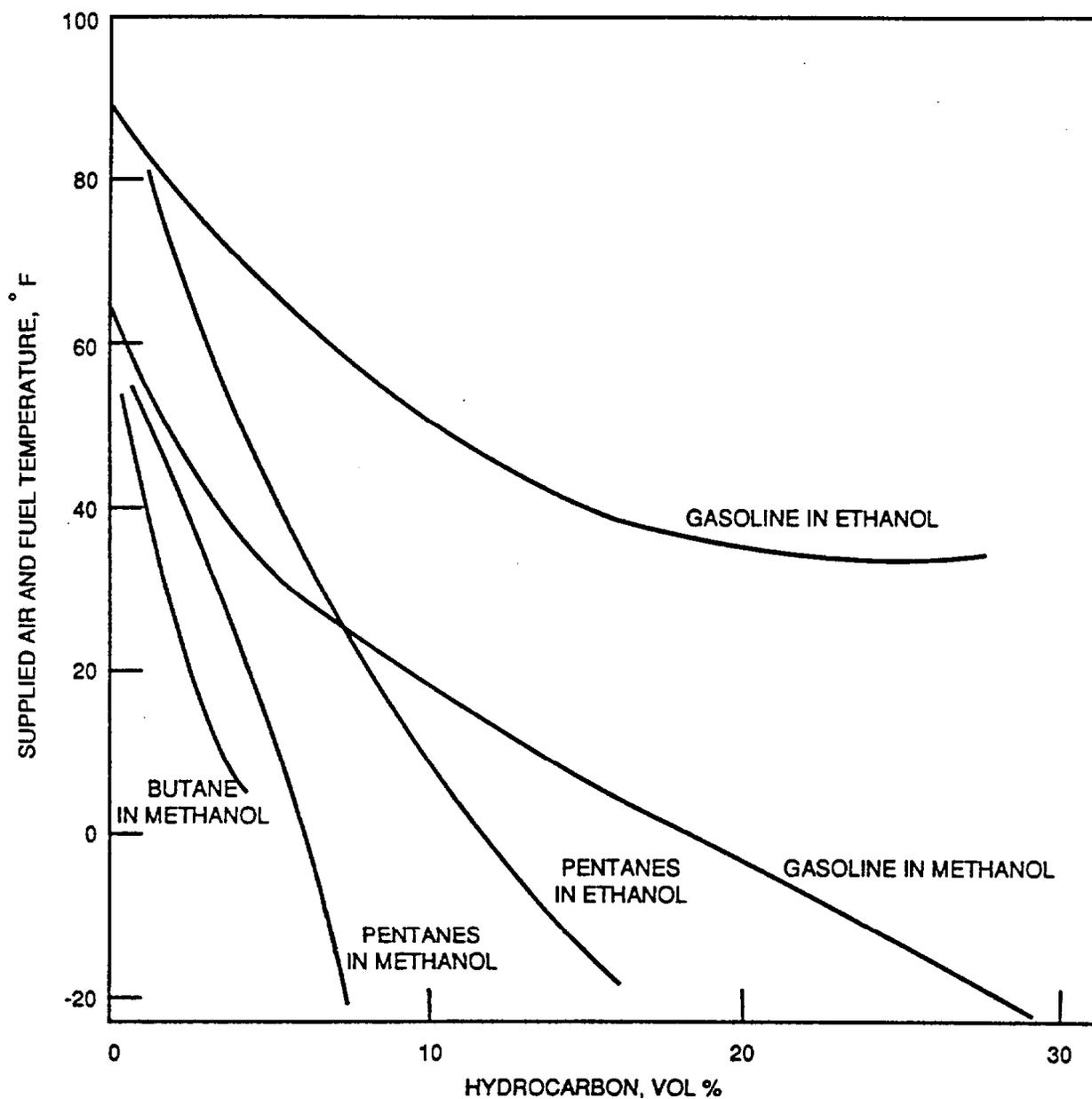


FIGURE 2. SIMULATED COLD-STARTING MINIMUM TEMPERATURES
 BASED ON LABORATORY MEASUREMENTS(3)

- Methanol flame visibility is an important safety characteristic which must be addressed, probably through the use of additives.

In brief, Freeman, et al, publication is a definitive general treatise on alcohols and ethers. This reference serves as a good introductory publication for anyone entering this technological area, or desiring an update of the national effort.

Paul A. Machiele of the U.S. EPA at Ann Arbor provided an excellent general perspective on flammability, toxicity, and environmental safety aspects of methanol.⁽⁵⁾ Comparisons of key properties of M100 and M85 to diesel fuel and gasoline were tabulated and discussed for ullage and ventilated vapor spaces as flammability hazards. These comparisons were related to national statistics on car fire rates, fatality indices, and damage distances for methanol and gasoline pool fires. Figure 3 illustrates the relative safety in terms of fatalities and damage from methanol fuels versus gasoline. This figure shows the differences between gasoline, M85, and M100 pool fires. A 100 percent fatality limit is shown by the shaded area. As the distance from the center of the fire increases, the number of fatalities decreases. With M85 and M100, an individual can come much closer to the pool fire and survive when compared to a similar sized gasoline pool fire.

Machiele emphasized luminosity or flame visibility for M100 as a key issue for safety. A roughly 1000:1 ratio between gasoline and M100 luminosity was cited. The characteristic luminosity was described for M85 burns. He stated that many luminosity additive candidates are ineffective at low concentrations, but some positive results were seen with various organic dyes at concentrations in the hundred ppm range. This reference also mentioned that the introduction of 15 percent gasoline significantly changes other safety characteristics of the fuel. Machiele clearly advocated the enormous potential for M100 with regard to environmental factors, while presenting a balanced picture of safety, toxicity, and operational factors.

C. Engine Wear

Acknowledging that M100 without additives tends to increase engine wear rates above those for gasolines, DeJovine, Drake, and Maize⁽⁷⁾ of Atlantic Richfield Company employed the ASTM Sequence V-D engine test procedure (a test for rating sludge, piston varnish, average engine varnish, and cam wear), to examine wear characteristics of the following:

- Base unleaded gasoline
- Base plus OXINOL® - 50 at 5.5 volume percent (OXINOL® - 50 contains a blend of 50 volume percent methanol and 50 volume percent gasoline grade tertiary butyl alcohol - GTBA)
- Base plus GTBA at 9.1 volume percent
- Base plus OXINOL® - 50 blending component at 9.6 volume percent
- Base plus GTBA at 16 volume percent.

These fuels were tested with four multi-grade commercial lubricants (10W/20W40SF, 10W30SF, and 10W40SF formulations). Data from this study indicated that gasolines containing methanol and GTBA at the stated levels did not cause increased engine wear or deposits over that for normal gasoline. All four commercial lubricants exhibited adequate lubrication characteristics. Other factors such as sludge and

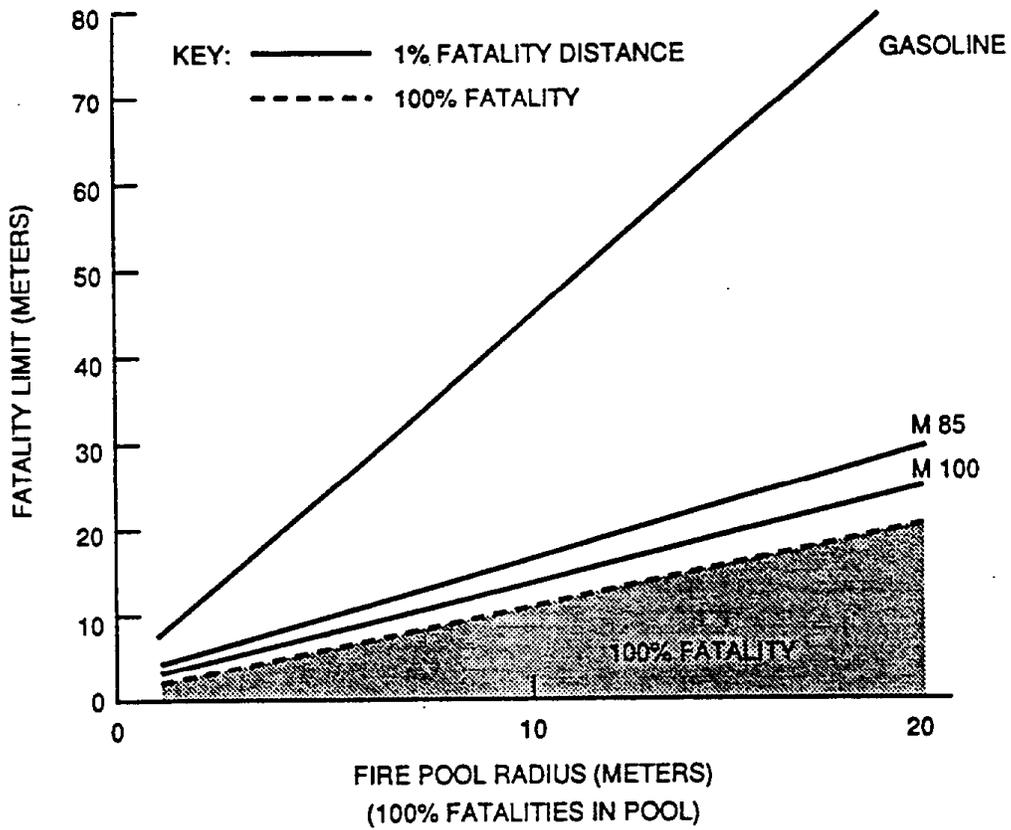


FIGURE 3. FATALITY AND DAMAGE DISTANCES FOR METHANOL AND GASOLINE POOL FIRES⁽⁶⁾

varnish were also unaffected or slightly reduced with the addition of the alcohol(s) to the base test fuel. This study, coupled with parallel studies on 50,000 mile durability tests at ARCO plus other fleet test work, formed a strong basis for optimism in utilizing conventionally-formulated engine oils for alcohol-containing fuels of modest concentration.

Chaibongsai, Howlett, and Millard of Paramins Technology Division Exxon Chemical Company⁽⁸⁾ also employed the ASTM Sequence VD engine (1980 2.3 liter Ford) and procedure to develop a methanol fuel wear test with certain modifications:

- Oil filter added
- Rapid flush mechanism added
- Dual carburetors for either gasoline or methanol fuel
- Reduced ring gaps
- Increased number of thermocouples for temperature monitoring.

This study concluded that this Methanol Fuel Engine Screening Test (MFEST) could discriminate wear under certain specified conditions in under 22 hours of testing, particularly for iron, molybdenum, and chromium. The MFEST correlated with standard Sequence VD test data and limited field testing data. The presence of detergent inhibitor type additives and zinc dithiophosphate (ZDP) was found to be important in controlling bore and ring wear. Also, commercially available (at that time) viscosity improvers were incompatible with methanol fuel dilution. The authors emphasized the inappropriateness of standard ASTM Sequence testing for adequately predicting field performance of methanol fuel. They recommended both a new oil classification when methanol fuel becomes widely adopted in the marketplace and the introduction of a new specification for methanol fuel. Through other channels, ASTM has now drafted such a specification.

In a program jointly sponsored by the U.S. Department of Energy and the U.S. Army, Naegeli and Owens⁽⁹⁾ of SwRI studied methanol and ethanol wear effects, for both neat and gasoline blended alcohols. They employed single-cylinder research engines and production multi-cylinder engines operating on dynamometer test stands. A 20-hour steady-state engine test was developed for use in lubricant formulation work. The test results indicated several findings:

- Pure ethanol and methanol fuels reduced the buildup of engine deposits
- M100 greatly increased engine wear rates at engine temperatures below 75°C
- Neat anhydrous ethanol and alcohol-gasoline blends showed no difference in wear rate from that of unleaded gasoline.

One experimental lubricant formulation was identified to be superior in reducing methanol-related cylinder bore wear, but still not to acceptable levels. Further, engine testing and bench experiments identified the presence of liquid methanol in the combustion chamber to be a primary factor in interfering with the formation of lubricant films on the cylinder walls. The 20-hour steady-state test was employed to investigate the role of nitrogen in the wear process. Wear (as indicated by iron wear-particle buildup in the oil) was the same for nitrogen-free environments as for baseline testing (wear testing involved the combustion of methanol-air mixtures). This observation strongly indicated that nitric acid does not play

a role in the corrosion of the upper-cylinder bore and ring areas of methanol-fueled engines. Subsequent bench experiments revealed that formic acid and peroxides are formed as methanol combustion proceeds. Owens postulated the following sequence of occurrences for methanol corrosive wear:

- Liquid methanol droplets deposit on the cylinder wall
- Liquid methanol rapidly penetrates/removes oil film on the wall
- During combustion, formic acid, formaldehyde, peroxides, and water are formed in the gas phase
- These products diffuse to the liquid surface; because methanol is polar, they dissolve in the methanol
- Formic acid and peroxides react with iron, yielding iron formate
- Iron formate may decompose to form iron oxide
- Material (oxides, etc.) are removed by (ring) abrasion.

This mechanism provides a strong indication that corrosion inhibitor type additives might be effective in improving methanol lubricity. Owens later summarized these findings and extended his conclusions to include a variety of approaches to solving the methanol wear problems.⁽¹⁰⁾ These suggestions included fuel additives, oils and oil additive formulations, material changes, design changes, and engine operation modifications.

Schwartz of General Motors Research Laboratories⁽¹¹⁾ formulated synthetic blowby condensates containing methanol and its combustion products, and placed them on iron surfaces pretreated with acids (acetic, formic, hydrochloric, nitric) and engine oils. This study confirmed that the presence of methanol on a metal surface prevents the lubricant from wetting the surface, thus inhibiting lubrication. The mechanism of corrosion and the subsequent scraping away of corrosion debris was similar for methanol and gasoline fuel wear at cold engine temperatures. Water and acids were identified as the probable corrosive agents. An important discussion and closure to this paper concerned the role of peroxides in this process. The author referred to the work of Naegeli and Owens,⁽⁹⁾ emphasizing the possible role of hydrogen peroxide in increased corrosion.

Ryan of SwRI and Bond and Schieman of Standard Oil Company (now BP Oil)⁽¹²⁾ made a major contribution to this technical area with their study of the methanol corrosive wear mechanism. They performed three types of experiments:

- Combustion experiments designed to identify the combustion products of methanol at various locations within a confined methanol flame
- Exposure studies designed to define the specific role of each combustion product on the corrosion mechanism
- Lubricant screening experiments designed to identify the mode of penetration for the oil film, and the location of the surface attack on the microscale.

Performic acid was identified as the major corrosive agent. Further, corrosion prevention was accomplished through additive formulations designed to prevent the accumulation of the precursors to performic acid formation (formaldehyde, hydrogen peroxide, formic acid, water) on the metal surfaces. Six lubricant formulations were employed with varying results. The lubricant formulations were not described for proprietary reasons. Nevertheless, this study identified the need for additives in neat and near-neat methanol fuels. These additives should work in combination with additives in crankcase lubricants specially formulated for methanol fuel applications.

D. Luminosity

The luminosity of a burning substance is in part related to the formation of submicroscopic soot particles during the combustion process. These carbonaceous particles are heated by the flame and emit "gray-body" radiation at visible light wavelengths. Methanol is unusual because it burns with a cooler flame, and its combustion produces no carbonaceous particles. Since no "gray-body" radiation occurs with methanol, the flame radiates at infrared wavelengths derived from the heated gaseous combustion products. Neat methanol has one of the lowest radiation characteristics during combustion compared to other hydrocarbon materials. The addition of hydrocarbons is one means of enhancing the luminosity of methanol in a flame by increasing the tendency to produce "gray-body" radiation.⁽¹⁾

Anderson, Magyari, and Siegl of Ford Motor Company⁽¹³⁾ studied the luminosity of methanol-hydrocarbon formulations using both wick flames and small pool fires (Petri dish). Concentration ranges were on the order of 10-20 volume percent hydrocarbon additives, using a photomultiplier for luminosity measurements and a bolometer to measure total radiation from wick flames. Hydrocarbon and other compounds included:

- | | |
|---------------|-----------------------|
| • Isooctane | • Benzene |
| • Heptane | • Acetone |
| • Isopentane | • Methyl ethyl ketone |
| • Cyclohexane | • Ethyl acetate |
| • Toluene | |

and alcohols included:

- | | |
|--------------------|--------------|
| • 1-Octanol | • 1-Propanol |
| • 2-Butanol | • Ethanol |
| • 2-Methylpropanol | • Methanol |
| • 2-Propanol | • n-Hexanol |

This study emphasized two important phenomena:

- A "concentration threshold," in which the concentration varies for different hydrocarbon additives, was observed where the flame luminosity rapidly increased with increases in concentration. Those compounds which burn individually to form large amounts of soot (e.g., xylene) exhibit lower thresholds (lower concentration for visibility) than those which burn and form little soot (e.g., n-hexanol).
- The effect of destructive distillation on luminosity varied with time during a pool burn. Low-boiling hydrocarbons (relative to methanol) are selectively vaporized out of the pool, burned, and produce high initial flame luminosity which later decreases as the residual pool liquid is enriched in methanol. High-boiling hydrocarbons reverse this process, with

initial flame luminosity being dominated by methanol vapor (and consequently very low luminosity) followed by latter stages of the pool fire governed by residual, low-volatility hydrocarbons (and consequently higher luminosity).

Infrared imaging using a bolometer provided a rapid, efficient means of detecting methanol flames under conditions where they are virtually imperceptible to visible light monitoring systems (human eye). This device might serve as a practical means for detecting methanol fires in a road-accident situation but would obviously require training and indoctrination of state highway patrol professionals, etc.

Kirshenblatt and Bol of Sypher-Mueller International, Canada⁽¹⁴⁾ confirmed the 1000:1 ratio of gasoline luminosity to methanol luminosity. They examined some 26 simple and complex combinations of methanol with hydrocarbon and chemical dopants. These materials included:

- Winter grade gasoline
- Regular unleaded gasoline
- Nigrosine
- Avocet
- Armeen O
- Neo-fat 94-96
- n-Pentanol
- Mixtures of n-propanol, n-butanol, ethanol, n-pentanol, and n-octanol.
- 2-Butanol
- n-Butanol
- Isooctane
- Isopentane
- Benzene
- Diesel fuel
- Octane

Concentrations ranged from 0.01 to 9 volume percent. Ten milliliter quantities were used for all burns. Luminance in foot-lamberts as well as burn time was recorded. In addition, subjective observations were recorded (e.g., yellow orange-flame for first 10-20 seconds and during last 5 seconds). These researchers described the importance of distillation effects in flame luminosity variation. They identified nigrosine as a potential methanol luminosity enhancer that does not suffer from distillation effects. However, a later study⁽¹⁵⁾ (in publication), revealed that nigrosine is not 100 percent soluble in methanol under certain conditions, resulting in non-filterable residue at concentrations down to 0.01 percent on a weight per volume basis. In addition, nigrosine dyed the fuel jet black and showed a great propensity to form ash residues. In general, these additives, at the concentrations used, did not raise the average luminance of methanol near to that of gasoline, and the luminosities reported may be well below human visibility thresholds in most lighting conditions.

Wang, Sawyer, and Muniz of the University of California at Berkeley⁽¹⁶⁾ conducted an experimental program on pool burning (100mm diameter) of 7 fuels:

- Methanol
- M95
- M85
- M50
- Unleaded gasoline
- Diesel fuel
- n-Heptane

Quantitative measurements were made of flame height, burning rate, and flame luminosity. Burns were made under steady and unsteady conditions. Unsteady burning entailed total burnout of 70 mL samples, while steady burning used a level-maintaining flow device for 20-30 minutes duration. This latter was a novel and ingenious way to eliminate the attenuation in flame luminosity for any burn which accompanies the reduction in remaining liquid mass [usually in the last 1/4 or so of burn]. The researchers employed a Minolta T-1 illuminosity meter which closely mimics the response of the human eye. Relative ranking of luminosities was quite consistent with that reported elsewhere. The report concludes that the unsteady pool burning test method is preferable, since it "captures the important

time-varying character of the luminosity of the blended fuels". Conclusions of relevance to this present study were:

- A commercial illuminance meter provides a sensitive, repeatable means of quantifying flame luminosity
- An unsteady burning technique was best for showing time variations with blended fuels
- The visibility is not simply related to luminosity.

Kucharczuk, Miller, Mummert, and Ressler⁽¹⁷⁾ were senior engineering students at Widener University at the publication time of their senior project, "Flame Luminosity of Primed Methanol Fuels". This team employed a United Detector Technology Model 40X optimeter with a luminescence probe. The results of their pool-burning experiments indicated the following acceptable formulations:

- 10% toluene, 5% Indolene in methanol
- 10% toluene, 5% reformat in methanol
- 10% reformat, 5% toluene in methanol
- 5% toluene, 5% reformat, 5% Indolene in methanol
- 5% toluene, 5% reformat, 5% MTBE in methanol
- 15% reformat in methanol.

These formulations provided a luminosity greater than that of 15 percent Indolene in methanol used as a standard. No data were taken at lower concentrations. This project developed and demonstrated a simple, reproducible technique to measure flame luminosity and used this method to identify luminosity-enhancing co-fuels.

Considerable work was done during the period of 1987 to 1989 by BP Oil Company⁽¹⁸⁾ on luminosity additives. Some of the proprietary additive formulations evaluated by BP Oil have shown great promise. Most of the additives consisted of alcohol-soluble solid dyes in a variety of colors and contained only carbon, hydrogen, oxygen, and nitrogen. Test burns were performed on many of these materials to demonstrate their effectiveness. There were several concerns and observations presented by BP Oil regarding the use of these organic dyes to improve the flame luminosity which included:

- Residue after completion of the burn
- Lower flame luminosity due to flame color
- Possible engine deposits
- Solubility of the solid when combined with the gasoline portion of M85
- Decomposition temperature of the solid
- Functional groups which affect or improve luminosity

- Carriers to increase additive solubility and reduce residue
- Differences resulting from luminosity measurement methods
- Other ways to improve luminosity.

BP used two methods to conduct burns in a metal pan and a glass dish. Burns in the metal pan produced more visible flames than those conducted in the glass dish. These differences may have been due to:

- Temperature of the flame
- Volatility in the different dishes
- Surface effects from the different dishes
- Temperature of the burning liquid
- Synergistic effect between the additive and the dish material
- Light reflection from the metal pan.

No resolution was provided for these differences.

Burns were conducted on neat methanol and on M85 with light iso-crackate as the blending agent. The effect of solid concentration (0.005 to 0.5 weight percent), fuel temperature, and the carrier for the solid component in M85 were investigated. Combinations were burned under controlled laboratory conditions and outdoors to determine subjectively the effect of sunlight on the visibility of the flame. With the BP Oil additives, methanol burns with a visible orange flame. Although the luminosity of these flames in foot-candles was low, the visibility to the human eye was good. This situation illustrated that flame luminosity and flame visibility were not identical measurements; one is an actual measured value based on the radiated energy of the burning liquid, and the other is subjective to the observer (human eye).

E. Lubricity

Lubricity or the film strength of a fluid is the ability of a liquid to lubricate. Most fuel lubricity research has concerned jet fuel lubricity and has been performed over the past 5 to 10 years. This work was associated with increased demand for jet fuels of higher thermal stability. These fuels require a more severe hydrotreatment to remove so-called heteroatoms and aromatic organic compounds which cause degrading effects on thermal stability (deposit-formation). Removal of these species has introduced the problem of decreased lubricity since the very compound classes which degrade thermal stability quite often act as excellent solid film lubricants. The class of corrosion inhibitors typically specified on the Qualified Products Lists for military specifications showed great promise for this project, since they not only have been designed to inhibit corrosive activity, but they also adsorb on metal surfaces and serve as lubricity improvers. The only question, then, was of compatibility with methanol. References cited in this report discuss lubricity improvement of jet fuels rather than methanol, since their origins stem from this area of fuels technology.

Russell, Campbell, Burton, and Ku of SwRI⁽¹⁹⁾ utilized a pin-on-disk apparatus capable of measuring the coefficient of friction and wear from near absolute zero to 1000°F in a variety of oxidizing,

inert, and reducing atmospheres. They employed single compounds of super-purified quality to measure lubricity of hydrocarbons such as paraffins, fatty acids, and the lower molecular weight alcohols. This pioneering work demonstrated the lack of lubricity for high purity methanol coupled with the fact that lubricity could be improved almost instantly by any polar impurity at extremely low concentration. Stearic and dilinoleic acids were particularly effective in reducing friction and wear in the boundary lubrication regime. Dilinoleic acids as corrosion-inhibitors were the dominant class of compound on most of the Qualified Products Lists for military specification.

Grabel of the Naval Air Propulsion Test Center⁽²⁰⁾ demonstrated the effectiveness of a device (then in prototype configuration) originally called the "Ball-on-Cylinder Machine" (BOCM) as a lubricity tester. In general, he found that corrosion inhibitors, organic acids, and nitrogen-containing compounds improve lubricity, while sulfur compounds, non-acid oxygen-containing compounds, and anti-oxidants had little or no effect on lubricity. This work was done with jet fuels supported by parallel test method development at SwRI. This BOCM apparatus has evolved over the last 15 years with minor modifications and is now popularly known as the BOCLE, the device used in this study. Typically, a 15-20 percent reduction in "wear scar diameter" is considered significant for overall repeatability and reproducibility of the procedure.

Lykov, et al,⁽²¹⁾ demonstrated that synthetic fatty acids produced in the USSR can have good lubricity properties. This class of compounds is produced in industrial-scale quantities in Russia by methanol extraction which implies their compatibility with methanol. Their effectiveness was demonstrated in jet fuel at concentrations down to 0.002 weight percent. Lykov's work with fatty acids in experimental conditions of a high water concentration also showed that they were effective corrosion inhibitors.

In an internally-sponsored program at SwRI, Fischer and Estefan⁽²²⁾ utilized the above-mentioned BOCM wear tester and the ASTM Sequence V-D engine test to identify effective anti-wear additives for methanol fuel. They employed 104 single compounds and one fully-formulated commercial additive package in their study. Many compounds did not reduce wear; however, the fatty acid category did result in significant wear reduction on the bench test apparatus. Unfortunately, the full scale engine test phase of this study provided largely disappointing and sometimes catastrophic results because rapid buildup of wear metals in the crankcase oil terminated the useful life of the test engine. The authors recommended development of a new engine test to provide even more rapid and severe wear conditions than the Modified Sequence V-D to differentiate pure methanol wear from wear with additives.

Lubricity is very relevant to the satisfactory operation of diesel engines, which rely on the fuel to lubricate many of the moving and rubbing metal parts of the fuel injection equipment. Currently, lubricity is not included in diesel fuel specifications, but it is considered that some injection equipment may be at risk if operated on fuels of low viscosity or of non-petroleum origin.^(22A) Although a great deal of testing has been carried out by fuel injection equipment makers and other researchers, no agreement has yet been reached on the applied loads and limiting wear scar values that would be considered acceptable.^(22B) Lubricity is not considered as important in Otto cycle engines because the injection pressures are not as high even though the lubricity of gasoline is less. With methanol, the concern is from the washing away of the lubricant by the alcohol resulting in metal-to-metal contact and the formation of corrosive agents during combustion which directly attack the iron.

F. Cold-Starting and Flammability

Keller⁽³⁾ studied the effect of hydrocarbon addition to methanol for reducing the cold-starting temperature. This study avoided the high cost of engine experiments by using a bench apparatus to

determine the vapor-air flammability. The experiments were designed for adiabatic, rather than isothermal fuel evaporation. The cooling effect of the evaporating methanol resulted in lower temperatures than the initial air/fuel temperatures. Compressive heating was not accounted for, so the results should be considered conservative. Additives of C₄ to C₇ hydrocarbons were effective in reducing the flammability temperatures as shown in Figure 2. Butane was the most effective. Keller reported that his results were similar to General Motors⁽²³⁾ vehicle results.

Other researchers' engine results were also similar to the findings of Keller. Goetz⁽²⁴⁾ obtained unaided starts (no heat addition prior to or during cranking) at 32°F using 10% gasoline as an additive, which was slightly above the prediction of Keller. Goetz also found a mixture of gasoline (9%), dimethyl ether - DME (5%) and butane (1%) was the most effective for obtaining cold-starts to -18°F. Nichols⁽²⁵⁾ reported cold-starting in less than 10 seconds at 32°F using 5% isopentane, while 10% isopentane was required to start at 5°F. For comparison, Keller⁽³⁾ predicted 14°F for the 5% isopentane mixture using the bench apparatus. Menrad⁽²⁶⁾ found 5% isopentane produced 23°F starts and 10% isopentane yielded engine starting at -18°F. His data indicates that 7% isopentane is needed to cold-start at 0°F. Menrad⁽²⁶⁾ and Bernstein⁽²⁷⁾ have concluded that the cold-starting temperatures for hydrocarbon additives in methanol correlate to the Reid Vapor Pressure (RVP). Based upon Menrad's data, an RVP of 8 psi will result in a 23°F starting temperature. This prediction is also in good agreement with Keller's data.

Closely related to the addition of hydrocarbons for improving cold-start is the safety issue of the explosive methanol vapor/air mixtures existing in the vehicle fuel tank ullage. Keller⁽³⁾ demonstrated this in the laboratory at 73°F. Ignition could occur in a vehicle fuel tank with a submerged fuel pump if the pump were exposed when the tank was run empty. This observation may affect the design of vehicle fuel tanks and fuel pumps.

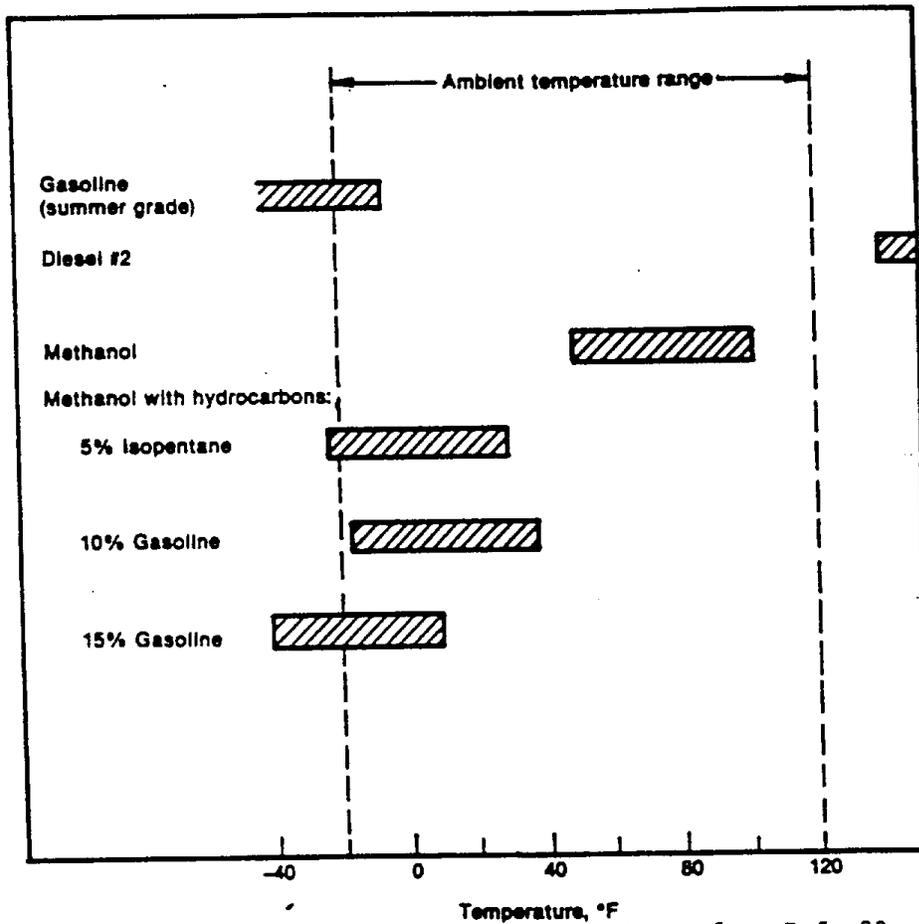
Anderson⁽²⁸⁾ experimentally obtained the results for several methanol/hydrocarbon blends which are reproduced in Figure 4. Isopentane, the most volatile of the hydrocarbons evaluated, was the most effective. At 5% isopentane concentration, the rich flammability limit was 30°F which is above the -8°F rich flammability limit of the summer grade gasoline.

Battista⁽²⁹⁾ found that the flammability limits for M85 using a winter grade gasoline were lowered to the range of -40°F to -5°F. This researcher also noted the fill level in the test apparatus influenced the upper flammability limit result. The near empty limit was generally 9°F higher than the near full results. The lower limits were not affected by the fill level.

A final concern of volatile additives in methanol is the effect of water contamination and weathering. Bernstein⁽²⁷⁾ conducted a study of these effects on methanol with three different additives; butane, dimethyl ether (DME), and pentane. He found that low concentrations of water, typically 4%, could result in a sharp rise in RVP. This effect was more pronounced for the hydrocarbon additives, butane, and pentane, than for the oxygenated additive DME. Bernstein⁽²⁷⁾ also conducted comparative weathering tests between the fuel blends by partially filling a vehicle fuel tank and thermally cycling its contents from 5°C to 29°C. The loss of additive was greatest for the butane at 0.7% and least for the DME at 0.5%. Gasoline lost 0.64% of its C₄ and C₅ hydrocarbons under these test conditions.

G. Taste Deterrents

Of the three major routes of methanol poisoning (ingestion, inhalation and subcutaneous absorption), direct ingestion is the quickest. Methanol does not have a strong or distinctive taste to identify its presence. In fact, methanol has been mistaken for ethanol innumerable times throughout history and has been consumed with sometimes disastrous consequences. The addition of a bitter or foul



NOTE: This figure was taken in its entirety from Ref. 28.

FIGURE 4. VAPOR SPACE FLAMMABILITY LIMITS OVER LIQUID FUELS

tasting substance may deter accidental poisoning and possibly even prevent some intentional ingestion of methanol fuel.

The practice of adding taste deterrents to products available to the public has been used by manufacturing companies for several years to increase the safety of their products. Taste deterrents have been added to everything from laundry detergents to perfumes, to prevent unintentional ingestion. Denaturants (which include taste deterrents) have been used routinely to prevent the consumption of ethanol. In addition to imparting a foul or bitter taste, an additive to methanol in a motor fuel application must be compatible with the engine and fuel system components, difficult to separate from the methanol, and economical in cost.

Hagen⁽³⁰⁾, and Wimer, Russell, and Kaplan⁽³¹⁾ stated that the usual fatal dose by direct ingestion of methanol was between 50 and 100 mL (2-4 oz.), although 25-50 mL (1-2 oz.) has often been fatal if not treated promptly. The symptoms of acute poisoning usually occur 12 to 48 hours after ingestion with visual disturbances, cerebral aberrations, severe acidosis, abdominal pain, nausea, vomiting, weakness, shortness of breath, dizziness, and a lowering of the CO₂-combining power in the blood. Target areas for the symptoms of methanol poisoning include eyes, skin, central nervous system, and gastrointestinal system. The lowest reported fatal dose was 3 teaspoons (about 15 mL) of 40% methanol (approximately 6 mL of pure methanol) and the highest dose for a survivor was one pint (500 mL) of the same material (approximately 200 mL of pure methanol). Midwest Research Institute stated that the chance of a 6 mL dose causing death was exceedingly low.⁽³²⁾

The toxicity of methanol is attributed to the metabolites produced after ingestion. In primates, methanol oxidation to formaldehyde is catalyzed by enzyme alcohol dehydrogenase (ADH). Formaldehyde is considered responsible for some of the toxicity that methanol exhibits. The formaldehyde is then oxidized to formic acid in a reaction mediated by formaldehyde dehydrogenase. Formic acid is either oxidized to carbon dioxide and water or eliminated in the urine. The consumption of ethanol prior to or in conjunction with methanol has been found to decrease the toxic effect because ethanol competes effectively for the enzyme which converts methanol to formaldehyde and formic acid. The competitive preferential ratio of ethanol to methanol is 9:1 with this enzyme. This enzyme is suspected of being responsible for some of the toxic effects of methanol. Therefore, ethanol greatly lessens the poisonous effect of methanol.⁽³¹⁾

Although little information exists on the addition of materials to methanol to make it undrinkable, denaturants have been added to commercial ethanol for over 60 years to render ethanol unfit for human consumption. A list of denaturants used in ethanol is presented in Table 4. Although denaturants are most commonly involved with ethanol, many of these substances are also soluble in methanol and could be used as a taste deterrent.

The two categories of denaturing formulas for ethanol are: (1) completely denatured alcohol (C.D.A.), and (2) specially denatured alcohol (S.D.A.). Completely denatured alcohol is ethanol which has denaturants added to render it entirely unfit for human consumption. This type of denatured alcohol may be handled for legitimate purposes without filing a bond, obtaining a permit, or paying a tax. Specially denatured alcohol is ethanol denatured for special purposes and may be received and blended at bonded facilities that are subject to rigorous inventory control and government supervision. Two C.D.A. and three S.D.A. formulas have been authorized by the Federal government for ethanol use as a motor fuel. Many other S.D.A. formulas have been authorized by the Federal government, but they have specific uses ranging from the production of adhesives and binders to the production of vitamins. The Southwest Alabama Farmer's Cooperative Association also evaluated a denatured ethanol formula for use in farm equipment.⁽³⁴⁾ In addition, several foreign patents exist for denaturing fuel and ethanol. Table 5 presents the list of denaturing formulas which have been used as motor fuels. Methanol is included as

**TABLE 4. U.S. GOVERNMENT-AUTHORIZED DENATURANTS FOR
COMPLETELY DENATURED ALCOHOL (C.D.A.) AND
SPECIALLY DENATURED ALCOHOL (S.D.A.)(33)**

DENATURANT	USED IN	DENATURANT	USED IN
Acetaldehyde _____	S. D. 29	Methyl violet (methylosaniline chloride) _____	S. D. 33
Acetone N. F. _____	S. D. 23-A; 23-H	Methyl violet (methylosaniline chloride) U. S. P. _____	S. D. 33
Acetaldoi _____	C. D. 18	Mustard oil, volatile (allyl Isothiocya- nate), U. S. P. XII _____	S. D. 38-B
Almond oil, bitter N. F. _____	S. D. 38-B	Nicotine solution _____	S. D. 4
Ammonia solution, strong U. S. P. _____	S. D. 36	Peppermint oil U. S. P. _____	S. D. 38-B
Anethole U. S. P. _____	S. D. 38-B	Phenol U. S. P. _____	S. D. 38-B; 46
Anise oil U. S. P. _____	S. D. 38-B	Phenyl mercuric benzoate _____	S. D. 42
Bay oil (myrcia oil) N. F. _____	S. D. 23-F; 38-B; 39-D	Phenyl mercuric chloride N. F. IX _____	S. D. 42
Benzaldehyde N. F. _____	S. D. 38-B	Phenyl mercuric nitrate N. F. _____	S. D. 42
Benzene _____	S. D. 2-B; 2-C; 12-A	Phenyl salicylate (salol) N. F. _____	S. D. 38-B
Bergamot oil N. F. _____	S. D. 23-F; 38-B	Pine needle oil, dwarf N. F. _____	S. D. 38-B
Bone oil (Dipple's oil) _____	S. D. 17	Pine oil, N. F. _____	S. D. 38-B
Boric acid U. S. P. _____	S. D. 38-F	Pine tar, N. F. _____	S. D. 3-B
Brucine alkaloid _____	S. D. 40	Potassium iodide, U. S. P. _____	S. D. 25; 25-A; 42
Brucine sulfate N. F. IX _____	S. D. 40	Pyridine bases _____	S. D. 6-B
n-Butyl alcohol _____	S. D. 44	Pyronate _____	C. D. 18
tert-Butyl alcohol _____	S. D. 39; 39-A; 39-B; 40; 40-A	Quassia, fluid extract of, N. F. VII _____	S. D. 39
Camphor U. S. P. _____	S. D. 27; 27-A; 38-B	Quassin _____	S. D. 40
Caustic soda, liquid _____	S. D. 36	Quinine, N. F. _____	S. D. 39-A
Chloroform _____	S. D. 20	Quinine bisulfate N. F. _____	S. D. 39-A; 39-D
Chlorothymol N. F. _____	S. D. 38-B; 38-F	Quinine hydrochloride U. S. P. _____	S. D. 39-A
Cinnamon oil (cassia oil) U. S. P. _____	S. D. 38-B	Quinine sulfate U. S. P. _____	S. D. 39-D
Citronella oil, natural _____	S. D. 38-B	Resorcin, U. S. P. _____	S. D. 23-F
Cinchonidine _____	S. D. 39-A	Rosemary oil, N. F. _____	S. D. 27; 38-B
Cinchonidine sulfate N. F. IX _____	S. D. 39-A	Rubber hydrocarbon solvent _____	S. D. 2-B; 2-C
Cinnamic aldehyde (cinnamaldehyde) N. F. IX _____	S. D. 38-B	Safrol _____	S. D. 38-B
Clove oil U. S. P. _____	S. D. 27-A; 38-B	Salicylic acid, U. S. P. _____	S. D. 23-F; 39
Coal tar U. S. P. _____	S. D. 38-B	Sassafras oil, N. F. _____	S. D. 38-B
Diethyl phthalate _____	S. D. 39-B; 39-C	Shellac (refined) _____	S. D. 45
Ethyl acetate _____	S. D. 35; 35-A	Sodium iodide, U. S. P. _____	S. D. 25; 25-A
Ethyl ether _____	S. D. 13-A; 19; 32	Sodium, metallic _____	S. D. 2-C
Eucalyptol U. S. P. _____	S. D. 37; 38-B	Sodium salicylate, U. S. P. _____	S. D. 39; 39-D
Eucalyptus oil N. F. _____	S. D. 38-B	Soap, hard, N. F. _____	S. D. 31-A
Eugenol U. S. P. _____	S. D. 38-B	Soap, medicinal soft, U. S. P. _____	S. D. 27-B
Formaldehyde solution U. S. P. _____	S. D. 22; 38-C; 38-D	Spearmint oil, N. F. _____	S. D. 38-B
Gasoline _____	S. D. 28-A	Spearmint oil, terpeneless _____	S. D. 38-B
Glycerol U. S. P. _____	S. D. 31-A	Spike lavender oil, natural _____	S. D. 38-B
Guaiacol N. F. _____	S. D. 38-B	Storax, U. S. P. _____	S. D. 38-B
Iodine U. S. P. _____	S. D. 25; 25-A	Sucrose octa-acetate _____	S. D. 40-A
Kerosene _____	C. D. 18; 19	Thimerosal, N. F. _____	S. D. 42
Lavender oil U. S. P. _____	S. D. 27-B; 38-B	Thyme oil, N. F. _____	S. D. 38-B
Menthol, U. S. P. _____	S. D. 37; 38-B; 38-C; 38-D; 38-F	Thymol, N. F. _____	S. D. 37; 38-B; 38-F
Mercuric iodide, red N. F. _____	S. D. 42	Tolu balsam, U. S. P. _____	S. D. 38-B
Methylene blue N. F. _____	S. D. 4	Turpentine oil, N. F. _____	S. D. 38-B
Methyl alcohol _____	S. D. 3-A; 30	Vinegar _____	S. D. 18
Methyl isobutyl ketone _____	C. D. 18; 19; S. D. 23-H	Wintergreen oil (Methyl salicylate) U. S. P. _____	S. D. 38-B, 46
		Wood alcohol _____	S. D. 1

TABLE 5. DENATURANT FORMULAS FOR ETHANOL AND OTHER FUELS

1. C.D.A. Formula No. 18: to every 100 gallons of ethyl alcohol of not less than 160 proof, add:
 - 2.50 gallons of methyl isobutyl ketone;
 - 0.125 gallon of pyronate or a compound similar thereto;
 - 0.50 gallon of acetaldol (b-hydroxybutyraldehyde); and
 - 1.00 gallon of either kerosene, deodorized kerosene, or gasoline.
2. C.D.A. Formula No. 19: to every 100 gallons of ethyl alcohol of not less than 160 proof, add:
 - 4.0 gallons of methyl isobutyl ketone; and
 - 1.0 gallon of kerosene, deodorized kerosene, or gasoline.
3. S.D.A. Formula No. 1: to every 100 gallons of ethyl alcohol of not less than 185 proof, add:
 - 5.0 gallons wood alcohol.
4. S.D.A. Formula No. 3-A: to every 100 gallons of ethyl alcohol of not less than 185 proof, add:
 - 5.0 gallons methyl alcohol.
5. S.D.A. Formula No. 28-A: to every 100 gallons of ethyl alcohol of not less than 185 proof, add:
 - 1.0 gallon of gasoline.
6. Southwest Alabama Farmers' Cooperative Association⁽³⁴⁾ Formula is 10 gallons of denaturant blended with 90 gallons of methanol.
 - 89.5 gallons of S.D.A. Formula No. 28-A,
 - 5.0 gallons gasoline,
 - 0.5 gallon methyl isobutyl ketone or tertiary butyl alcohol,
 - 5.0 gallons methyl alcohol,
 - a dye to color the solution.
7. French patent for denaturing fuel⁽³⁵⁾
 - 100 wt. parts dye (1-(2'-methyl-1'-phenyl-4-azophenylazo)-2-naphthalenol or 1,4-bis(butylamino)anthraquinone)
 - 500 wt. parts diphenylamine
 - 5-30 wt. parts 3-(oleylamino) propyl amine dioleate
 - dilute to 1 g dye/hectoliter of fuel
 - sometimes add 0.5-1 g furfural/hectoliter fuel.
8. Polish patent⁽³⁶⁾

The following by-products of the chemical industry are used as denaturants. One part denaturant added to 99 parts ethanol colored with 18 mg/L of crystal violet. The denaturant is a mixture of two or more components:

 - aromatic fraction obtained by separation of gasoline and pyrolysis products
 - ketone oil isolated from wood tar containing alcohols, aldehydes and ketones
 - cumene fraction obtained by alkylation of C₆H₆
 - fraction of higher aliphatic alcohols from oxo synthesis
 - gasoline fraction with boiling point between 90-150°C containing 70% paraffins and 20% naphthenes.

a denaturant for ethanol in several of these formulas. Ethanol, on the other hand, cannot be used as a denaturant for methanol. Ethanol has, however, been used in the treatment of methanol poisoning victims. All formulas in Table 5 contain gasoline or methanol as part of the denaturant.

In the 1920's, two ethanol base fuels were produced. One, called Alcogas, was manufactured by the U.S. Industrial Alcohol Company of New York and Baltimore. Alcogas contained 33% of 180-190 proof ethanol, 35% gasoline, 25% benzene, and 7% ether. The other fuel, Natalite, was made from molasses at Natal, South Africa. Natalite consisted of 54-60% 190 proof ethanol, 39-45.8% ether, 0.15-1% pyridine, ammonia or trimethylamine, and 0.5% arsenious acid.⁽³⁴⁾ During the 1930's, ethanol was denatured in England by adding a small percentage of pyridine and wood naphtha.⁽³⁷⁾ However, this formula was not released from the surveillance of the Excise authorities until at least 35% hydrocarbons (benzene or gasoline) was mixed with the ethanol.

Mueller Associates, Inc.⁽³⁴⁾ listed several important technical factors involved in choosing a suitable denaturant for alcohol fuels. The alcohol fuel additive:

- Should closely match the thermal and physical properties of the alcohol to ensure compatibility with the combustion characteristics.
- Should add to the energy content; preferably in an amount greater than that required to produce the substance.
- Should impart a taste or smell sufficiently disagreeable to discourage human consumption even if diluted, sweetened or flavored.
- Should not be capable of being eliminated easily by filtration, distillation or any other process.
- Should be capable of being easily and reliably detected.
- Should not increase combustion products.
- Should not leave any objectionable residue to clog or corrode fuel systems.
- Should be readily available.
- Should not appreciably increase the cost.
- Should not complicate the regulatory compliance.

The Muller Associates, Inc. paper was primarily concerned with ethanol; however, the technical factors should also be applicable to methanol.

Nakaguchi, Keller, and Wiseman⁽³⁸⁾ conducted recovery experiments on various denatured ethanol blends (C.D.A. 19-A, S.D.A. 28-A, and the Southwest Alabama Farmers' Cooperative Association formula with the t-butyl alcohol option). The blends were washed with water to remove the gasoline and extracted with a volatile stove and lantern fuel. The extracted alcohol was air blown until no hydrocarbon odor was detected. The results showed that the ethanol recovered from the blends was sufficiently palatable to drink by a determined consumer even though small amounts of noxious compounds remained. Similar experiments were conducted with six additional compounds as denaturants. These compounds were N,n-

dimethylformamide (DMF), isopropyl alcohol, n-butyl alcohol, iso-amyl alcohol, t-butyl mercaptan, and an odorant (Sindar deodorant oil GD-64262). Of these six compounds, the most effective denaturant was DMF, which imparted a highly objectionable and bitter taste to the extracted alcohol. Once again, these tests were conducted with ethanol, and similar results may be expected with methanol.

The addition of gasoline to methanol as a taste deterrent has been suggested by some researchers, and it meets some of the criteria established for additives to fuel alcohols. Gasoline has also been used as a denaturant for ethanol in some applications. Keller, Nakaguchi, and Ware⁽³⁾ stated that the toxicity of a blend of gasoline and methanol was only slightly more hazardous than ordinary gasoline because of the prominent gasoline odor in the blend and the difficulty in separating methanol in a potable or consumable form from the blend by "casual" means. For example, the addition of water to a gasoline (5 or more volume percent) and methanol blend produced an unattractive milky mixture. Lower concentrations of gasoline were not as objectionable, although the gasoline odor was still noticeable. They also stated that one must be "determined" to drink methanol with even as little as 1 to 2 percent gasoline added as a denaturant.

Methylal, which has been added to fuel methanol to increase the engine cold-starting properties, was another additive considered as a taste deterrent. In April, 1983, the New Gasoline Corp, of Arlington, Massachusetts was preparing to market the fuel Hydrolene, which contained up to 10% dimethoxymethane (methylal) blended with methanol.⁽³⁹⁾ Celanese and Bank of America also expressed interest in producing blends of methylal and methanol.⁽⁴⁰⁾ Although no claims were made by any of these companies about the effect on the taste of methylal/methanol blends, methylal should act as a deterrent to the ingestion of methanol because of its pungent taste and chloroform-like odor.

Several compounds have been proposed and used as additives to produce a foul- or bitter-tasting product. Several compounds are listed in Table 6, along with their bitterness thresholds (if available), an indication of the minimum concentration required to produce a bitter taste. Proctor and Gamble uses the additive Bitrex (denatonium benzoate) in several of its detergent and household cleaning products to prevent unintentional ingestion.⁽⁴²⁾ Bitrex is 20 times as bitter as strychnine,⁽⁴³⁾ and is considered the most bitter substance known.⁽⁴¹⁾ In one study, the addition of 0.0011% Bitrex significantly reduced the amount of liquid dishwashing detergent consumed by 18- to 47-month-old children from accidental ingestion.⁽⁴⁴⁾ Bitrex is used as a taste deterrent in other applications, including paints,^(45,46,47) herbicides,⁽⁴⁸⁾ insecticides,⁽⁴⁹⁾ nail biting and thumb sucking deterrent drugs,⁽⁵⁰⁾ rubbing alcohol,⁽⁴³⁾ vegetable oils,⁽⁵¹⁾ and ethanol used for alcoholic toilet preparations and related articles.^(52, 53, 54) The use of Bitrex is effective in concentrations of 2 to 3 mg/liter and is desirable due to the minimal residue left after evaporation. Brucine, quassin, and sucrose octaacetate are other commonly used taste deterrents which have been used in some or all of the following products: hair and scalp preparations, lotions and creams for the head, face and body, deodorants for the body, perfumes, shampoos, soap and bath preparations, external pharmaceuticals, disinfectants, insecticides, fungicides and other biocides, and cleaning solutions including household detergents.

H. Dyes and Colorants

Dermal contact with methanol is one route in methanol poisoning. The addition of a dye would serve to identify the fuel as poisonous and deter the improper use of methanol as a degreaser or cleaning agent, during which skin contact and subsequent absorption could result. If a dye temporarily colored the skin, one would probably not use the treated methanol as a cleaning solvent. In addition, an intense or repulsive color would deter the ingestion of methanol and appear unpalatable even when diluted.

TABLE 6. COMPOUNDS FOR FOUL TASTE(41)

<u>Compound</u>	<u>Bitterness Threshold</u>	<u>Comments</u>
Absinthin	1:70,000	very bitter; chief bitter principle of wormwood
Aldehol		disagreeable odor; for denaturing alcohol (ethanol)
Benzyl alcohol		sharp burning taste; faint aromatic odor
Benzyl benzoate		sharp burning taste; pleasant aromatic odor
Benzthiazide		bitter taste
Bitrex	1:1,000,000	most bitter substance known to man. Added to toxic substances as a deterrent to accidental ingestion
Brucine	1:220,000	very bitter taste; very poisonous; used in denaturing alcohols and oils
Capsaicin	1:100,000	burning taste
Collinsonia extract		peculiar odor; bitter, astringent taste
Columbin	1:60,000	major bitter principle from the root of <i>Jatrorrhiza palmata</i> Miers; very bitter
Conduragin	1:20,000	bitter principle from Condurango bark, astringent, aromatic bitter
Dimethylformamide		universal organic solvent; faint amine odor
Ethyl citrate		bitter oily liquid
Furfuryl alcohol		bitter taste, faint burning odor; poisonous
Humulon		bitter taste especially in alcoholic solutions
Isoquassin		bitter principle from Jamaica quassia
Isovaleric acid		acid taste; disagreeable rancid-cheese odor
Lupulon		bitter taste especially in alcoholic solutions
Marrubiin		diterpene lactone principle isolated from white horehound

Some investigators examined the cutaneous exposure of human subjects to methanol. Dutkiewicz, Konczalik, and Karawacki⁽⁵⁵⁾ determined a mean value for the absorption rate of methanol through the skin of 0.192 mg/cm²/min. Using this value, the researchers calculated the absorption from immersing the whole hand (about 440 cm² surface area) in methanol for twenty minutes. This immersion would result in the absorption of 1.7 mg (2 mL) of methanol. The absorption of 2 mL of methanol is approximately 5 percent of the usual fatal dose, and 33 percent of the smallest reported fatal dose (6 mL) by ingestion. Although it is unlikely that one would immerse a hand in methanol for twenty minutes without some discomfort, case studies have shown that industrial workers (painters, varnishers, hatters, etc.) have experienced blindness or even death from cutaneous exposure to methanol. Case histories of cutaneous methanol poisoning include a painter who went blind after spilling methanol on his clothes and shoes, and infants who died from a methanol soaked compress applied to their chests or under their rubber pants.

Dutkiewicz and coworkers also determined that the rate of methanol absorption was time-dependent.⁽⁵⁵⁾ Table 7 illustrates the absorption rate of methanol. The absorption rate consisted of two parts (Figure 5). In the first part, the absorption rate increases with longer exposure times until about 30 minutes have elapsed. The increase in absorption rate for the first part is approximately 0.0053 mg/cm²/min². The second part showed a slight decrease in absorption rate for the remainder of the 60 minute exposure time. No data was available for exposures longer than 60 minutes. In addition, the overall absorption rate of methanol was comparable to benzene, xylene, and carbon disulfide.

TABLE 7. METHANOL ABSORPTION RATE THROUGH THE SKIN AT DIFFERENT EXPOSURE TIMES⁽⁵⁵⁾

Exposure Time (min.)	Number of Experiments	Range of absorbed doses, mg	Absorption Rate Through the skin (mg/cm ² /min)	
			Average	Range
15	3	22-27	0.146	0.131-0.161
20	3	38-40.8	0.175	0.169-0.182
30	6	65-81	0.225	0.193-0.241
35	3	81-92	0.220	0.206-0.234
45	3	92-108	0.198	0.182-0.214
60	4	119-130	0.187	0.176-0.193
Mean Value: 0.192				

Tada, et al,⁽⁵⁶⁾ conducted absorption experiments on male subjects using methanol, 10 volume percent toluene with methanol, and 50 volume percent methylchloroform with methanol. The blood methanol content was monitored during the experiments at regular intervals. The work demonstrated that methanol was rapidly absorbed through the skin, and that cutaneous absorption is a major route for methanol intake.

Ferry, Temple, and McQueen^(57, 58) investigated the influence of combinations of methanol and petrol (gasoline) on dermal absorption. Blends of 85%, 50%, and 15% gasoline with methanol were

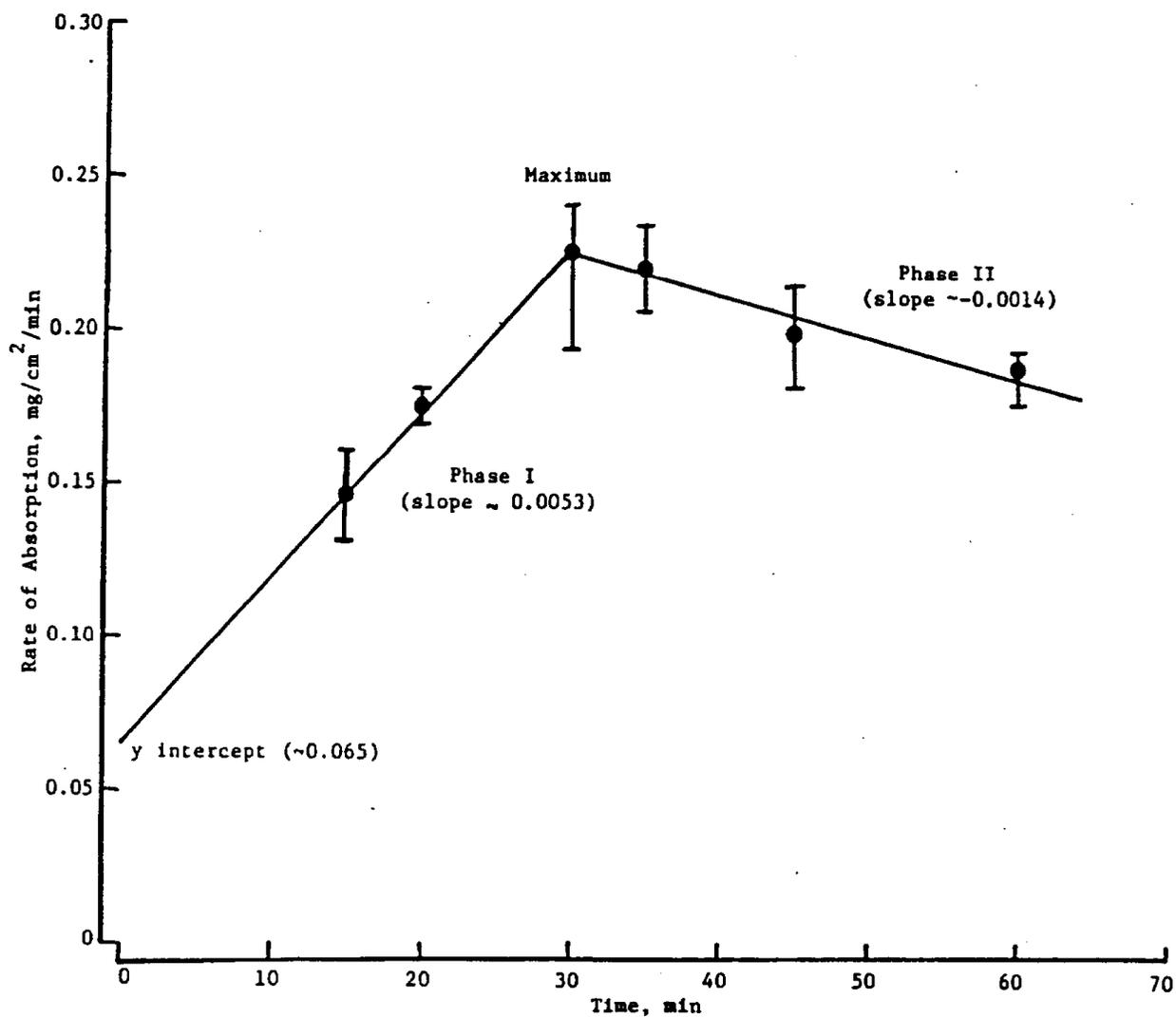


FIGURE 5. EXPERIMENTAL RATE OF METHANOL SKIN ABSORPTION VERSUS EXPOSURE TIME(56)

examined. The effectiveness of barrier creams for preventing methanol absorption was also studied. After exposure, the change in skin appearance was noted for each test subject. Methanol alone caused the least dermal change, while the methanol/petrol blends caused the skin appearance to be very white and dry. Several hours were required for the skin to return to its normal appearance. The methanol/gasoline blends were described by the test subjects as irritating, with most discomfort caused by the 50% mixture. The gasoline mixtures modified the absorption process and allowed greater amounts of methanol to be absorbed. The use of barrier creams did not protect the skin from methanol penetration, and appeared to reduce the capacity of normal skin to resist the absorption of methanol. In other experiment, 15% methanol in gasoline was applied to a 75 cm² area of the forearm on two human subjects. After one minute, an increase in the sensation of heat occurred and the experiment had to be terminated after five minutes because the condition became severe. The skin remained inflamed for three days but did not blister. In each experiment, the absorption of methanol from a mixture with gasoline was more likely to be irritating because of the de-fating effect caused by the petroleum distillate.

The addition of a dye or colorant to identify and to deter the improper use of fluid is a common practice. The addition of a dye to stain temporarily the skin, however, is not a common practice. A methanol fuel containing a dye to stain the skin could result in irreversible coloration of clothing and vehicle components, cause excess engine wear due to deposits (although this has not been thoroughly investigated), and lead to additional exposures when trying to remove the dye from skin or clothing.

Several alcohol-soluble dyes are available on the market in a rainbow of colors. The addition of dyes has historically identified various fluids, especially in automotive applications, and commercial methanol products have typically been blue in color.⁽⁵⁹⁾ Table 8 presents a general list of fluids and the colors used for identification. The only colorants previously used in denaturing ethanol are methyl violet (S.D.A. 33) and iodine. Both the colorants produce a deep blue to violet color.

One company, the Lindele Corporation in Orange, California, has produced two methanol fuels containing dyes. One product was for racing applications (Racing Blue), and the other was for street vehicles (Red fuel). Both contained proprietary additive packages, however, the dyes used in these fuels were added as a method of leak detection rather than as a stain for the skin.

The use of dyes in methanol would probably have little or no impact on the exhaust emissions, if the dyes were used at concentrations equal to or lower than those currently used in gasoline (up to 40 mg/gal). The impact on the exhaust emissions from higher dye concentrations would depend on the chemical makeup of the dye. Dyes containing metals such as manganese (permanganate) or halogens (chlorine, bromine, iodine) should be avoided because they may damage the emission control devices and may result in exhaust emissions that could represent human health hazards.

I. Odorants

Another major route of methanol poisoning is inhalation. Methanol does not have a strong or distinctive odor to identify its presence, and when pure, has such a low odor intensity that one could be exposed to hazardous levels without realizing it. The addition of odorants would serve to identify the presence of methanol, and as a warning of possible hazardous conditions. A suitable odorant should co-evaporate with methanol and be detectable at a much lower concentration than the methanol vapor alone.

The Occupational Safety and Health Administration (OSHA) set a workplace ceiling level standard of 150 ppm (200 mg/m³) for methanol in air. Other standards for methanol exposure include the American Conference of Governmental Industrial Hygienists (ACGIH) and OSHA threshold limit value (TLV) of 200 ppm (260 mg/m³), ACGIH short term exposure limit of 245 ppm (310 mg/m³), and the American National Standard Institute (ANSI) ceiling concentration of 600 ppm (760 mg/m³) and an eight

TABLE 8. GENERAL AUTOMOTIVE FLUID COLORS(60,61)

Fluid	Color
Antifreeze	yellow-green blue
Automotive transmission	red
Aviation gasoline(61)	
Grade 80	red-max. 0.5 mg/gal blue ^a + max. 8.65 mg/gal red ^b
Grade 100	green-max. 4.7 mg/gal blue ^a + max. 5.9 mg/gal yellow ^c
Grade 100LL	blue-max. 5.7 mg/gal blue ^a
Brake	
DOT 3 and 4	colorless to amber
DOT 5	blue
Gasoline	orange-red green blue clear bronze
Hydraulic	green
Window washer solvent	light blue

^a1,4-dialkylamino-anthraquinone.

^bmethyl derivatives of azobenzene-4-azo-2-naphthol (methyl derivatives of Color Index No. 26105).

^cp-diethylaminoazobenzene (Color Index No. 11020).

hour, time weighted concentration of 220 ppm (260 mg/m³). The IDLH (Immediately Dangerous to Life or Health) value for methanol is set at 25,000 ppm, and the lower explosive limit is approximately 67,000 ppm. The values for the odor threshold have been reported to range from 100 to 2000 ppm.⁽²³⁾ Varying levels of impurities in methanol may account for this discrepancy; since compounds of low odor are greatly influenced by the presence of odorous impurities. If the odor threshold was at the upper end of the range, then one might not be able to detect levels where physiological effects could result.

Keller, Nakaguchi and Ware⁽³⁾ screened eight substances for their effect on the odor threshold of methanol. These substances were screened initially by preparing solutions with methanol in open volumetric flasks (Table 9). The more promising of these substances for cost effectiveness and odor threshold were tested further in a closed room. A measured quantity of each solution was allowed to evaporate in the room to give a 480 ppm (610 mg/m³) concentration of methanol. The odor in the room was then evaluated by two or more individuals. The results of this second experiment are presented in Table 10. The odor threshold for reagent grade methanol was approximately 400 ppm (505 mg/m³).

TABLE 9. ODORANT TESTS: ODOR OF VARIOUS ODORANTS ABOVE A SOLUTION IN METHANOL (In An Open Volumetric Flask)

Compound	Molarity in Methanol	Odor
Toluene	1.0	very strong
	0.1	slight
	0.01	not detectable
"Xylenes"	1.0	strong
	0.1	slight
Gasoline (estimated mol. wt. 100)	0.7 ^a	strong
	0.14 ^b	slight
	0.07	very slight
Ethyl acrylate	1.0 x 10 ⁻³	strong and irritating
	1.0 x 10 ⁻⁴	strong
	1.0 x 10 ⁻⁵	slight and not irritating
	1.0 x 10 ⁻⁶	slight and not irritating
Acrolein	0.01	slight
Crotonaldehyde	0.01	slight
n-Butyl mercaptan	5.4 x 10 ⁻⁴	strong and very unpleasant
t-Butyl mercaptan	5.1 x 10 ⁻⁴	strong and unpleasant

^a10 vol % or 9 wt % gasoline.

^b2 vol % or 1.8 wt % gasoline.

TABLE 10. ODORANT TESTS: EVAPORATION OF A SOLUTION IN METHANOL INTO A CLOSED ROOM^a

Odorant	Concentration in Methanol, Molarity	Approximate Concentration of Odorant in Air, ppm by Vol.	Observations
Gasoline	4 ^b	6	no noticeable odor odor "like old paint," "sweet," not very alarming ^d
	12 ^c	18	
Ethyl acrylate	1.0 x 10 ⁻⁴	0.002	odor very noticeable, distinctive, rather sweet, "like plastic"
t-Butyl mercaptan	5.1 x 10 ⁻⁴	0.01	odor strong, unpleasant, "like natural gas"
	1.7 x 10 ⁻⁴	0.003	odor fairly strong, unpleasant, "like natural gas"
	5.1 x 10 ⁻⁵	0.001	odor noticeable, unpleasant
n-Butyl mercaptan	5.4 x 10 ⁻⁴	0.01	odor very strong, very unpleasant
	1.8 x 10 ⁻⁴	0.004	odor very strong, unpleasant
	5.4 x 10 ⁻⁵	0.001	odor noticeable, more unpleasant than t-butyl mercaptan
Methanol only	--	330 ^e	odor noticeable, rather sweet but irritating to nose and throat

^aSufficient to give 480 ppm (vol) methanol in the air.

^b5 wt % gasoline.

^c15 wt % gasoline.

^dThe odor was not recognizable as that of gasoline to anyone.

^eMethanol did not completely evaporate.

The most effective odorants tested in the study were determined to be n-butyl mercaptan and ethyl acrylate. Gasoline, giving an "old paint" odor to the blend, was not considered as effective as the others. At very low concentration levels, the odor of ethyl acrylate was described as pleasant, while at higher concentrations, the odor was found to be extremely irritating. The two mercaptans screened in the study produced very distinctive odors even at very low concentrations, however, n-butyl mercaptan was considered more unpleasant than t-butyl mercaptan.

While the mercaptans were found to be effective odorants in Keller's work, their odor could produce confusion about the source since mercaptans are also added to natural gas. Mercaptans are also thought to be susceptible to oxidation in methanol. This oxidation process would convert the mercaptans to sulfur oxides, which have a much lower odor intensity. Organic sulfides (i.e., methyl sulfide, ethyl sulfide) have an odor slightly different from, but equivalent in intensity to mercaptans. Organic sulfides are also more resistant to oxidation, and would be viable alternatives to odorous additives to methanol. Vehicles using methanol fuel with mercaptans or organic sulfides as odorant additives would produce exhaust emissions containing sulfur dioxide and sulfate. These exhaust emissions would be nonexistent when using pure methanol; however, the levels of sulfur dioxide and sulfate emissions would be on the order of one-tenth those from the sulfur in conventional gasoline.

The use of mercaptans or organic sulfides at the levels necessary to produce a strong and unpleasant odor in methanol should not provide any problems with vehicle operation or with the health of people using the fuel blend. The use of ethyl acrylate as an odorant may not be as practical as the sulfur-containing odorants, since ethyl acrylate levels that were high enough to be detected were also irritating. This irritation of the eyes and mucous membranes could be a problem in itself.

In addition to identifying the presence of methanol vapor, the use of odorants would also act as deterrents for the ingestion and for the dermal contact of ethanol fuel. Before 1880, the only commercially available source of methanol was in the form of wood alcohol, which had a vile taste and disgusting odor. For this reason, methanol was rarely ingested or used in contact with the skin. After an inexpensive method of deodorizing wood alcohol was introduced, methanol became a substitute for ethanol and as many as one thousand cases of poisoning were attributed to methanol between 1888 and 1913.⁽³¹⁾ An odorant added to methanol fuel should discourage the ingestion and dermal contact of methanol fuel as did the unpleasant odor of wood alcohol. Table 11 lists several malodorous substances which could be used as odorants in methanol fuel.

TABLE 11. MALODOROUS SUBSTANCES

<u>Compound</u>	<u>Odor</u>	<u>Source</u>
Aldehol	disagreeable odor	1
Acrolein	pungent odor	3
Bis(methylthio)methane	odorous principle of white truffle	1
trans-2-Butene-1-thiol	scent of skunk	64
n-Butyl mercaptan	heavy skunk odor	3
sec-Butyl mercaptan	heavy skunk odor	1, 65
t-Butyl mercaptan	heavy skunk odor	3, 65
Crotonaldehyde	vapor extremely irritating	3
Dimercaprol	pungent offensive odor of mercaptans	1
Ethyl acrylate	acrid, penetrating odor	3
Ethyl mercaptan	penetrating leek-like odor	1
Ethyl sulfide	etheral odor	61
Gasoline	characteristic odor	3, 65
Isoamyl mercaptan	repulsive odor, striped-skunk defensive secretion	1
Isoamyl sulfide		1
Isobutyl mercaptan	heavy skunk odor	3
Isobutyl sulfide		1, 65
Methyl acrylate	acid odor	1
3-Methylbutanoic acid	disagreeable, rancid-cheese odor	1
3-Methyl-1-butanethiol	scent of skunk	64
2-Methyl-2-butene	disagreeable odor	1
3-Methylbutenyl thioacetate	striped-skunk defensive secretion	1

TABLE 11 (CONT'D). MALODOROUS SUBSTANCES

<u>Compound</u>	<u>Odor</u>	<u>Source</u>
Methyl mercaptan	odor of rotten cabbage	1
2-Methylquinoline	quinoline odor	1
Methyl sulfide	disagreeable odor	1, 65
2-Naphthyl mercaptan	disagreeable odor	1
1-Octanol	penetrating, aromatic odor	1
2-Octanol	aromatic, yet somewhat unpleasant odor	1
1-Pentanethiol	penetrating, unpleasant odor	1
1,3-Propanedithiol	disagreeable odor	1
Pyrazine	strong pyridine-like odor	1
Pyrazole	pyridine-like odor	1
2-Pyrazoline	faint amine odor	1
Pyridine	characteristic disagreeable odor	1
Pyrrolidine	unpleasant ammonia-like odor	1
3-Pyrrolidine	unpleasant ammonia-like odor	1
Quinoline	penetrating odor, not as offensive as pyridine	1
2-Quinoline methanethiol	striped-skunk defensive secretion	1
2-Quinoline thioacetate	striped-skunk defensive secretion	1
Thiophene	slight aromatic odor resembling that of benzene	66
Trans-2-butene-1-thiol	striped-skunk defensive secretion	1
Trans-2-butenyl thioacetate	striped-skunk defensive secretion	1
Toluene	benzene-like odor	3
Xylenes		3

III. EXPERIMENTAL PROGRAM

The experimental portion of this program has been broken down into a number of tasks. Initially, Task 1 - Literature Search and Additive Evaluation was designed to perform a literature search and laboratory screening of potential additive candidates. Laboratory screening involved the evaluation of potential candidates for flame luminosity, fuel lubricity, and flammability limit. Task 1 was later expanded to include additional laboratory evaluation, outdoor burns, and hydrocarbon speciation of vehicle exhaust emissions. This section discusses the results of the experimental program for Task 1 and the Task 1 Expansion.

A. Additive Candidates from Literature Search

As a result of the literature search and contacts with representatives of the additives manufacturing industry, plus previous experimental programs at SwRI, an extensive list of potential additives for the improvement of flame luminosity, flammability limits, and lubricity/corrosion was developed. Table 12 lists all additive candidates investigated in this program grouped according to these three categories. Many compounds on this list were screened initially to determine their effect on flame luminosity. From this screening, many potential compounds were eliminated due to poor luminosity. Compounds listed by CARB as known or suspected toxic air contaminants (Table 13) or substances which could react to form these listed compounds as combustion products were avoided during the experimentation phase of this task. Commercial additive manufacturers, who expressed interest in supplying candidate additives, were furnished with this list. Many additives listed in Table 12 from commercial manufacturers were identified only by a code number at the request of the manufacturer. In the Task 1 Expansion, additional compounds were tested. These compounds were also included in Table 12. Results for the additive evaluations are given in the appropriate sections below.

B. Peer Review Meeting

On Thursday, August 23, 1990, a project review meeting was held at the SCAQMD office in El Monte, California. The purpose of this meeting was to discuss the results from the Task 1 - Literature Search and Additive Evaluation and to provide an opportunity for the scientific, technical, and commercial communities to make comments and suggestions on these results. This meeting was an open forum for the presentation and exchange of ideas on the topic of additives for methanol fuel property improvement and safety. Representatives from all areas involved with methanol fuel were invited, including:

- Engine and vehicle manufacturers
- Fuel and additive suppliers
- Individuals/companies working in safety-related areas
- Government officials.

Specific individuals within these areas were sent invitations to attend this meeting as well as a copy of the Task 1 Interim Report, titled "Methanol Fuel Additive Demonstration," before the meeting for their review. Table 14 lists many of the people who attended the meeting.

The results from Task 1 for flame luminosity, fuel lubricity, and flammability limit were discussed in detail with the participants. The meeting was hosted by Manjit S. Ahuja, CARB. After reviews of the

TABLE 12. LIST OF CANDIDATES USED FOR LUMINOSITY,
LUBRICITY, AND FLAMMABILITY SCREENING

A. Luminosity Improvers

1-Butene
1-Hexyne
1-Indanone
1-Pentyne
1-Phenyl octane
1-Propanol
1,2,4,5-Benzenetetracarboxylic acid
1,3-Butadiene
2,2-Dimethylbutane
2,4-Pentanedione
3-Methylpentane
4-Methyloctane
4-Tertiary butylpyridine
7-Trans-7-tetradecene
90 RON reformat
AB^a
Acetone
Acetonitrile
Acetylferrocene
Aluminum stearate
Aniline
AO^a
BBR^a
Benzaldehyde
Benzoic acid
Benzophenone
Benzoylpyridine
Borane-pyridine complex
Boric acid
Boron oxide
Butane
Butyl ether
Butylethyl ether
Calcium stearate
Carbazole
Cyclohexane
Cyclohexanol
Cyclohexene
Cyclooctane
Cyclopentane
Cyclopentene
D1280X^b (Omstar)
DB7^a
Decahydronaphthalene
Decalin

TABLE 12 (CONT'D). LIST OF CANDIDATES USED FOR LUMINOSITY,
LUBRICITY, AND FLAMMABILITY SCREENING

Dicyclohexylamine
Dicyclopentadiene
Dicyclopentadiene 97^b
Diethanolamine
Dimethoxymethane
Dimethoxytetraethylene glycol
Dimethyl ether
Dimethylnaphthalene
DP5-160^b
DP6-46^b
Ester based synthetic lubricant, O-149^b (USAF)
Ester based synthetic lubricant, O-148^b (USAF)
Ester based synthetic lubricant, O-160^b (USAF)
Ethanol (reference compound for luminosity)
Ethyl ether
Ethyl acetate
Ethyl alcohol
Ethyl tertiary butyl ether (ETBE)
Ethyl formate
Ethylacetoacetate
Ethylene glycol
F^a
Ferrocene
Formamide
Furan
Furfurylamine
G1280X^b (Omstar)
H229^b (Howell Hydrocarbons, C7-C9 hydrocarbon mix, boiling range 240 - 360°F)
H400^b (Howell Hydrocarbons, middle distillate solvent extract, C10-C13 aromatics, boiling range
340-490°F)
Heptane
Hexane
HSR naphtha
Hydrocarbon grade DCPD^b
Indan
Indene
Iron stearate
Isoamyl acetate
Isooctane
Isopentane
Isopropyl alcohol
Jet Fuel (Jet A)
Light hydrocrackate (BP Oil)
Lithium acetate
Lithium stearate
Mesitylene
Methacrylic anhydride

TABLE 12 (CONT'D). LIST OF CANDIDATES USED FOR LUMINOSITY,
LUBRICITY, AND FLAMMABILITY SCREENING

Methacrylic acid
Methyl tertiary butyl ether (MTBE)
Methyl naphthalene
Methylcyclopentane
Methylsulfoxide
MO^a
Naphthalene
Nigrosine
Nitrobenzene
N,N-Dimethylformamide
Normal butanol
Normal-Butyl acetate
Normal-Butyl benzene
Normal-Propyl benzene
Octane
OS 85801^a
OS 85803^a
OS 85800^a
OS 85802^a
PBVF^a
Pentamethylbenzaldehyde
Pentamethylbenzene
Pentane
Pentane
Phenol
Phenylcyclohexane
Piperidine
Polyester grade DCPD^b
Polyphenol ether
Pyridine
Pyrrole
Pyrrolidinone
Refined peanut oil
Secondary butylbenzene
Sodium stearate
Sodium acetate
Tertiary amyl alcohol
Tertiary butyl alcohol (TBA)
Tertiary amyl methyl ether
Tertiary utylethyl ether
Tetrahydrofuran
Tetrahyrdonaphthalene
Tetralin
Toluene
Trans cinnamic acid
Tricresyl phosphate (TCP)

TABLE 12 (CONT'D). LIST OF CANDIDATES USED FOR LUMINOSITY,
LUBRICITY, AND FLAMMABILITY SCREENING

Tridecyl alcohol
Trimethyl borate
Unleaded gasoline (35% aromatics)
VX 3181^a
VX 3194^a
VX 3174^a
VX 3195^a
VX 3182^a
Zinc stearate
Zinc dithiophosphate

B. Lubricity-Corrosion Improvers

D1280X^b (Omstar)
DCI-4A^b (DuPont)
FC-708^b (3M)
G1280X^b (Omstar)
IPC 4410^b (ChemLink, Inc.)
Ketjenlube 135^b (Akzo Chemicals, Inc.)
Metacor 704^b (Cortec)
OS 83934^a
OS 85798^a
OS 85800^a
OS 85801^a
OS 85802^a
OS 85803^a
Paranox 15^b, zinc dithiophosphate (Exxon)
RBUK AG^b (submitted by Acurex from Rheinische Braunkohlen Union Kraftstoff AG)
Tricresyl Phosphate (FMC Corp)
Unicor J^b (UOP, Inc.)
VX 3181^a
VX 3182^a
VX 3174^a

C. Flammability Limit Improvers

1-Butene
90 RON reformat
Butane
Butene
Cyclohexane
Cyclopentane
D1280X^b (Omstar)
Dimethyl ether
Ethyl tertiary butyl ether (ETBE)
G1280X (Omstar)
Methyl tertiary butyl ether (MTBE)

**TABLE 12 (CONT'D). LIST OF CANDIDATES USED FOR LUMINOSITY,
LUBRICITY, AND FLAMMABILITY SCREENING**

Pentane
Pentene
Tetralin
Toluene
Unleaded gasoline

^aCoded sample

^bCommercial product or product name

TABLE 13. CARB LIST OF KNOWN AND SUSPECTED
TOXIC AIR CONTAMINANTS⁽⁶⁹⁾

Acetaldehyde	Polynuclear aromatic hydrocarbons including:
Allyl chloride	Acenaphthene
Acrolein	Acenaphthylene
Asbestos	Anthracene
Benzene	Benzo(a)anthracene
Benzyl chloride	Benzo(a)pyrene
Beryllium	Benzo(b)fluoranthene
1,3-Butadiene	Benzo(ghi)perylene
Cadmium	Benzo(k)fluoranthene
Carbon tetrachloride	Chrysene
Chloroform	Dibenzo(a,h)anthracene
Chlorobenzene	Fluoranthene
Chlorophenols	Fluorene
Chloroprene	Indeno(1,2,3,-cd)pyrene
Chromium	Naphthalene
Cresol	Nitro PAHs
Dialkylnitrosamines	Phenanthrene
Dibenzofurans	Pyrene
p-Dichlorobenzene	Polychlorodioxins
Dimethyl sulfate	Polychlorinated biphenyls
1,4-Dioxane	Propylene oxide
Dioxins	Radionuclides
Di(2-ethylhexyl)phthalate	Styrene
Ethyl acrylate	Toluene di-isocyanates
Ethylene dibromide	Trichloroethylene
Ethylene dichloride	2,4,6-Trichlorophenol
Ethylene oxide	Vinyl chloride
Formaldehyde	Vinylidene chloride
Glycol ethers	Xylenes
Hexachlorobenzene	
Inorganic arsenic	
Inorganic lead	
Maleic anhydride	
Manganese	
Mercury	
Methyl bromide	
Methyl chloroform	
Methylene chloride	
4,4-Methylenedianiline	
N-Nitrosomorpholine	
Nickel	
Nitrobenzene	
Perchloroethylene	
Phenol	
Phosgene	

TABLE 14. LIST OF ATTENDEES FOR THE PEER REVIEW MEETING

<u>Name</u>	<u>Organization</u>
Howard L. Sargent	Omstar Products
Morton Z. Fainman	MZF Associates
L. M. Gibbs	Chevron Research and Technology
Wendy Clark	BP Oil
Wolfgang Groth	Volkswagen of America
Sandy Minner	Unocal
Jeffrey Herzog	EPA
T. A. Coultas	WJSA
L. M. Reese	CEC
Mike Tamayo	Toyota Technical Center
Tony Martino	GM
Richard Skaggs	CBA
Vittoria Battista	Transport Canada
Richard Meyer	Nalco Chemical
Clarence Collier	CARB
Michael Berg	Petrolite
Michael Jackson	Acurex
Dick Cooke	Omstar
Paul Machiele	EPA
Ken Stamper	NREL
Avtar S. Bining	CARB
Michael Hinton	Morton International
Don Kopinski	EPA
Geeta Patel	CARB
Michael McCormack	CEC
Jason McMillen	SCAQMD
Sarah Santoro	CARB
Jerry Wiens	CEC
Roberta Nichols	Ford

program by Dr. Lawrence Smith, and Messrs. E. Robert Fanick, and John Russell, SwRI; presentations were made by Jeff Herzog and Paul Machiele, EPA; Vittoria Battista, Transport Canada; and Howard Sargent, Omstar Products. Jeff Herzog showed a video of indoor and outdoor burns to illustrate additives for enhanced flame luminosity. These burns included additives such as triboryl stearate, sodium hydroxide, and allyl alcohol. Vittoria Battista showed a video on burns in actual vehicles with gasoline and methanol. These burns were performed at various locations on the vehicle including the engine compartment and underneath the vehicle as well as on two surfaces (on gravel and in the grass). Each burn demonstrated the differences between the flame luminosity of the two fuels and the damage caused by the burning fuel at these locations.

C. Discussions with Participants from Peer Review Meeting

Several participants at the peer review meeting were contacted after the meeting concerning their in-house methods for examining flame luminosity, fuel lubricity, and flammability limits as well as their ideas on how to improve the procedures employed by SwRI in this program. Each company had specific interests in the various analytical procedures. Comments from each company are summarized as follow.

1. Fuel Suppliers

- Unocal was concentrating its efforts toward reformulated fuels and natural gas. They also wanted to see additional emission tests.
- Chevron was waiting on the development of a luminosity test by ASTM. Chevron has been looking at the exhaust emissions from methanol fueled vehicles, and they are participating in the CEC program to dispense M85 in California stations. They want to see more work done on optimizing the vehicle. They also saw a need to find a correlation between outdoor burns and the laboratory test procedures.
- BP Oil was concerned that the SwRI flame luminosity procedure was measuring flame brightness rather than visibility; visibility was considered more important than brightness in the detection of a flame. Flame color was also an important contributor to flame visibility. BP Oil has been working closely with the ASTM on the luminosity procedure, and they had also been working on designer additives that may produce the desired effects in the flame, but this work was never completed.

2. Engine and Vehicle Manufacturers

- Volkswagen felt that flame luminosity was only a perceived problem today because the general public is not experienced with fuel methanol. They were more interested in an alternative solution to the perceived problem such as placing a substance like a plastic under the vehicle that would ignite and burn with a visible or smokey flame in the event of a fire.
- GM was concerned about fuel lubricity. They suggested that the technique should be similar to the type of motion being studied. They were also concerned about additive weathering, and the loss of volatile components for cold-starting, and low temperature flammability. Some research on flame luminosity has been done by GM. Their procedure involved a photometer with a response similar to the human eye and a pyroelectric detector for infrared (heat). The fuel was burned in a burner which produced a laminar flame and avoided intermittent boiling of the liquid fuel. A black chimney was placed around the flame with small holes of about one mm in diameter along the length of the cylinder and the tests were performed in the dark. The luminosity and heat along the entire column of the flame were integrated to provide the flame luminosity. In addition, the evaluation of any fuel formulation should include vehicle cold-starting and fuel weathering. Cold-starting of a vehicle should be one of the major considerations in selecting additives. A fuel should cold-start down to -20 °F; if not then the fuel should be ruled out. For lubricity, they considered two vehicle components susceptible: the fuel pump and more importantly the fuel injector. In addition, they suggested that the exhaust emissions from M85 were better than M100.
- Ford suggested that the development of additives should continue and that the CARB fuel blend should be included in the Auto/Oil Air Quality Improvement Study.

3. Additive Suppliers

- Atomergic Chemetals produces a bitter agent called Vilex which is reported to be about 2 to 4 times more bitter than the previously discussed Bitrex. They were very interested in evaluating this material as a potential fuel additive.
- Nalco was mostly concerned with lubricity; they do not have any procedures for testing the luminosity. For lubricity, they suggested a spindle corrosion test or ASTM D-665.
- Petrolite was mainly concerned with fuel lubricity, corrosion, and how the BOCLE test related to real world situations. They wanted additional basic research with emissions testing before continuing with luminosity evaluations.
- Morton was more concerned about the loss of market share for their colorants that would result from the trends toward different fuels than about analytical procedures.
- Omstar wanted to reopen the issue of boundary layer for lubricity improvement. They also wanted additional emission tests of the lubricity additives.

4. Governmental Agencies

- Transport Canada was concerned about performance, especially cold-starting. They were interested in an educational approach as a means of improving the safe use of methanol. They are also interested in work being performed by the EPA to place foams in the fuel tank to reduce the tank flammability. They had some concern about the deterioration of the foam with long term exposure to the fuel.
- EPA was interested in all aspects of methanol including luminosity, flammability, fuel tank explosions, taste, odor, contamination in ground water, cold-starting, fuel lubricity, and upper cylinder wear. They wanted to see requirements for taste deterrents to allow for the dilution of the fuel in an underground aquifer. The dye, denaturant, and odorant should still be effective even after dilution to a very low concentration. A need was expressed to standardize on a single color and odor so that the general public will know and identify the fuel as potentially hazardous. Each issue should be taken by itself and considered for problems individually.

5. Miscellaneous Organizations Involved with Methanol Fuel

- NREL was interested in basic research into the radicals in the flame that cause flame visibility. They also highlighted engineering solutions to solve some of the methanol related problems (e.g., anti-siphoning devices). They also wanted to know what was the ultimate fuel goal (pure methanol or something else?).
- Acurex felt that the improvement of methanol fuel properties was a difficult problem. They wanted more basic research into the structure of additives and suggested engineering the vehicle to help with the problems. Some suggestions included a double wall fuel tank to prevent a spill or a fuel tank made of a material that would burn with a visible flame when ignited.

Some interesting observations resulted from the peer review meeting and from conversations with the individuals listed above. Most companies adopted a wait and see attitude toward developing procedures for flame luminosity. Companies that were looking at flame luminosity improvers were using modified versions of the procedure used in the previous work under this program (which is similar to the proposed ASTM procedure).⁽⁶⁷⁾ Details of the improvements in the flame luminosity procedure will be discussed in the appropriate section below.

D. Lubricity Additives

There are many potential forms of wear with M100 related to corrosion and contact of fuel-wetted engine parts. Some forms of wear include:

- bore and ring
- fuel injectors
- fuel pumps.

Lubricity problems with M100 are caused by washing away of the normal oil film by the liquid alcohol. Removal of the oil film causes increased metal-to-metal contact, with nothing remaining to serve as the lubricant. Excessive wear results. Another problem is corrosion. Corrosion is caused by dissolved combustion products from the fuel, which cause the exposed surfaces to deteriorate.^(9,12) Therefore, fuel lubricity is a concern in developing an additive package for improving the characteristics of the fuel.

1. Apparatus and Procedures

Lubricity experiments employed the BOCLE, an apparatus widely used in military jet fuel lubricity programs.⁽⁶⁸⁾ The BOCLE consisted of a non-rotating, one-half-inch diameter ball held in a vertically-mounted chuck and loaded against the outer surface of a standard Timkin bearing ring. Ball and ring were positioned inside a rectangular reservoir containing 50 mL of test fluid, enough to cover the lower portion of the ring. The ring was mounted axially by a mandrel on a horizontal shaft that passed through the sides of the reservoir's upper section and was connected to a variable-speed motor. BOCLE test conditions included:

Load: 1000 g
Speed: 240 rpm
Duration: 30 min.
Sample volume: 50 mL
Sample temperature: $75 \pm 1^\circ\text{F}$

After completing the 30 minute test, the ball was examined under a microscope, and the characteristic elliptical wear scar was taken as the measure of the fluid's lubricating characteristic under these test conditions. The major and minor axes of the ellipse were determined using an optical microscope with a graduated eyepiece. The average of the two axes was reported as the Wear Scar Diameter (WSD) in millimeters. Figure 6 shows the BOCLE apparatus.

2. Test Results

The WSD was determined for M100, M85, several commercially available corrosion inhibitors and lubricity improvers, and several potential proprietary compounds designed for use in

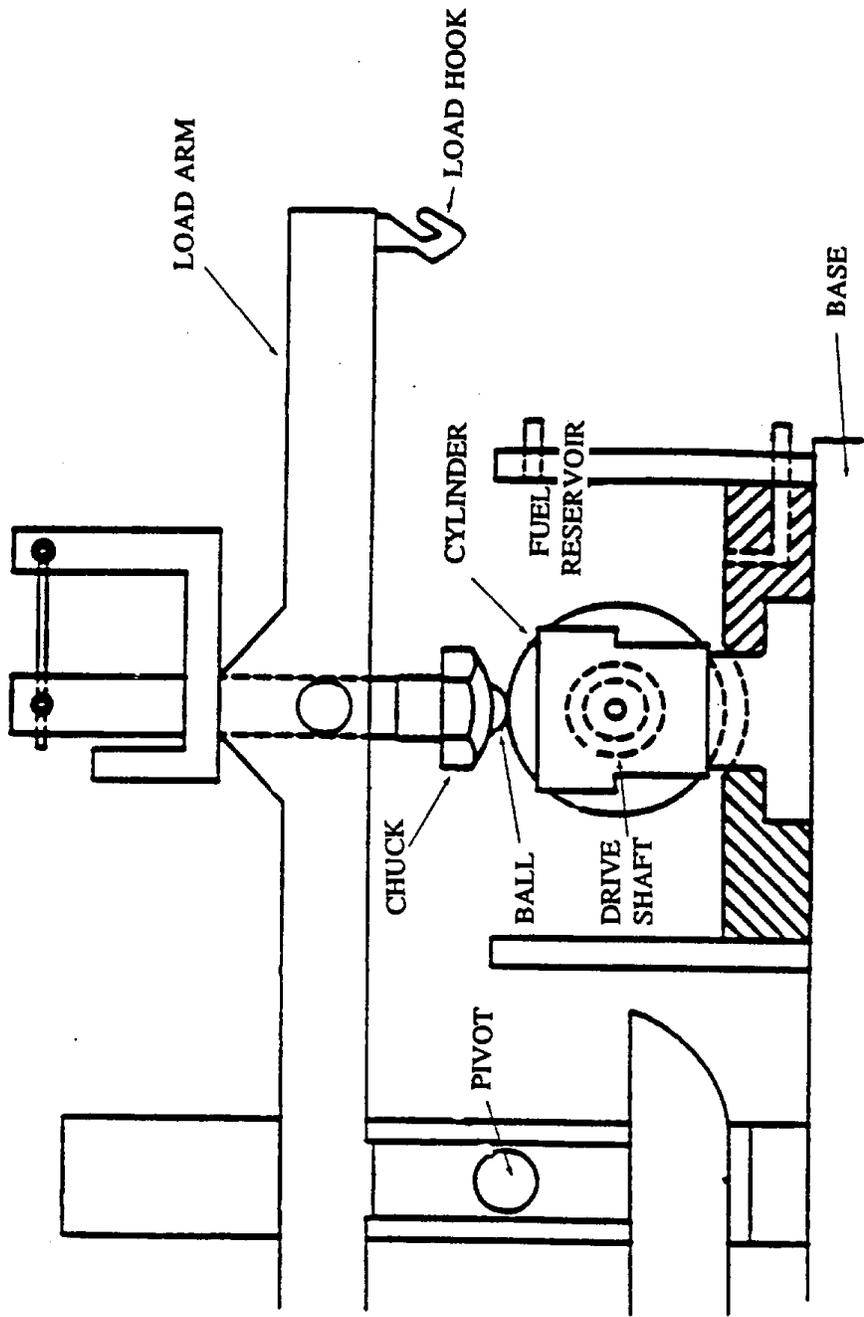


FIGURE 6. SKETCH OF BOCLE APPARATUS

methanol fuel by commercial suppliers. Most of these additives contained proprietary components of either fatty acids or organic amine salts. All lubricity measurements are presented in Table 15. The final column is the net reduction in wear, reported as "% Change." Since M100 provided an average wear scar diameter of 0.55 mm, the calculated improvement in lubricity (negative percent change) was given by:

$$\% \text{ Change} = \left[\frac{WSD_i - WSD_{MeOH}}{WSD_{MeOH}} \right] \times 100$$

Where:

WSD_i = wear scar diameter of compound

WSD_{MeOH} = wear scar diameter of M100 as standard for comparison (0.55 mm)

The WSD for M100 was measured as the reference, and the WSD for M85 was measured as the standard of comparison (diesel and jet fuels typically give WSD of between 0.4 and 0.5 mm when they contain corrosion inhibitor packages). Any wear reduction from M100 was due to the additive, or in the case of M85, the hydrocarbons and lubricity agents in the gasoline. Several additives yielded similar or better WSD as compared to M85, with a percent change greater than negative 15 percent (15 percent less wear than M100).

3. Discussion

Extensive work with the BOCLE on alcohols, gasolines, distillates, and jet fuels indicated that an improvement in lubricity (decrease in WSD) of negative 15 percent or more is significant.⁽⁶⁸⁾ On this basis, the following lubricity improving additives were effective and essentially interchangeable in their potential for a combination of corrosion inhibition and lubricity improvement:

- DCI-4A
- Metacor 704
- Unicor J
- IPC 44210
- VX 3181
- VX 3182
- OS85798
- OS86453
- OS86454
- OS86455
- OS86456
- OS86457
- OS86458
- OS86460

This procedure simulated wear from metal-to-metal contact under load. In actual application, these additives will likely attenuate fuel pump wear where metal-to-metal contact occurs. The effect of these additives on fuel injectors, upper cylinder lubricity, and corrosion were not investigated in this study. Other test procedures must be used to investigate wear in these cases.

E. Flame Luminosity Additives

Flame luminosity is a desirable property for a motor fuel because it allows the detection of flames in the event of an accidental fire.^(1,2) A visible flame allows steps to be taken in avoiding or extinguishing the flame. Conversely, a non-luminous flame may result in danger to victims, observers, and fire fighters when in close proximity to the flame. The mechanisms involved with flame luminosity were discussed in detail in Section II. D. In brief, the luminosity of burning carbon-containing fuels is related to the formation of submicroscopic soot particles during combustion. These carbonaceous particles are heated by the flame, which causes them to emit light at visible wavelengths in a process called "gray-body" radiation. Since methanol burns with a cooler flame and few soot particles are formed, methanol has a low flame luminosity when compared to the luminosity of gasoline and many other flammable hydrocarbons.⁽³⁾

TABLE 15. LUBRICITY MEASUREMENT USING BOCLE

Formulation	Wear Scar Diameter, mm			
	Major Axis	Minor Axis	Average	% Change ^a
Methanol	0.60	0.49	0.55	--
M85	0.48	0.42	0.45	-18
0.6 wt% DCI-4A	0.48	0.40	0.44	-20
0.12 wt% DCI-4A	0.50	0.39	0.45	-18
0.6 wt% Metacor 704	0.47	0.39	0.43	-22
0.6 wt% TCP	0.57	0.47	0.52	-5
0.6 wt% Paramox15	0.85	0.75	0.79	+43
0.6 wt% Unicor J	0.47	0.33	0.40	-27
0.6 wt% FC-708	0.59	0.47	0.53	-3
0.6 wt% KJL	0.56	0.44	0.50	-9
0.6 wt% IPC 4410	0.49	0.36	0.43	-22
0.6 wt% VX 3181 ^b	0.48	0.39	0.44	-20
0.12 wt% VX 3181 ^b	0.47	0.38	0.43	-22
0.6 wt% VX 3182 ^b	0.49	0.40	0.45	-18
0.12 wt% VX 3182 ^b	0.45	0.34	0.40	-27
0.6 wt% VX 3174 ^b	0.59	0.43	0.51	-7
0.12 wt% OS 85798 ^c	0.53	0.37	0.45	-18
0.03 wt% OS 85798 ^c	0.52	0.43	0.48	-13
0.01 wt% OS 85798 ^c	0.56	0.43	0.50	-9
0.03 wt% OS 83934 ^c	0.58	0.45	0.52	-5
5 vol% OS 85800 ^c	0.67	0.53	0.60	+9
5 vol% OS 85801 ^c	0.54	0.42	0.48	-13
1 vol% OS 85801 ^c	0.54	0.45	0.50	-9
5 vol% OS 85802 ^c	0.57	0.46	0.52	-5
7.5 vol% OS 85803 ^c	0.57	0.47	0.52	-5
0.12 wt% OS 86453 ^c	0.49	0.41	0.45	-18
0.12 wt% OS 86454 ^c	0.49	0.40	0.45	-18
0.12 wt% OS 86455 ^c	0.45	0.37	0.41	-26
0.12 wt% OS 86456 ^c	0.49	0.41	0.45	-18
0.12 wt% OS 86457 ^c	0.47	0.35	0.41	-26
0.23 wt% OS 86458 ^c	0.46	0.36	0.41	-26
0.12 wt% OS 86459 ^c	0.58	0.50	0.54	-2
0.12 wt% OS 86460 ^c	0.51	0.40	0.46	-16
0.15 wt% G1280X ^d	0.55	0.46	0.51	-7
0.15 wt% D1280X ^d	0.53	0.48	0.51	-7
0.015 vol% RBUK AG ^e	--	--	0.54	-2
0.5 vol% RBUK AG ^e	--	--	0.52	-5

^aNegative percent change indicated lubricity improvement.

^bAdditive provided by Nalco - coded samples.

^cAdditive provided by Lubrizol - coded samples.

^dAdditive provided by Omstar.

^eAdditive provided by Acurex from Rheinische Braunkohlen Union Kraftstoff AG.

In Task 1 - Literature Search and Additive Evaluation, many compounds were screened for their effect on improving the luminosity of a methanol flame. As part of the expanded Task 1 effort, continued procedural development experiments were conducted to optimize the laboratory procedure for evaluating flame luminosity. The experiments addressed the following questions:

- What is the optimum distance from the flame for the detector?
- Which filters should be used?
- Should the cosine diffuser be used?
- What is the best angle to position the detector?
- What is the best height for the detector?
- What volume should be burned?
- Is there any difference or improvement by using a watch glass rather than a Petri dish?

Similarities and differences between Task 1 and the Task 1 Expansion are presented below.

1. Apparatus and Procedures - Task 1

Figure 7 presents a sketch of the experimental apparatus for flame luminosity measurements. The luminosity instrument consisted of a UDT Instruments Model 40X Opto-Meter™ with a Model 248 Uniprobe detector. This instrument was used in both the Task 1 and the Task 1 Expansion. A No. 111 photometric filter simulated the human visual response to light sources (visible spectrum), and a No. 112 cosine diffuser accounted for the peripheral vision (scattered light response) of the human eye. The diffuser permitted the system to be calibrated in foot-candles with a milliamp output to drive a recorder. Characteristic foot-candle versus time traces were generated during each burn. Some of the more promising candidates were videotaped using a color video camera.

Pre-formulated test samples were introduced from calibrated glass burettes into a Pyrex Petri dish set into an insulating block to inhibit heat loss through the Petri dish. The dish and block were placed under a ventilated hood with a calibrated air flow of 750 cfm (1 mph as measured by hot wire anemometer). The insulating block and all interior surfaces of the hood were painted flat black, and dark room conditions were established before each ignition. In the Task 1 - Literature Search and Additive Evaluation experiments, the optometer sensing head was positioned 18 inches from the vertical center line of the Petri dish. Flames were ignited with an ordinary wooden kitchen match struck and waved over the test sample to start the burn or with a cotton swab dipped into the liquid and ignited with a lighter. Five-mL samples were used for all burns, which resulted in typical durations from 45 to 60 seconds. Some burns occurred for longer periods if the volatility of the liquid was lower. Ethanol was designated as the standard of comparison for luminosity measurements. Amplifying scales on the luminometer and chart recorder were selected and adjusted to provide a 1.0 foot-candle full-chart deflection for ethanol.

No standard specification has ever been established for the minimum perceptible flame luminosity, but a value was requested as part of this project. To identify the minimum perceptible flame luminosity or the estimated minimum threshold visibility as the term will later be referred, numerous burns were performed at SwRI, and a consensus opinion was formed for the estimated minimum threshold

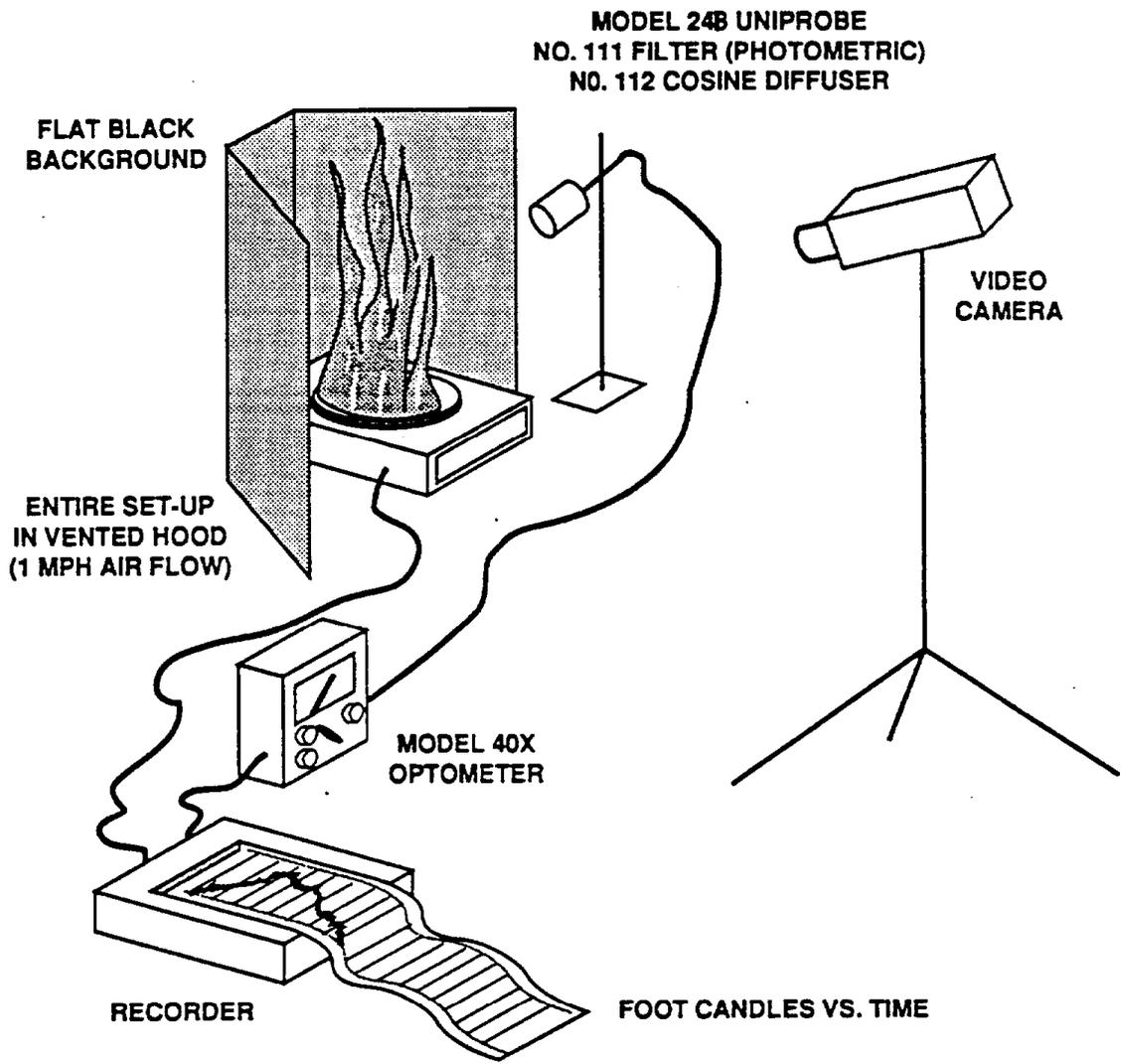


FIGURE 7. LUMINOSITY MEASUREMENT APPARATUS

visibility. This threshold visibility is the lowest resolvable luminosity by the human eye under twilight conditions, and was based on a "subjective consensus" of the observers from burns of many different mixtures with methanol. This limit is also based on the lowest perceptible luminosity during the middle portion of an M85 burn. Since a flame flickers while burning, the estimated minimum threshold visibility as measured with the instrumentation described above was between 0.1 and 0.2 foot-candles with the lower limit selected at 0.2 foot-candles.

2. Apparatus and Procedures - Task 1 Expansion

In the Task 1 Expansion, test burns were performed to address each of the questions which arose from the peer review meeting. As a result of these experiments, the final test conditions were similar to those described previously, with a few exceptions. The best position for the detector was determined by placing 10 mL of ethanol in a Petri dish and igniting the liquid. The detector was positioned at different angles (45°, 70°, 90°) from the horizontal, several distances from the center of the Petri dish, and various heights above the bottom of the Petri dish. An average luminosity of 1 foot-candle was achieved with the detector positioned at a 45° angle and 15 in. from the center bottom of the sample receptacle. Under these conditions, the sensor was about 10.6 in. vertically above the bottom and about 10.6 in. horizontally from the center of the dish. Figure 8 illustrates the optimum conditions for the sensor. Additional experiments conducted with and without the filter and cosine diffuser revealed that the photometric filter with the cosine diffuser produced the most consistent results.

Experiments were also performed to determine the best sample size and sample receptacle (Petri dish or watch glass). Sample sizes of 2, 5, and 10 mL were burned in both sample receptacles. The sample size was found to influence the length of burn rather than the height of the flame or the flame luminosity. A 5 mL sample size for the Petri dish gave a burn time of about one minute. In the watch glass, a 2 mL sample size produced burn times of about 1.5 to 2 minutes. Longer burn times did not increase the information obtained from the burn (Note: 5 mL samples in a Petri dish had been used in Task 1).

The sample receptacle was found to have a large effect on the flame character. With the Petri dish, the liquid spread unevenly across the bottom of the dish; while in a watch glass, the liquid tended to pool in the center. Longer burn times were recorded for the watch glass with smaller amounts of liquid due to this pooling. In the Petri dish, the flame was larger and was inclined to flicker or "breathe" as the burn continued. With the watch glass, the flame was much lower in height, less luminous, and less flame flickering was observed. The greater extent of flame flickering in the Petri dish probably occurred due to continuously changing oxygen concentrations near the liquid surface. The flux in oxygen concentration in the flame apparently helped improve the luminosity. The Petri dish was selected for subsequent testing because the uneven burning was probably more consistent with real world conditions. When a burning liquid spills on the ground or some other flat surface, the liquid would tend to spread rather than pool. In addition, variable air currents in real world conditions were probably better simulated by the Petri dish in laboratory experiments.

3. Test Results

A broad range of compounds were screened initially in Task 1 - Literature Search and Additive Evaluation. In the Task 1 Expansion, a more detailed testing program was performed and potential additive compounds were tested in laboratory burns at 5, 10, and 20 percent concentrations by volume for their improvement of the flame luminosity. Single component and multiple component methanol/additive combinations were tested in both efforts.

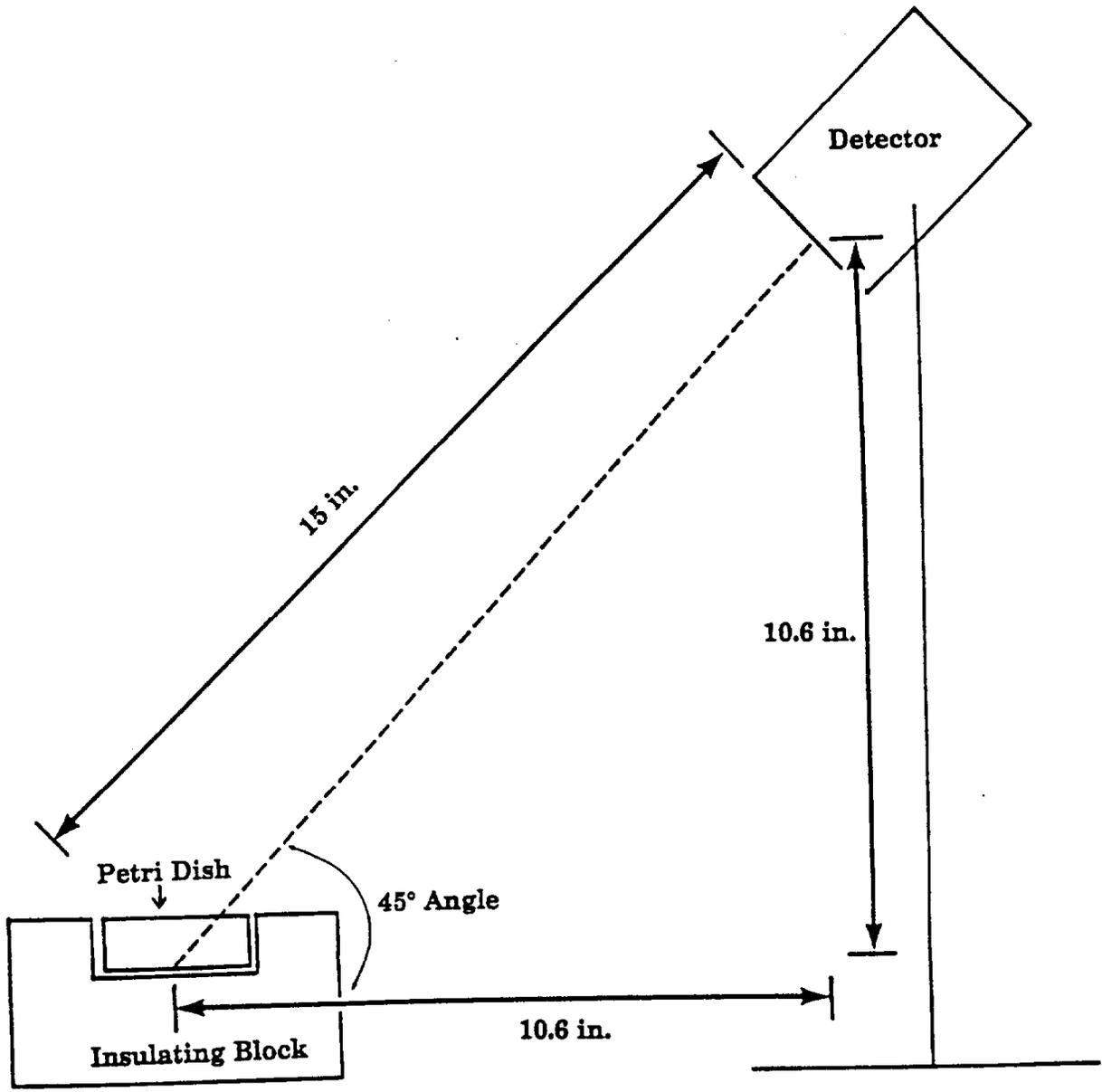


FIGURE 8. SKETCH OF DETECTOR POSITION (NOT TO SCALE)

Test results for luminosity measurements on single and multiple additive combinations are presented in Appendix A. Burn times in these tables refers to the length of time a flame was observed from a 5 ml sample in a Petri dish. The visibility duration is defined as the length of time the luminosity was above 0.1 foot-candles during the burn. Percent luminous flame is the percentage of time the luminosity was above 0.1 foot-candles. Larger or smaller samples sizes should have the same relative percent luminous flame in relation to the burn time and sample size. Appendix A also presents the luminosity curves versus concentration for each compound tested in the Task 1 Expansion. Results for both efforts cannot be combined because the procedure was modified in the Task 1 Expansion.

Several classes of compounds were identified as potential luminosity improvers.

- Aromatic compounds form submicroscopic soot particles during combustion and provide the most significant improvement to the flame luminosity as a group of compounds. These soot particles become heated by the flame and emit "gray-body" radiation at visible light wavelengths.
- Hydrocarbons also produce visible light upon combustion. Many hydrocarbons are soluble in methanol, but these compounds provided a limited improvement to the flame luminosity.
- Oxygen-containing compounds such as alcohols, ethers, esters, aldehydes, ketones, and acids were the third group. Most of these compounds are soluble in methanol and individually produce more luminous flames than methanol. In combination with methanol, these compounds may assist the flame luminosity through synergistic effects, but at lower concentrations the effect was negligible. In addition, alcohols and other oxygen-containing compounds are considered clean fuels because their combustion products produce lower exhaust emissions and less reactive hydrocarbons for ozone formation.
- Organometallic compounds and metal organic salts are another group of compounds which form luminous flames. These compounds have metal atoms attached to organic molecules (ligands). Many of these compounds, when burned in a flame, emit visible light at specific colors which correspond to the line spectrum of the excited state for the metal atom in the molecule.
- Some organic dyes and alcohol-soluble solids produce visible flames in methanol. These compounds typically have many functional groups that serve to increase the number of excited states for the molecule.
- Boron compounds produce a characteristic green flame when burned. However, many boron compounds are moisture-sensitive, corrosive, and leave a residue when burned.
- Several miscellaneous compounds containing nitrogen and sulfur with various functional groups were also tried, but these compounds had limited success.

Each group was investigated individually, and the more promising ones were tested in combination with others to determine their effect on flame luminosity.

a. Single Component Blends

In Task 1 - Literature Search and Additive Evaluation, single component blends were made at concentrations of 5 percent by volume. This effort was expanded in the Task 1 Expansion to include concentrations of 10 and 20 percent by volume. The concentration versus luminosity curves for each single component blend show that the luminosity increases with increasing additive concentration. Some compounds have a sharp increase in the luminosity as the concentration increases past a certain point (normally above 5 or 10 percent by volume). Cyclopentane is a good example of an additive with a sharp increase in the luminosity curve. Between 10 and 20 percent concentration by volume, the flame luminosity increases significantly. Other compounds such as ethanol have very flat luminosity curves until very high concentrations were reached. Although neat ethanol served as the standard of comparison, it did little to improve the flame luminosity when blended with methanol in low concentrations.

Several boron-containing compounds were tested to determine the extent of luminosity improvement from this group of compounds. Trimethyl borate and two other similar compounds (boric acid - H_3BO_3 and boron oxide - B_2O_3) were tested for their effects on the flame luminosity. Trimethyl borate is soluble in methanol and is stable in the absence of water, but hydrolyzes with water to form methanol and boric acid. Boric acid was tested because it is the product of hydrolysis from trimethyl borate, and boron oxide was tested because it is the anhydrous form of boric acid. In addition, a borane-pyridine complex was also tested. This complex offers handling convenience over other boron compounds because of its relative stability in air. Laboratory burns were performed at 5, 10, and 20 percent concentrations by volume for trimethyl borate and borane-pyridine complex, and at 0.001, 0.003, and 0.006 percent by weight for boric acid and boron oxide.

Each boron compound produced a green flame when burned. Boric acid and boron oxide at low concentrations caused the flame tips to be green. At higher concentrations, the entire flame was green, and a small residue (probably boric acid) was left in the bottom of the Petri dish. With trimethyl borate, the minimum threshold visibility was achieved for about 50 percent of the burn at the 5 percent concentration by volume. As with boric acid and boron oxide, a white residue remained in the Petri dish after burning. The borane-pyridine complex produced a green flame, as expected, in the initial part of the burn, and a yellow flame toward the end of the burn. Pyridine is the probable cause of the yellow flame in the latter part of the burn. The minimum threshold visibility was not achieved until the concentration of borane-pyridine complex in the methanol reached 10 percent by volume. Although the minimum threshold visibility was not reached until a concentration of 10 percent by volume was added, the flame was quite visible to the observers. The increase in visibility with respect to luminosity is probably due to the higher sensitivity of the human eye to wavelengths in the green to yellow portion of the spectrum. These compounds showed some promise as luminosity enhancers, but some concern remains about the residue left behind after burning. This residue may cause excessive wear or other problems in the engine or fuel handling system of an actual vehicle.

Three additives were investigated for their effect on flame luminosity based on their low Carter Maximum Incremental Reactivity (MIR). One compound was a C_{11} monoalkyl benzene (pentamethylbenzene), which had an MIR value of 1.70 g O_3 /g non-methane organic gases (NMOG). The other compound was benzaldehyde, the only compound with a negative MIR (-0.55 g O_3 /g NMOG). Another homologous compound to both of these compounds, pentamethylbenzaldehyde, was also tested. If these compounds pass through the combustion process unburned, a lower potential for ozone formation may occur.

Pentamethylbenzene and pentamethylbenzaldehyde resulted in very little increase in the flame luminosity compared to methanol. Both were solids at room temperature, and their volatility

in the flame was not sufficient to enhance the luminosity. Benzaldehyde, a liquid at near room temperature, increased the flame luminosity above the minimum threshold visibility toward the latter part of the burn at the 5 percent by volume concentration and throughout the majority of the burn at higher concentrations. This compound was unique, because most oxygen-containing compounds yielded lower flame luminosities than the homologous compounds without oxygen. A blend of toluene or cyclopentene with about 5 percent benzaldehyde should result in a visible flame throughout the majority of the burn and may contribute to lower ozone formation in the exhaust.

b. Multiple Component Blends

To reach the minimum threshold visibility throughout the burn, multiple component blends were required. Since unsaturated, branched-chain, and cyclic hydrocarbons improved the luminosity in the initial part of the burn and aromatics improved the luminosity toward the end of the burn, a properly blended mixture of these two components should result in an adequate flame luminosity throughout the majority of the burn.

The literature was searched for possible sources of feedstocks or commercial products that would be high in olefins and low in aromatic concentrations. A low aromatic content would allow the mixture to be blended with a specific aromatic and avoid the toxic substances such as benzene and xylene. At least one industrial product was found that met these criteria. Chevron developed a process called the Paragon Process which yielded a feedstock with a high degree of unsaturation (about 75 percent olefins). The major products of this process included:

- Normal and slightly branched paraffins
- Highly branched iso-paraffins
- C₃-C₈ olefins
- Gasoline-boiling iso-paraffins.

Artificial mixtures were blended based on information obtained from the literature and on the availability of specific chemicals in the laboratory. The luminosities of several olefin blends similar to known feedstocks and process streams were studied to determine if these mixtures could improve the flame luminosity. Most olefin blends improved the luminosity above the minimum threshold visibility, but they required concentrations above 20 percent by volume. In general, mixtures of olefins did not improve the luminosity as well as selected single olefins such as cyclopentene.

Several multiple component blends of ethanol plus t-butyl alcohol (TBA) and ethanol plus methyl t-butyl ether (MTBE) mixed in methanol were burned to determine the luminosity with other common oxygenates, molecules that contain oxygen in one form or another. Both multiple component blends did not reach the minimum threshold visibility until the concentration of TBA or MTBE exceeded 20 percent by volume. In addition, the ethanol concentration apparently had little effect on the flame luminosity in either blend. These results agreed with the luminosity curves for ethanol, TBA, and MTBE. Concentrations of greater than 20 percent by volume of TBA and MTBE were required to reach the minimum threshold visibility. Unless higher concentrations of these oxygenates are desired as co-solvents or as a blending stock, these oxygenates should not be considered solely as additives to improve the flame luminosity.

Five grades of dicyclopentadiene (DCPD) and a hydrocarbon resin oil called DP5-160 containing indene, methylindene, and dimethylindene were investigated for their effect on flame luminosity. The five grades of DCPD were tested to evaluate the degree of chemical processing required for these components to improve the flame luminosity. These samples were provided as a possible source of cyclopentene derived from DCPD. If the lower grades of DCPD would serve as a luminosity improver without additional processing, then extra steps could be saved in the production of the additive.

Three lower grades of DCPD were obtained from Texmark Chemicals, Inc. The lowest grade (Product Name DP6-46) contained mostly DCPD and several other minor components. The major constituents were 61.8 percent DCPD, 8.1 percent cyclopentane plus 2-methylcyclopentane, 1.9 percent cyclopentene, and 1.1 percent cis-piperylene. The balance of the sample had less than 1 percent each of trans-piperylene, n-pentane, isoprene, 1-pentene, 2-methyl-1-butene, 2-methyl-2-butene, benzene, other C₆ hydrocarbons, and other undetermined compounds. The next grade, called hydrocarbon grade, contained 76.0 percent DCPD, 15.8 percent C₁₀ codimers, 4.8 percent C₁₁ codimers, 2.1 percent C₉ codimers, 0.8 percent cyclopentadiene (CPD), and 0.4 percent C₅ and C₆ hydrocarbons. The DCPD polyester grade contained 81.6 percent DCPD, 12.5 percent C₁₀ codimers, 3.9 percent C₁₁ codimers, 1.6 percent C₉ codimers, and 0.3 percent cyclopentene. Exxon Chemical provided a sample of their Dicyclopentadiene 97 which was a mixture of 95 percent DCPD, 2 percent CPD, 1.5 percent C₅ acyclic dienes, and 1.5 percent cyclic diene and trimers. A small quantity of reagent grade DCPD was obtained from Aldrich Chemical Company, Inc. This grade of DCPD was about 95 percent pure and inhibited with 200 ppm p-tert-butylcatechol.

A sample of hydrocarbon resin oil was also obtained from Texmark Chemicals, Inc. The product name was DP5-160, and it contained about 40 percent C₁₀ hydrocarbons, 25 percent methyl and dimethyl indenenes, 17 percent C₉ aromatics, 16 percent indene, and 2 percent C₈ aromatics. This mixture was obtained as a commercial blend containing indene and methylindenenes which could be processed into indan.

In general, the DCPD and indene containing blends were not successful in improving the flame luminosity. The various grades of DCPD and DP5-160 improved the luminosity later in the burn. Concentrations above 5 percent by volume were required to improve the luminosity above the minimum threshold visibility (0.2 foot-candles) for the majority of the burn.

4. Discussion

Each burn had a characteristic luminosity "signature" (foot-candles versus time) which varied immensely, depending upon the volatility and the soot-forming tendency of the additive. With gasoline-methanol mixtures, the "signature" was a "U-Shaped" trace, likely caused by the destructive distillation of the gasoline components relative to the volatility of methanol (shown in Figure 9). For example, M85 yielded an average luminosity of 0.90 foot-candles for the initial phase, 0.15 foot-candles for the methanol-dominant mid-segment, and 0.70 foot-candles for the final phase of the burn. Early in the burn, the gasoline light ends evaporated and combusted, producing a highly visible flame. During the middle portion of the burn, a relatively low luminosity time segment was observed where the predominant burning element was methanol. Toward the end of the burn, the heavier gasoline constituents evolved, resulting in an increase in luminosity. For reference, neat methanol gave a uniform luminosity of 0.001 foot-candle. The luminosity "signature" changed depending on the various components, their tendency to form gray-body radiation, and their volatility. Therefore, the concentration and type of luminosity additives were very important when trying to improve the flame luminosity throughout the entire burn.

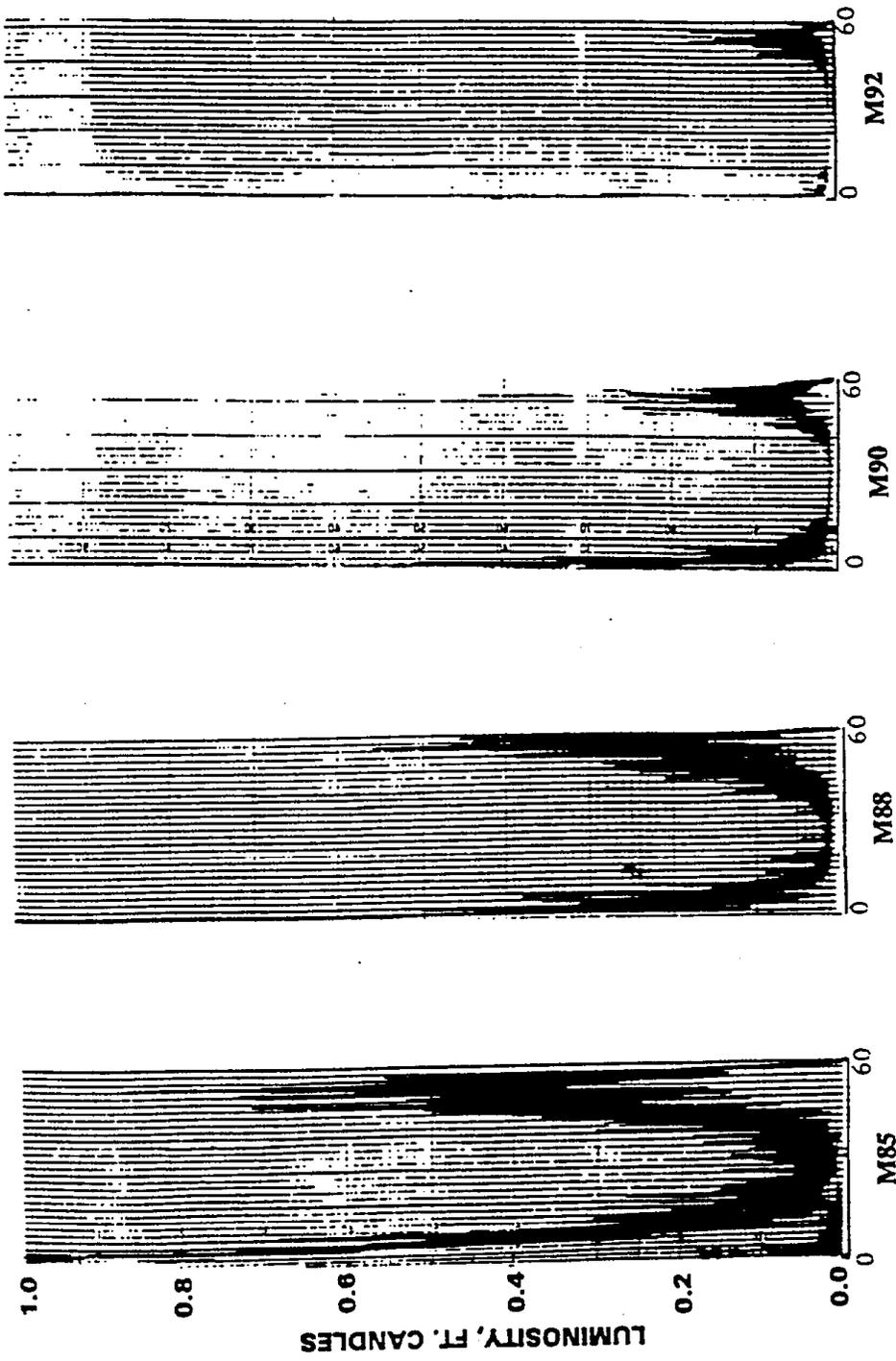


FIGURE 9. M85, M88, M90 AND M92 LUMINOSITY, FT.-CANDLES

a. Task 1 - Literature Search and Additive Evaluation

The measurement of luminosity was also found to be "container-dependent." Experiments showed that replacement of the glass petri dish with a slightly smaller (50 mm) aluminum weighing pan resulted in increased luminosity, and different luminosity "signatures." This phenomenon appeared to depend on reflections from the shining surface of the pan, a shorter path length for the flame, the heat from the flame causing more rapid evaporation of the contained liquid, the shape of the container, and possibly some synergistic effects from interactions with the container. Since the lowest luminosity was obtained in a glass dish, this method was selected as the worst case for a methanol fire.

Concentration effect studies were performed for some of the more promising candidates, including gasoline as a reference. Figure 10 illustrates the increase in luminosity with increasing additive concentration. When gasoline was blended with methanol in concentrations between 5 and 15 percent by volume, the flame luminosity increases from essentially equivalent to methanol with M95 to almost 75 percent of the luminosity of the neat ethanol with M85. Toluene yielded poor luminosity at concentrations below 2 percent, and at concentrations above 2 percent, the luminosity exceeded the minimum threshold visibility. Between 2 and 4 volume percent toluene, a dramatic breakpoint occurred in the luminosity. Concentrations above 4 volume percent toluene resulted in the luminosity increasing to levels which approached neat ethanol and actually exceeded ethanol at concentrations above 8 volume percent.

Ethanol and other oxygen-containing compounds blended in methanol resulted in only modest increases in luminosity at higher concentrations. The substitution of an oxygen atom into the molecule greatly changes the luminosity when compared to homologous compounds. At concentrations between 15 and 20 volume percent, higher molecular weight alcohols began to show some improvement in the flame luminosity, but not enough to serve as a single component additive.

Two coded additives provided by BP Oil (MO and AO) provided luminosities greater than 0.2 foot candles at concentrations of 0.5 to 1.0 volume percent in methanol. A third coded additive, F, provided a luminosity of 0.1 foot-candle at 1.0 volume percent. Concentrations above 1.0 percent were not investigated, since this concentration was very close to the saturation level for these three additives. Nevertheless, these coded alcohol-soluble dyes enhanced the luminosity in the last 1/3 to 1/4 of the burn, but these additives provided no luminosity during the early and mid portions of the burn and large amounts of residue remained in the Petri dish after each burn. The residue cause some concern about the practicality of these additives for flame luminosity enhancement due to possible deposition in an engine.

At the peer review meeting, the leading candidates for flame luminosity were:

- Toluene
- Coded additive MO
- Ethanol (at 10-20% concentrations).

These constituents improved the flame luminosity above the minimum threshold visibility separately and in combination with one another at a total concentration of 5-7 percent by volume (exclusive of ethanol), but no single compound was successful in improving the flame luminosity for the entire burn. Further work was considered necessary for the improvement of flame luminosity for the entire length of the burn. This effort resulted in the Task 1 Expansion.

LUMINOSITY CHARACTERISTICS FOR SINGLE-ADDITIVE FORMULATIONS IN METHANOL

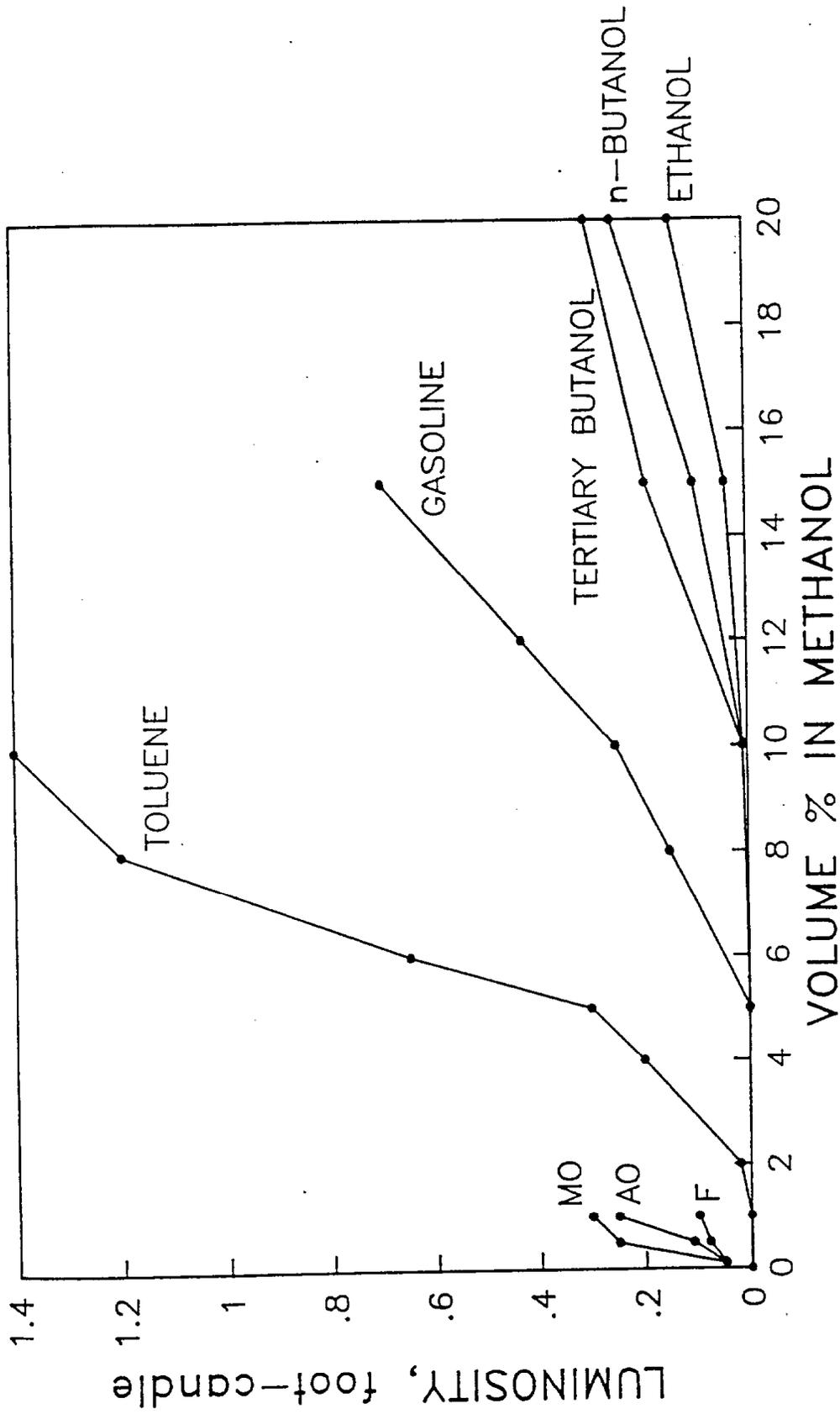


FIGURE 10. LUMINOSITY CHARACTERISTICS FOR SINGLE-ADDITIVE FORMULATIONS IN METHANOL

b. Task 1 Expansion

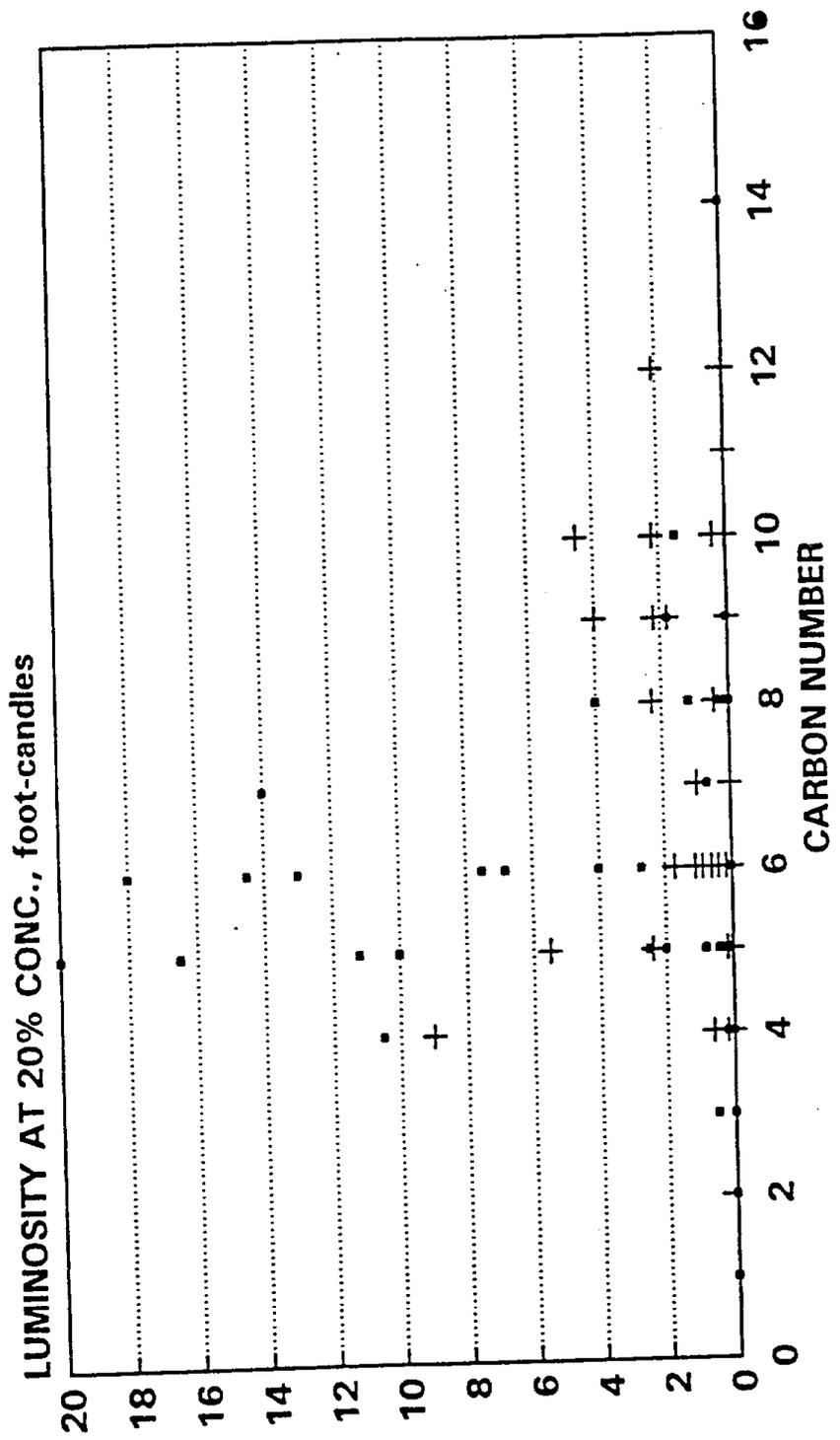
The best combinations for improving flame luminosity were those with unsaturation, cyclization, and aromaticity. Carbon chain branching also increased the luminosity; but in combination with methanol, higher concentrations were required. Most of these structures resulted in molecules with lower hydrogen/carbon number ratios. Unsaturated, branched-chain, and cyclic hydrocarbons typically increased the flame luminosity in the initial part of the burn more than straight chain hydrocarbons; however, many of these compounds required concentrations above 10 volume percent to raise the luminosity to the level of the minimum threshold visibility (0.2 foot-candles). Aromatics and certain substituted cyclic hydrocarbons improved the flame luminosity in the latter part of the burn. Toluene and cyclopentene provided the highest flame luminosity at the lowest concentration during the initial part of the burn, while indan, an aromatic with a cyclic side chain produced good luminosity at a low concentration in the latter part of the burn. Indan meets the minimum threshold visibility at a concentration as low as 1 percent by volume for a short time near the end of the burn. Alcohols and ethers provided limited improvements in the luminosity except at very high concentrations. One exception was cyclohexanol, but even this compound had a lower luminosity than its homologous cyclic hydrocarbon, cyclohexane.

The differences between compounds which enhanced the luminosity at the beginning of the burn and those that improved the luminosity near the end of the burn were related to the volatility of the compounds and the ability to form azeotropes with methanol. When the carbon number and the hydrogen/carbon number ratio were plotted against the flame luminosity of the various additives at a 20 percent by volume concentration (Figures 11 and 12), compounds with a carbon number of 5 or 6 yielded the highest luminosity in the early part of the burn. Above and below carbon numbers of 5 and 6, the luminosity during the early part of the burn dropped off dramatically. Compounds with a hydrogen/carbon number ratio between 1.5 and 2.5 (olefins/paraffins) produced the highest luminosity in the early part of the burn, while compounds with a hydrogen/carbon number ratio less than 1.5 (aromatics) exhibited higher luminosity in the latter part of the burn.

As a result of the Task 1 Expansion, the leading candidates for luminosity improvement at low concentrations were:

- Toluene
- Cyclopentene
- Indan
- Benzaldehyde

Trimethyl borate showed some potential as an additive at low concentrations, but a residue was left after burning which may cause problems with excessive engine wear. Trimethyl borate also produced a characteristic green flame which would indicate that boron compounds were present in the additive package. At slightly higher concentrations, methylcyclopentane (early in the burn) and mesitylene (late in the burn) improve the luminosity above the minimum threshold visibility. Two of the additives (MO and ethanol) from Task 1 were not included in the Task 1 Expansion because MO left a residue in the Petri dish after burning and ethanol was necessary in higher concentrations to enhance the flame luminosity.



▪ EARLY + LATE

FIGURE 11. CARBON NUMBER VERSUS PEAK LUMINOSITY

F. Flammability Additives Evaluation

Additional concerns about methanol as a fuel included the potential flammability of fuel vapors in underground and vehicle storage tanks, and the lack of sufficient fuel volatility to allow good cold-start and warm-up performance. For gasoline, the air-vapor mixture in the vapor space of a fuel storage tank typically exceeds the rich flammability limit at temperatures above -15°C . Spark-ignition engines need a volatile fuel for ease of starting, rapid warm-up, and good driveability; too light a fuel leads to poor fuel economy, carburetor icing, and vapor lock in the fuel pump and too heavy a fuel causes poor cold starting, inferior driveability, excessive engine deposits, and crankcase oil dilution. With diesel, the air-vapor mixture is typically below the lean flammability limit at temperatures less than 54°C . Volatility of a diesel fuel has little influence on the engine performance except as the volatility affects exhaust smoking tendencies. For M100, however, the flammability potential exists over a temperature range from about 9°C to 42°C . The addition of volatile components to methanol serves to shift the flammability limits of methanol toward lower temperatures. These components help saturate the vapor space above the liquid in a closed volume. Similar principles apply to the cold starting process in an Otto cycle engine where the vapor in the intake manifold and combustion chamber are enriched by the volatile components. This enrichment assists cold starting. The addition of volatile components to methanol serves to shift the flammability limits of methanol toward lower temperatures. These components help saturate the vapor space above the liquid in a closed volume. Similar principles apply to the cold starting process in an Otto cycle engine where the vapor in the intake manifold and combustion chamber are enriched by the volatile components. This enrichment assists cold starting.

1. Apparatus and Procedures

The apparatus for determining the flammability limits of the methanol fuel tank vapor space (Figure 13) consisted of five major components, which were:

- Reaction vessel
- Igniter
- High voltage source
- Temperature-controlled bath
- Temperature measurement instrumentation.

The reaction vessel consisted of a 100 mL Pyrex flask. The flask was spherical with two necks designed to accept cork stoppers. The igniter was mounted to one stopper, which placed the spark gap at the approximate center of the flask. The igniter was fabricated by passing two 4-inch lengths of 14-gauge copper wire through two holes of a stopper. The wires were parallel and separated 1/2-inch along their length. The spark gap was formed using two lengths of 0.006-inch diameter nichrome wire, each attached to a 14-gauge wire. A gap of 0.1 inch existed between the ends of the thin wires. The thin wire electrodes minimized the heat transfer from the spark kernel. Spark energy was generated using a vibrator and induction coil. This system provided 70 mJ of energy per spark at a repetition rate of 400 hz.

A commercial laboratory bath provided the necessary heating or cooling for the flask during the experiment. A thermocouple entered the flask through the other stopper and extended to the bottom of the flask to monitor the flask temperature. The temperature of the bath was measured using a calibrated mercury thermometer. Flask thermocouple calibration was checked against this thermometer for each temperature at which the methanol blends were tested.

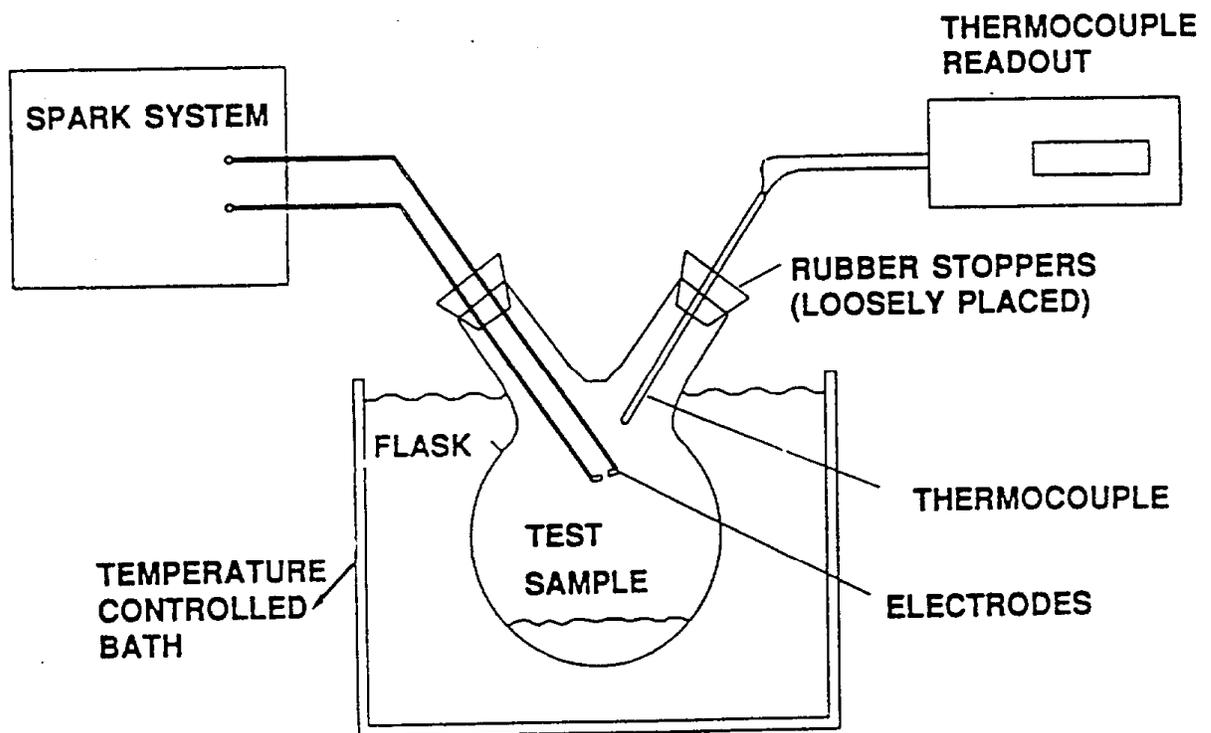


FIGURE 13. FLAMMABILITY TEST APPARATUS

For each test, a 5 mL sample was pipetted from the sample container into the 100 mL flask. The igniter and thermocouple were then placed in position. The flask was lowered into the bath which had been set at the desired temperature. When the sample temperature agreed with bath temperature (usually 5-10 minutes), the system was at equilibrium. The spark electrodes were then connected to the high voltage supply, the ignition system was energized, and the results (ignition or no ignition) were recorded at the sample temperature.

Flammability limits of test samples were determined by first stepping through the temperature range from -50° to 0°C in 10°C intervals. The temperatures which bracketed the transition from an ignitable to a non-ignitable mixture were noted, and a test was then performed at an intermediate temperature. The flammability limits are defined by the temperature range where the vapor in a confined space is combustible. Between these temperatures, the air-vapor mixture could ignite under the proper conditions. The temperature where the gases in the vapor space are too lean (insufficient fuel) to ignite is defined as the lean flammability limit. This condition typically occurs at a low temperature. Conversely, the rich flammability limit is the temperature where the gases in the head space are too rich (insufficient oxygen) to ignite which occurs at a higher temperature. Flammability limits were determined within 5°C accuracy in most cases.

2. Test Results

The test results are given in Table 16 for the fuel blends containing a total of 5% additive or less except for the M85. Data are represented as "Yes" or "No" to indicate ignition at a given temperature. A few fuel blends containing a total of 6% additives or 6% additives and 15% ethanol (with a balance of methanol), are given in Table 17.

3. Discussion

The addition of volatile components for cold-starting and flame luminosity lowers the flammability limits of methanol. Results from the flammability limit experiments listed in Table 16 were plotted in Figure 14. Examination of these data reveals that only the C_4 hydrocarbons (butane, and butene) provide the necessary vapor pressure at 5 volume percent (or less) to lower the rich flammability limit to -18°C (0°F) or colder. Pentane, at 5 volume percent, lowered the rich flammability limit to only -5°C , (23°F), and DME, at 5 volume percent, lowered the rich flammability to -20°C .

From the luminosity data, butane was found to be ineffective at improving the luminosity; therefore, blends of toluene and butane were evaluated for their combined effect on the flammability limit (See Table 17). Blends containing 1% and 2% butane, with 4% and 3% of toluene, respectively, by volume, yielded a higher temperature for the rich flammability limit than the corresponding two component systems containing only butane and methanol. The rich flammability limit for these butane/toluene/methanol blends were above -18°C . Since the 5% additive blends of butane and toluene did not provide a rich flammability limit below -18°C , a series of 6% total additive blends were evaluated (See Table 17). Those blends containing 2.5% or 3% butane lowered the rich flammability limit to below -18°C .

A limited amount of RVP data was taken for the butane and butene mixtures (see Table 18). Interpolation of this data indicated that a 2.5% butane mixture results in an RVP of 8.45 psi. This amount of butane or butene should improve the vehicle cold-starting while lowering the flammability limit below -18°C (0°F), which is a significant improvement over M85. A mixture of 2.25% butane would result in an RVP of 8.00 psi. Based upon the findings of Menrad,⁽²⁶⁾ a cold-start temperature of 23°F is predicted for this mixture, which should provide adequate cold-starting in the Southern California area.

TABLE 16. FLAMMABILITY LIMIT DETERMINATIONS

Sample, except as noted	Ignition Temperature																							
	68°F 20°C	59°F 15°C	50°F 10°C	41°F 5°C	32°F 0°C	23°F -5°C	14°F -10°C	5°F -15°C	0°F -18°C	-2°F -18.9°C	-4°F -20°C	-8°F -22°C	-9°F -23°C	-13°F -25°C	-22°F -30°C	-28°F -33°C	-30°F -34°C	-35°F -37°C	-40°F -40°C	-49°F -45°C	-58°F -50°C	-67°F -55°C	-73°F -58°C	
95% MEOH, 5% Sample, except as noted																								
Butane	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
3% Butane ^a	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
2% Butane	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
1% Butane	No ^f	No	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No								
Butane	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
3% Butane	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
2% Butane	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
1% Butane	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No								
Pentane	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
1-Pentene	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
Pentene	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
MES ^b	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
Toluene	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
ETBR	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
MTBR	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
Tol/Tol ^c	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
MEOH ^d	Yes ^{g,h}	Yes	Yes	Yes	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
1,3-Butadiene	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
DME	No	No	No	No	No	No	No	No	No	No	No	No	Yes							
Cydrpentane	No	No	No	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	No	No	No	No	No	No	No	No	No	No	No	
Cyclohexane	Yes	Yes	Yes	Yes	Yes	No	No	No	No	No	No	No	No	No	No	No	No	No	No	No	No	No	No	
Reformax	No	No	No	No	No	No	No	No	No	No	No	No	No	No	No	No	No	No	No	
GT280X (Omnistar)	Yes	No	

TABLE 17. FLAMMABILITY DETERMINATIONS OF 6% ADDITIVE BLENDS AND ADDITIVES WITH 15% ETHANOL

°F	77	68	59	50	41	32	23	14	5	-4	-13	-22	-31	-40	-49	-58	-67	-76	-85	
	25	20	15	10	05	0	-5	-10	-15	-20	-25	-30	-35	-40	-45	-50	-55	-60	-65	
Sample ID																				
5% Toluene/ 2% Butane	No	No	Yes	Yes	Yes	Yes	Yes					Yes	No							
4% Toluene/ 2% Butane					No	No	Yes							Yes	Yes	No				
3% Toluene/ 3% Butane					No	No	No	No	No	Yes	Yes			Yes	Yes	Yes	No			
3.5% Toluene/ 2.5% Butane								No	No	Wk. Yes							Yes	No		
4% Toluene/ 2% Butane/ 15% EtOH					No	No	No	Yes						Yes	Yes	Wk. Yes	No			
3% Toluene/ 3% Butane/ 15% EtOH									No	No	Yes						Yes	No		
3.5% Toluene/ 2.5 Butane/ 15% EtOH										No	Yes					Yes	Yes	No		

FLAMMABILITY LIMITS FOR METHANOL MIXTURES

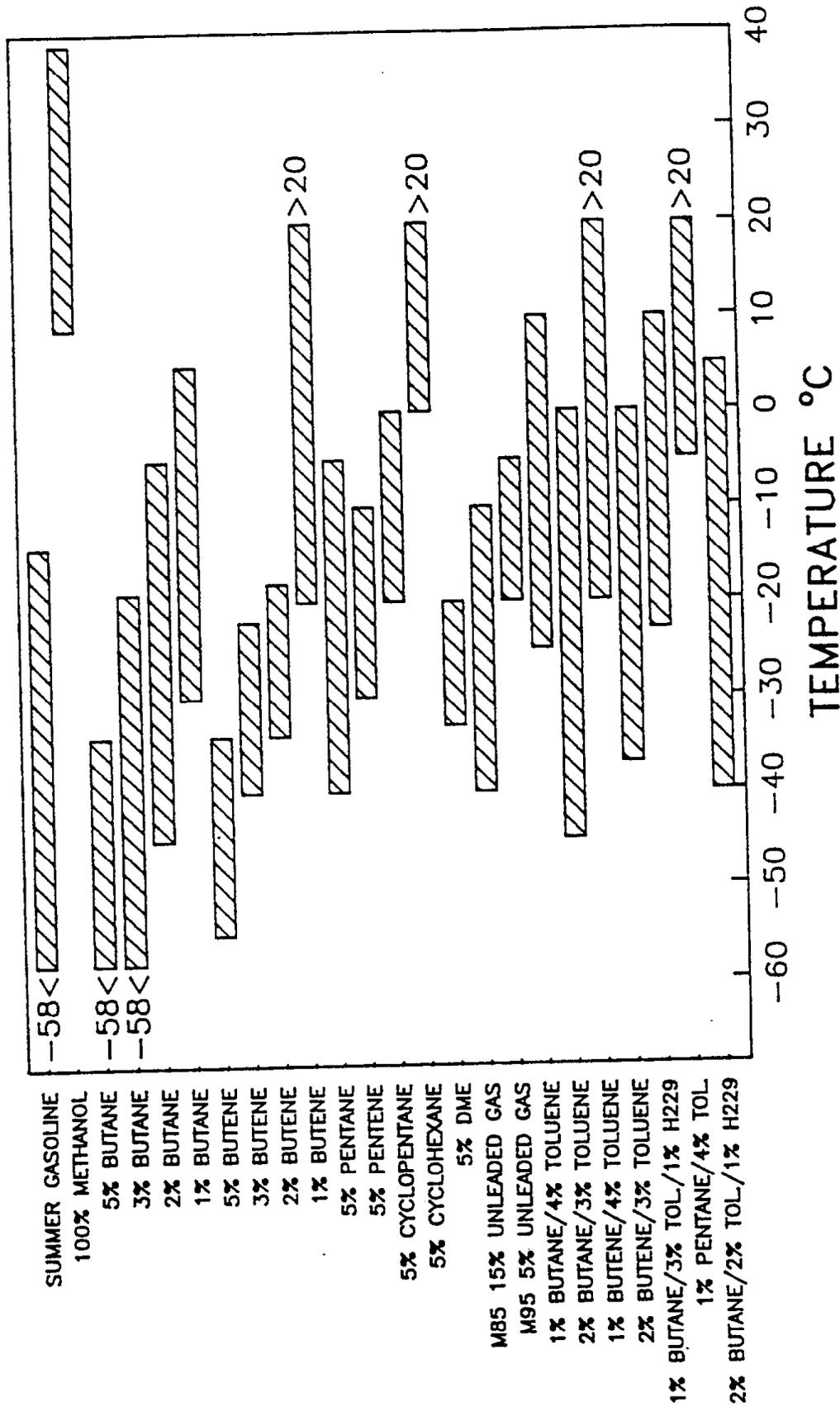


FIGURE 14. FLAMMABILITY LIMITS FOR METHANOL MIXTURES

TABLE 18. REID VAPOR PRESSURE MEASUREMENTS OF BUTANE AND BUTENE MIXTURES

Additive in Methanol	RVP, (psi)
5% Butane	13.55
3% Butane	9.35
2% Butane	7.55
1% Butane	6.50
5% Butene	11.40
3% Butene	9.30
2% Butene	7.00
1% Butene	6.20

Vehicle fuel weathering studies should be conducted to determine the extent of butane losses with time and the subsequent effect on cold-start capability.

G. Additive Package Components Selection

One important observation in both the Task 1 - Literature Search and Additive Evaluation and the Task 1 Expansion was that one single additive could not achieve all of the required properties for methanol. Combinations were necessary to meet each criterion. In Task 1 - Literature Search and Additive Evaluation, a group of compounds were selected to achieve the 5 percent by volume concentration limit. This criterion was later changed to include additives at higher concentrations which would not exceed 125 percent of the cost for the gasoline component of M85.

After the specific additives for flame luminosity, fuel lubricity, and flammability limits were identified and investigated in Task 1 - Literature Search and Additive Evaluation, the best additives within each category were combined and tested to determine any synergistic effects from the combination. The candidates included toluene, butane, butene, ethanol, DCI-4A (a DuPont lubricity/corrosion additive), and MO (coded BP Oil luminosity improver). Combinations of these compounds were tested at a total additive concentration of 5 volume percent, except ethanol, which was added at a concentration up to 20 volume percent. Test procedures for luminosity, lubricity, and flammability limit were performed on each combination. Table 19 presents the results from these experiments.

These data indicate that several combinations offer many advantages for improving the properties of M100. First, many additives yielded significant improvement in the lubricity of the fuel. Second, all combinations had a rich flammability limit below -18°C , and the combinations with ethanol had a rich flammability limit of -25°C . Finally, the luminosity varied with the time and the different components in the mixture. Toluene enhanced the luminosity in the initial part of the burn, and MO helped with the latter stages of the burn although MO left a residue after burning. These data suggested the additive combinations could provide adequate properties for fuel methanol, but the flame luminosity could not be maintained throughout the entire burn.

TABLE 19. CHARACTERISTICS OF COMPLEX ADDITIVE PACKAGES

<u>Additive</u>	<u>Luminosity</u>	<u>Lubricity</u>		<u>Flammability</u>	
	Average Luminosity, Foot Candles	Avg. Wear Scar Diam., mm	% Change	Lower Limit, °C	Upper Limit, °C
Target Values	0.1-0.2 minimum	0.47 max	-15 minimum	----	-18 max
2.8% Toluene 2.2% Butane 0% EtOH 0.12% DCI-4A	0.1/0.02	0.46	-16	-45	-20
2.8% Toluene 2.2% Butane 0% EtOH 0.12% DCI-4A	0.1/0.02	0.44	-20	-45	-20
2.8% Toluene 2.2% Butane 20% EtOH 0.12% DCI-4A	0.2/0.1/0.02	0.45	-18	-50	-25
2.0% Toluene 2.5% Butane 20% EtOH 0.12% DCI-4A 0.6% MO	0.05/0.02/0.18	0.44	-20	-55	-25
1.0% Toluene 2.5% Butane 20% EtOH 0.12% DCI-4A 1.0% MO	0.01/0.1/0.22	0.45	-18	-55	-25
2.8% Toluene 2.5% Butane 20% EtOH 0.12% DCI-4A 1.0% MO	0.08/0.14/0.25	0.43	-22	-55	-25

TABLE 19 (CONT'D). CHARACTERISTICS OF COMPLEX ADDITIVE PACKAGES

Additive	Luminosity	Lubricity		Flammability	
	Average Luminosity, Foot Candles	Avg. Wear Scar Diam., mm	% Change	Lower Limit, °C	Upper Limit, °C
2% Toluene 2.5% Butane 0% EtOH 0.12% DCI-4A 0.6% MO	0.02/0.1/0.18	0.45	-18	-55	-20
0% Toluene 2.5% Butane 20% EtOH 0.12% DCI-4A 0.5% MO	0.08/0.18	0.43	-22	-55	-25
0% Toluene 2.3% Butane 20% EtOH 0.12% DCI-4A 0.6% MO	0.01/0.08	0.44	-20	-50	-25
0% Toluene 2.3% Butane 0% EtOH 0.12% DCI-4A 0.6% MO	0.02/0.1/0.25	0.44	-20	-55	-20
0% Toluene 2.5% Butane 20% EtOH 0.12% DCI-4A 1.0% MO	0.001/0.15/0.32	0.45	-18	-55	-25

In the Task 1 Expansion, several compounds improved the flame luminosity during the beginning or at the end of the burn, but none increased the flame luminosity throughout the entire burn. To achieve a luminous flame throughout the majority of the burn, several of the compounds with the best luminosity improvement at low concentration were combined. Cyclopentene and toluene produced luminous flames at low concentrations during the initial part of the burn, and indan improved the luminosity toward the end of the burn. These hydrocarbons were combined in several concentrations and compared to M85. With M85, the flame luminosity was above the minimum threshold visibility of 0.2 foot-candles for about 75 percent of the burn. Two combinations of the above compounds yielded luminosities above the minimum threshold visibility and equivalent to or better than M85. These combinations were 4% toluene + 2% indan, and 5% indan + 5% cyclopentene. Two compounds recommended in Task 1 were not included in the Task 1 Expansion: MO and ethanol. These two compounds were not included because MO was found to leave a residue after burning, and ethanol was required in much higher concentration to improve the flame luminosity.

H. Outdoor Burns

The work with multiple component blends in the Task 1 Expansion led to a comparison of the laboratory results with real world situations. A set of experiments was designed to examine the effect of five different liquids in outdoor burns. In these experiments, the burns were performed on two different days because of the length of each burn and the time required to complete the experiment. One liter sample of liquid was burned on each of five surfaces:

- Concrete
- Asphalt
- Sheet metal
- Grass
- Soil.

These surfaces were coded with a letter which represented the first letter of each surface: C, A, M, G, and S, respectively. Each liquid was also coded with a number to prevent the panel from identifying the different samples. The five liquids with their test codes consisted of:

- 100% methanol - 1
- 100% ethanol - 2
- M85 - 3
- 4% toluene + 2% indan in methanol - 4
- 5% indan + 5% cyclopentene in methanol - 5.

In the subsequent text, the blend of 4 percent toluene + 2 percent indan will be designated as T&I, and the blend of 5 percent indan + 5 percent cyclopentene will be referred to as I&C.

Each mixture was poured onto the surface, ignited with a match or burning cotton swab, and videotaped throughout the burn. A sand barrier around the liquid contained the flame and prevented spreading. Some of each liquid was absorbed by the sand, but the majority of each liquid was concentrated on the desired surface. A panel of eight or nine observers watched the burns, rated the visibility, and answered questions about the lighting conditions, flame color, flame luminosity, flame height, background, and other distinguishing features. All observers were male except one, and one male observer was color blind.

All burns were performed during bright sunlight or partly cloudy conditions. The wind was variable and less than 5 mph for most of the burns, and the wind direction was not a factor because the observers were positioned around the flame. In addition, the background conditions depended on the position of the observer relative to the flame. Background objects included grass, trees, concrete, asphalt, and soil; and one observer reported that a metal dumpster served as the background. The background conditions affected the flame visibility, but it was difficult to correlate the visibility with the background conditions since these conditions were not consistent throughout the burns for each surface or for each observer. Appendix B summarizes the results for the outdoor burns on each surface.

1. Concrete

On concrete, none of the observers could see the methanol flame, but all observers were able to see a flame for the other four liquids. The colors for all flames except methanol were reported as yellow, orange, or orange-yellow (except for the observer who was color blind and for one observer who saw the flame for I&C as orange-blue). Most observers indicated that the ethanol, M85, and I&C flames were visible throughout the burn. Four out of seven observers saw a visible flame throughout the burn for T&I. Descriptions of the flames ranged from heat waves for methanol to bright, fast, or high at first fading to low or weak near the end of the burn for the other four liquids. Ethanol had the highest average flame height with almost 6 feet while the I&C had the lowest with less than 3 feet.

Methanol was observed to have an average flame height of 4.4 feet even though the flame was not visible. Most observers felt the heat from methanol and ethanol, but could not feel the heat from the other three liquids. While most could feel the heat from methanol, eight of the nine would not have seen the flame or taken steps to avoid it. The majority would have seen and taken steps to avoid the other flames.

Ethanol and M85 flames would have been recognized at an average distance of over 200 feet, while methanol would not have been seen until less than 8 feet from the flame. Both T&I and I&C had average recognition distances of greater than 50 feet. Three observers noted an odor or slight smell from methanol, and three observers suggested that ethanol had a burning plastic or toxic smell. M85 produced a "stink" or nauseating smell for three observers, and I&C yielded an aromatic smell for one observer. In most cases on the concrete, the burns for the two additive blends were equivalent to M85 burns except for the average recognition distance.

2. Asphalt

On asphalt, none of the observers was able to see the methanol flame, but all observers were able to see a flame for the other four liquids. The flame colors seen by the observers were yellow, orange, and orange-yellow (except the observer who was color blind). Most observers indicated that the ethanol, M85, and I&C flames were visible throughout the burn. Four out of seven observers saw a visible flame throughout the burn for T&I.

Descriptions of the flames were very different on this surface. Methanol was described as clear or invisible for three observers. M85 was bright at first and barely visible toward the end of the burn. For the solution of T&I, the burn was rapid and hard to see at the end. With I&C, six observers indicated that the flame was high, large, or heavy at first, and two observers suggested that the flame was low midway while increasing toward the end. M85 had the highest average flame height at almost 5 feet while the ethanol, T&I, and I&C had flames that averaged about 3 feet. Methanol was observed to have an average flame height of about 4 feet even though the flame was not visible.

Most observers felt the heat from all five liquids, but four out of nine for M85 and three out of seven for T&I did not feel the heat. All observers indicated that they would have seen the flames except for methanol and would have taken steps to avoid them. The ethanol, M85, and I&C flames would have been recognized at an average distance of over 150 feet while methanol would not have been seen until about 4 feet from the flame. With T&I, the average recognition distance was greater than 50 feet.

Two observers noted a sizzle or crackling sound, and one detected a smell from methanol. M85 produced a hissing sound and an odor for two observers, and I&C yielded a stink for one observer, a bad smell for three observers, and a slight smell for one observer. In most cases on the asphalt, I&C flames were equivalent to or better than those for M85. The T&I blend was equivalent to M85 in most areas except flame recognition distance and flame visibility throughout the burn.

3. Sheet Metal

On sheet metal, only one observer saw the flame burning for methanol, but all observers were able to see a flame for the other four liquids. Once again, the observed flame colors for all flames except methanol were yellow, orange, and orange-yellow. Two observers indicated that the methanol flame was clear or blue. Most observers indicated that the ethanol, M85, and I&C flames were visible throughout the burn; and one observer suggested that the methanol flame was visible throughout the burn. One observer also indicated that the M85 flame was barely visible throughout the burn.

Descriptions of the flames were different from the other surfaces. Methanol was described as having quick ignition, quick evaporation, and heat waves. Ethanol was described as quick ignition, with a bright orange or "thick" flame. M85 was a bright flame, slow burning, and a bubbling liquid. For T&I, the flame was large and quick burning with heat waves. With I&C, one observer saw soot. The flame height for all five liquids ranged from 3 to 4 feet. Methanol was observed to have an average flame height of about 4 feet even though the flame was not visible.

Most observers felt the heat from methanol and I&C, but most observers did not feel the heat from the other flames. While most could feel the heat from methanol, only two would have seen or taken steps to avoid the flame. All observers would have seen the other flames and taken steps to avoid them. The ethanol, T&I, and I&C flames would have been recognized at an average distance of over 200 feet, while methanol would not have been seen until about 7 feet from the flame. With M85, the average recognition distance was about 50 feet. For I&C, the recognition distance averaged almost 400 feet. Six observers noted a stink, burnt grass, or acrid smell from methanol while only one observer detected an odor from ethanol. M85 produced a sizzle and an odor for two different observers.

The two additive blends had the largest number of distinguishing characteristics. With T&I, five observers indicated a bad smell and one each suggested the smell of burning plastic and a sizzle sound. For I&C, three observers detected a burned plastic smell, two indicated that the odor stunk, and one indicated a toxic smell. Two other observers detected black smoke and a sizzling sound

for I&C. In most cases on sheet metal, burns for the two additive blends were equivalent to or more detectable than burns for ethanol and M85.

4. Grass

On grass, the observers saw different degrees of burning. For methanol, six out of nine observers saw a flame, and two indicated that they saw the flame sometimes. With ethanol, six out of nine saw the flame at some time during the burn while three of these indicated either barely, sort of, or occasionally. For T&I, five out of nine saw the flame at some time during the burn. The flame colors included yellow, orange, orange-yellow, yellow-orange, and light yellow. Six observers indicated that the methanol flame was orange, and two saw no flame. Most observers indicated that the methanol, ethanol, and T&I flames were not visible throughout the burn, while most observers suggested that the M85 and I&C flames were visible throughout the burn. One observer also indicated that the I&C flame was barely visible throughout the burn.

Descriptions of the flames were similar and included bluish or white smoke, smoldering, and burning grass. The M85 flame was described as dim at first or as a "heavy" flame on bottom with light flame on top. With I&C, the observers suggested a long burn or nothing at first, but that it got brighter later in the burn. The flame height for all five liquids ranged from 1.5 to 5.5 feet. Methanol had the highest average flame height with 5.5 feet. The two additive blends had the lowest average flame heights with less than 2 feet.

Most observers did not feel the heat from any of the flames, but two observers did feel the heat from the M85 flames. While most could see the flames during some portion of the burn, only with M85 and I&C would the observers have seen or taken steps to avoid the flame. The average recognition distances for methanol and T&I flames were about 11 feet, while the average recognition distances for M85 and I&C were over 30 feet. With ethanol, the average recognition distance was only about 7 feet.

During the burns, most observers noted either a crackling sound, smoke, or the smell of burnt grass. With ethanol, one observer detected an engine smell, and with M85, an acrid smell. The visibility of the I&C additive blend flames was equivalent to or better than M85, and the T&I flames were similar to ethanol.

5. Soil

On soil, most observers saw the flames burning for all five liquids. For methanol, six out of nine observers saw a flame, including one who indicated that he barely saw the flame. The flame colors ranged from yellow, orange, orange-yellow, and yellow-orange to orange-blue. Three observers saw no methanol flame. Most observers indicated that the methanol and T&I flames were not visible throughout the burn while most observers suggested that the M85 and I&C flames were visible throughout the burn. Four out of seven observers saw the flame throughout the burn with ethanol.

Descriptions of the flames for the five liquids varied considerably. Methanol was described as heat waves and smoke. The ethanol flame was described as either visible at first, weak then pale, or as "thin" flames; while the M85 flames were described either as less visible with time or after 30 seconds, or as easily seen. For T&I, the flames were described as either weak, flame at first, or as a quick burn. With I&C, six observers suggested a bright flame. All five liquids ranged from 1 to 2 feet for the average flame height with methanol having the lowest and M85 the highest.

Most observers did not feel the heat from any of the flames except M85 (five out of seven) and methanol (three out of eight). Except for methanol, most observers would have seen the flames and taken steps to avoid them. The average flame recognition distance ranged from 25 to 35 feet for ethanol, T&I, and I&C. With methanol, the average flame recognition distance was only about 15 feet, and the average flame recognition distance for M85 was over 150 feet. Other distinguishing characteristics listed by the observers included a sweet smell for ethanol, an aromatic smell for T&I, and aromatic or sweet smell for I&C. For M85 the observers noted either an aromatic, sweet, or chemical smell, or a unique odor. The additive blends were equivalent to or better than M85 and ethanol in all cases, except for the average flame recognition distance as compared to M85.

6. Discussion

In general, the additive blends performed as well as or better than ethanol and M85 on most surfaces. The additive blends were significantly better than methanol in all cases. Heat was felt from the methanol flames on the less porous surfaces (concrete, asphalt, and sheet metal), but the flames were not visible. On these surfaces, the recognition distances were also much shorter for methanol. While there was a significant difference of opinion between the various observers, most were able to detect and would have taken steps to avoid the flames from both additive blends on all surfaces except grass with T&I. These results, while limited to a small number of observers, indicated that the flame visibility of methanol can be improved through the use of selected additives even in bright sunlight.

I. Emission Testing

Based on the results of the literature search and the laboratory investigations for flame luminosity, fuel lubricity, and flammability limits, combinations of the most successful additives from both Task 1 - Literature Search and Additive Evaluation and the Task 1 Expansion were tested in actual vehicles to determine the effect on the exhaust emissions. In Task 1, a 1986 dedicated M85 fuel Toyota Camry served as the test vehicle. This vehicle had a 2.0 L, 4-cylinder engine with electronic fuel injection, three-way catalyst, standard oxygen sensor, and exhaust gas recirculation (EGR). This work was performed just prior to the peer review meeting. In the Task 1 Expansion, a 1989 dual-fuel Volkswagen Jetta was used as the test vehicle with a 1.8 L multi-point fuel injected engine, a single under-floor three-way catalyst, heated oxygen sensor, and a dashboard mounted switch to indicate fuel selection (gasoline or M85). This vehicle was unique because a switch allowed the vehicle to operate in either the gasoline or M85 mode. No on-board fuel sensor was employed on this vehicle. These two test vehicles were the only available vehicles that the respective manufacturer approved for use with methanol blends containing greater than 85 percent methanol.

The objectives of the emissions tests were:

- To determine the emissions impact of the additive combinations on toxic substances and regulated emissions as compared to M100
- To determine if the fuel additives resulted in no more than 50 percent of the exhaust hydrocarbons as compared to M85 without the additive.

M85 and M100 served as the standards of comparison, and the gasoline RF-A, (auto/oil Air Quality Improvement Research Program designation) was included to compare these results to an industry average gasoline in the same vehicle.

The measured emissions included a complete hydrocarbon speciation (C₁ - C₃ hydrocarbons plus benzene and toluene, C₄ hydrocarbons including 1,3-butadiene, and C₅ - C₁₀ hydrocarbons), aldehydes, and methanol. All exhaust emissions were measured on a bag by bag basis and compared for their ozone forming potential based on the Carter Maximum Incremental Reactivities (MIRs) as adopted by CARB prior to August 1990. Table 20 lists the test plan for evaluating the different fuels. Each vehicle was tested on separate occasions with different selections for the additive blends, and the results for each vehicle as well as the compositions of the blends are presented below.

TABLE 20. TEST PLAN FOR EVALUATING METHANOL FUEL BLENDS

Step	Description
1	Prepare the vehicle for testing. Fuel system should be changed to take fuel from a clean 5 gal can rather than the fuel tank. A separate fuel pump should be used to supply the fuel from the can to the engine. Connect a second clean charcoal canister to the canister purge line. The old canister should remain connected to the vehicle fuel tank. Confirm presence of OEM (original equipment manufacturer) catalyst.
2	Purge previous fuel from system into a separate container to prevent contamination of new fuel from the return line. Prepare vehicle for testing by conditioning vehicle with test fuel during one Federal Test Procedure (FTP) cycle. Do not run any longer than necessary because of limited amount of fuel available. Soak vehicle for 12 to 36 hours before testing.
3	Run 3-bag FTP emission test with complete hydrocarbon speciation (C ₁ - C ₃ hydrocarbons plus benzene and toluene, 1,3-butadiene, and C ₅ - C ₁₀ hydrocarbons), aldehydes, and methanol. (Note: Exhaust emissions should be taken on a bag by bag basis.)
4	Repeat Step 3.
5	Change to next fuel and repeat Steps 2 through 4 with each methanol fuel.
6	When testing the Volkswagen Jetta, switch back to gasoline mode and repeat Steps 2 through 4 with RF-A (EM-1026-F).

1. Toyota Camry

Emission testing for Task 1 - Literature Search and Additive Evaluation was performed on a 1986 Toyota Camry (dedicated M85 vehicle) fueled with an SwRI methanol blend and with an actual commercial blend of M85 fuel obtained from California. In these tests, the M85 served as the baseline. The SwRI methanol blend was made from an M100 methanol fuel (EM-850-F) and was blended to contain the following additives:

- 6 volume percent toluene
- 2.5 volume percent butane
- 0.12 weight percent DCI-4A (Dupont)

- 0.0001 weight percent Bitrex (denatonium benzoate)
- 0.007 weight percent odorant.

The California version of M85 was designated with fuel code EM-1120-F, and the fuel with the additive package was denoted EM-1125-F. MO was not included in the additive package tested in this vehicle due to possible residue formation which was noticed during the flame luminosity testing. Comparisons to M100 and gasoline were not performed on this vehicle because it was designed as an M85 dedicated fuel vehicle. Computer printouts of the FTP regulated emissions for the tests are included as Appendix C. The detailed hydrocarbon speciation data is presented in Appendix D. Table 21 presents the regulated emissions, and Table 22 summarizes the hydrocarbon emissions.

TABLE 21. SUMMARY OF FTP REGULATED EMISSIONS FOR TOYOTA CAMRY DEDICATED M85 FUEL VEHICLE

Test No.	Test No.	Emissions Results, g/mi			Fuel Economy, mpg
		HCA	CO	NO _x	
EM-1120-F ^b	1-2	0.31	1.64	0.33	17.16
	1-3	0.33	2.47	0.26	17.24
	avg.	0.32	2.06	0.30	17.20
EM-1125-F ^c	2-1	0.28	1.34	0.29	16.62
	2-2	0.29	1.55	0.27	16.73
	avg.	0.29	1.45	0.28	16.68

^aHCA results based on fuel composition (i.e. includes mass of oxygen) and do not include an FID response for methanol.
^bCalifornia M85.
^c6 vol. % toluene, 2.5 vol. % butane, 0.12 wt. % DCI-4A, 0.0001 wt. % Bitrex, 0.007 wt. % odorant with balance methanol.

a. Regulated Emissions

A comparison of the regulated emissions from the two fuels indicated some minor differences. When the regulated emissions from the additive blend were compared to the California M85, all exhaust emissions and fuel economy were lower for the additive blend: hydrocarbons about 9 percent, CO about 30 percent, NO_x about 7 percent, and fuel economy about 3 percent. The improvement in exhaust emissions was notable, but not sufficient to result in no more than 50 percent of the exhaust hydrocarbons as compared to M85.

b. Speciated Hydrocarbons

A comparison of the individual hydrocarbons from the hydrocarbon speciation of the exhaust reflected the specific compounds present in the fuel. As expected, the cold-start emissions constituted the majority of the hydrocarbon emissions for both fuels, and methanol was the major single component present in the exhaust for each fuel. Fuel enrichment required for vehicle starting in conjunction with an ineffective cold oxygen sensor and a cold catalytic converter lead to the majority of the hydrocarbon emissions being emitted during the cold-start of a vehicle.

TABLE 22. SUMMARY OF HYDROCARBON EMISSIONS FOR TOYOTA CAMRY DEDICATED M85 FUEL VEHICLE

Test No.	Run No.	Total Speciated HC, g/mi ^a	NMOG, ^b g/mi	Ozone Formation, g/mi	Ozone Formation Potential ^c	Toxics, mg/mi ^d
EM-1120-F ^e	1	0.33	0.32	0.45	1.41	28.2
	2	0.37	0.35	0.45	1.29	22.5
	avg.	0.35	0.34	0.45	1.35	25.4
EM-1125-F ^f	1	0.38	0.37	0.42	1.14	17.4
	2	0.40	0.39	0.42	1.08	17.0
	avg.	0.39	0.38	0.42	1.11	17.2

^aAHC results based on speciated gas chromatograph results.

^bNMOG, non-methane organic gases, includes mass of all measurable non-oxygenated hydrocarbons (except methane), ketones, aldehydes, alcohols, and ethene.

^cRatio of g/mi ozone to g/mi NMOG.

^dSummation of toxics - benzene, 1,3-butadiene, three isomers of xylene, formaldehyde, acrolein, and acetaldehyde.

^eCalifornia M85.

^f6 vol. % toluene, 2.5 vol. % butane, 0.12 wt. % DCI-4A, 0.0001 wt. % Bitrex, 0.007 wt. % odorant with balance methanol.

A higher concentration of paraffins, olefins, and aromatics except for toluene were detected from M85 when compared to the additive blend. Since toluene was one of the additives in the blend, these results also were not surprising. Total aldehyde emissions were similar for both fuels, but benzaldehyde was present in higher concentrations from the additive blend with toluene. In addition, the higher molecular weight aldehydes occurred at higher concentrations in the M85 samples. Toluene may have been the source of benzaldehyde from the additive blend, and partial oxidation of the components from the gasoline may have caused the increase in other aldehydes for M85. In general, the components in the fuel were reflected in the results from the hydrocarbon speciation.

c. Ozone Formation

Many components in the exhaust contribute to the formation of ozone when emitted into the atmosphere. The reactivity of the exhaust and amount of ozone expected from reactions in the atmosphere depends on the sum of the individual component concentrations in the exhaust and their individual reactivity factors. Olefins, aromatics, and certain aldehydes tend to produce more ozone per gram of component than paraffins. The Carter MIRs used in this study were obtained from Ms. Sarah Santoro and Mr. Bart Croes, CARB based on a FAX sent November 21, 1991. These factors are used by the State of California to estimate and predict relative levels of ozone formation based on the individual hydrocarbon components in the exhaust. Some reactivities for specific compounds were not available, so reactivities of similar compounds were selected and assigned to the compounds. In some cases, multiple compounds co-eluted from the gas chromatograph, so the reactivities were taken as the average of the reactivities of all known co-eluting compounds. These reactivities were reported in terms of grams of

ozone per gram of the individual component. Another method of comparing the fuels was through the ozone-forming potential of the exhaust, obtained by dividing the mass of ozone formed from each fuel by the mass of NMOG. Table 22 lists the mass of ozone formed per mass of NMOG and summarizes the ozone-forming potential for each test conducted on the Toyota Camry.

The ozone formation for the additive blend was 7 percent lower than the ozone formation from M85. This result correlates with a 9 percent reduction in total hydrocarbons. Benzaldehyde with a negative MIR was detected in higher concentrations in the exhaust from the additive blend, and lower concentrations of individual olefins (higher MIR values) were detected in the samples from the additive blend. These conditions contributed to the lower calculated value for ozone formation when compared to M85. These data also resulted in a lower ozone-forming potential for the additive blend (about 18 percent lower); however, the criterion in the original program of not producing more than 50 percent of the reactive exhaust hydrocarbons when compared to M85 was not met for the additive blend in this vehicle.

d. Toxic Emissions

Another comparison based on the hydrocarbon speciation data is the toxic emissions, defined here as the summation of benzene, 1,3-butadiene, the three isomers of xylene, formaldehyde, acrolein, and acetaldehyde. All of these compounds are on the CARB list of known and suspected toxic air contaminants (See Table 22). The toxic emissions for the additive blend when compared to M85 were about 32 percent lower. No comparison to M100 was performed because this vehicle was a dedicated M85 fuel vehicle. While this comparison could not be performed, the percentage of reduction in toxic emissions from this vehicle with the additive blend was a significant improvement over M85.

2. Volkswagen Jetta

A 1989 VW Jetta from another CARB program involved with the investigation of non-standard catalysts was tested in its OEM configuration with the two fuel blends from the outdoor burn experiments discussed above. The vehicle exhaust emissions from these two fuels were compared to M85 (fuel methanol blended with the Auto/Oil industry average gasoline - RF-A), M100, and RF-A gasoline. In addition to the objectives for measuring the exhaust emissions stated above, these tests were performed to determine the effect that the luminosity additives from the Task 1 Expansion had on the exhaust emissions.

A test code was developed to uniquely identify each fuel. The test codes were:

- 4% toluene + 2% indan - T&I
- 5% indan + 5% cyclopentene - I&C
- M85 blended from RF-A - M85
- Fuel methanol - M100
- RF-A gasoline - G.

Each fuel blend was analyzed for carbon, hydrogen, and oxygen as well as API gravity. These properties were necessary to compute the emission rates for each test. Table 23 lists the fuel properties for each fuel.

TABLE 23. FUEL ANALYSIS FOR VOLKSWAGEN JETTA

SwRI Fuel Code	Description	API Gravity at 60°F	Percent		
			Carbon	Hydrogen	Oxygen
EM-850-F	M100 ^a	46.9	37.48	12.58	49.94
EM-1386-F	M100 ^b	46.2	37.53	12.39	50.08
EM-1026-F	RF-A	57.4	86.74	13.22	0.00
EM-1367-F	M100 ^a with 4% toluene + 2% indan	44.8	40.65	12.16	47.19
EM-1368-F	M100 ^a with 5% indan + 5% cyclopentene	45.3	41.69	12.24	46.00
EM-1369-F	M100 ^a with 15% RF-A	47.7	42.65	12.30	45.05
EM-1403-F	M100 ^b with 15% RF-A	47.9	43.68	12.50	43.82

^aFirst batch of M100 (EM-850-F)
^bSecond batch of M100 (EM-1386-F)

Table 24 summarizes the FTP results for each fuel, and Appendix E presents the computer printouts for the individual tests. Duplicate tests were performed on each fuel to determine test to test variability. Additional testing was performed on a second batch of M85 and M100 fuel because there were some discrepancies in the initial data. Insufficient fuel was available from the first batch, so a second batch was prepared. The second batch of fuel was also blended from a new batch of M100. In general, the repeat tests with the new batches of fuel did not duplicate the previous results, indicating that some changes had occurred in the vehicle in the interim between the tests or some differences existed between the different batches of M100. No explanation was found for these differences. All results are presented here, but care should be taken when comparing the data between the different batches of fuel.

a. Regulated Emissions

A comparison of the regulated emissions using the five fuels indicated some differences resulting from the various components in each fuel. Figure 15 illustrates the average regulated emissions and fuel economy for each fuel. For comparison purposes, only the results from the first batch of M100 & M85 are presented in Figure 15. When the regulated emissions from the two additive blends were compared to M85 and M100, the average emission levels were generally within 10 percent, except for the repeat test on the new batch of M100.

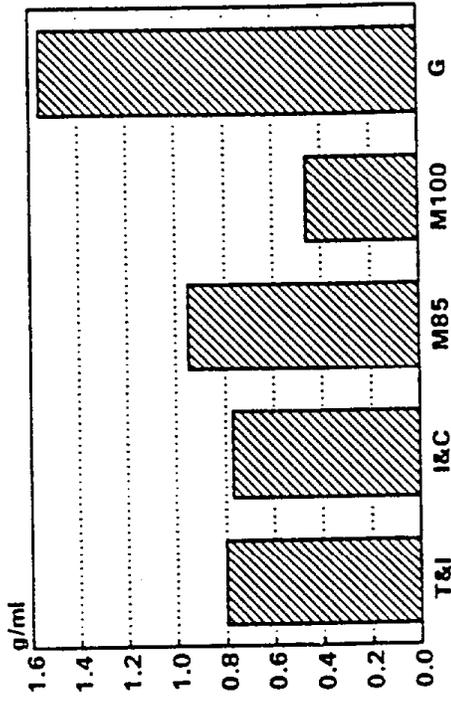
TABLE 24. SUMMARY OF FTP REGULATED EMISSIONS FOR VOLKSWAGEN JETTA

Test No.	Run No.	Emissions Results, g/mi			Fuel Economy, mpg
		HC ^a	CO	NO _x	
T&I	1	0.18	0.80	0.06	13.42
	2	0.20	0.79	0.06	13.38
	avg.	0.19	0.80	0.06	13.40
I&C	1	0.15	0.76	0.07	13.70
	2	0.17	0.78	0.07	13.64
	avg.	0.16	0.77	0.07	13.67
M85 (EM-1369-F)	1	0.17	1.04	0.08	13.85
	2	0.15	0.85	0.07	14.03
	avg.	0.16	0.95	0.08	13.94
M85 (EM-1403-F)	3	0.19	1.26	0.08	14.79
	4	0.23	1.65	0.08	13.91
	avg.	0.21	1.46	0.08	14.35
M100 (EM-850-F)	1	0.24	0.47	0.06	12.65
	2	0.20	0.44	0.06	12.55
	avg.	0.22	0.46	0.06	12.60
M100 (EM-1386-F)	3	0.32	0.73	0.07	12.30
	4	ND ^b	0.53	0.08	12.23
	avg.	ND ^b	0.63	0.08	12.27
G	1	0.18	1.48	0.10	25.08
	2	0.18	1.63	0.09	25.28
	avg.	0.18	1.56	0.10	25.18

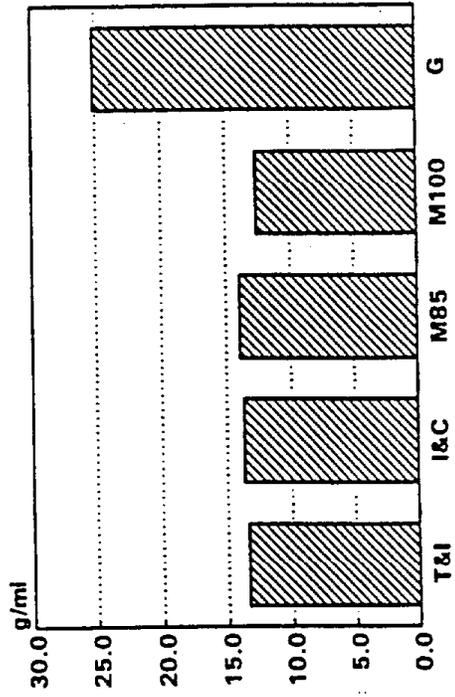
^aHC results based on fuel composition (i.e. includes mass of oxygen) and do not include an FID response correction for methanol.
^bNo data for this test because of problem with the total hydrocarbon instrument.

Only small exhaust emission differences were observed when comparing the results for the different fuels. The hydrocarbon emission rates for the two additive blends were greater than or equal to the results from the initial test on M85, and carbon monoxide (CO) and oxides of nitrogen (NO_x) emission rates were lower than M85. The hydrocarbons from the second batch of M85 were higher than

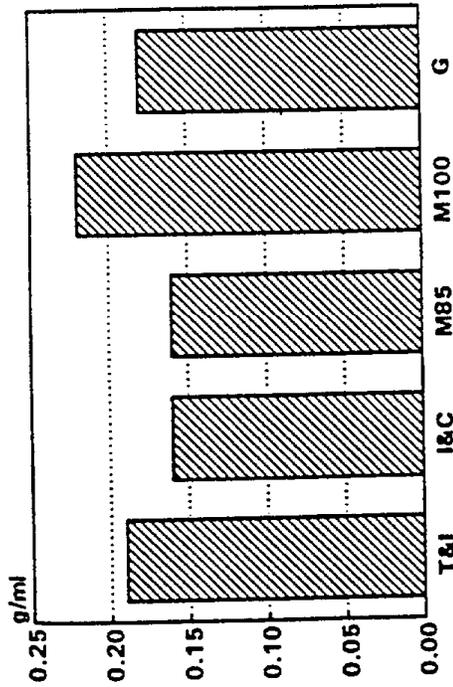
CO



FUEL ECONOMY



HC



*FID hydrocarbons only - not corrected for methanol response - does include oxygen

NOX

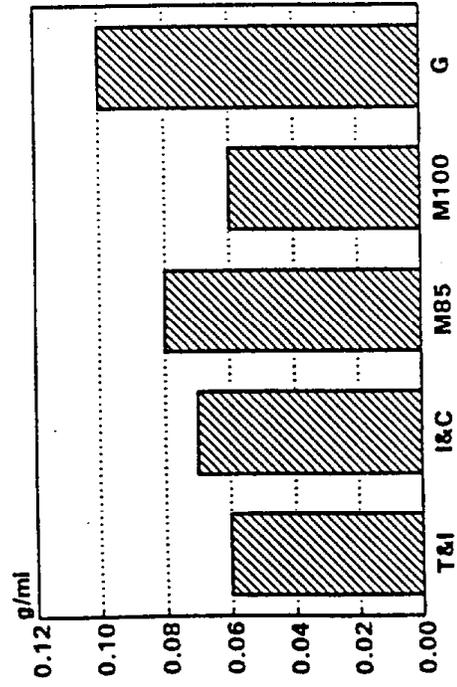


FIGURE 15. COMPARISON OF AVERAGE REGULATED EMISSION RATES AND FUEL ECONOMY

the two additive blends. Conversely, the hydrocarbon emission rates were lower and the CO rates were higher for the two additive blends than for those from either batch of M100. When the two additive blends were compared to gasoline, the CO and NO_x were significantly lower than the results from gasoline, but the hydrocarbon emission rates were split between the two additive blends. The blend with toluene and indan yielded slightly higher hydrocarbons, and the blend with indan and cyclopentene produced slightly lower hydrocarbons than gasoline. The fuel economy values for all four fuels containing methanol were about half of that for gasoline on a volumetric basis.

At the request of CARB, duplicate emission tests were repeated with a second batch of M85 and the new batch of M100 used to blend the M85 to confirm some anomalous results obtained during the previous testing. The only difference between the two fuel blends was that a newer batch of M100 was used as the blending stock. In general, the hydrocarbon and CO emissions were higher with the second batch of M85 and M100. The emissions impact on the regulated emissions from the two additive blends when compared to M100 was that the hydrocarbons were lower and the CO was higher for the additive blends when compared to either batch of M100. A similar comparison for the NO_x emissions was less clear due to the low levels of NO_x and the small differences observed in the emission results.

b. Total Hydrocarbons (Gas Chromatography)

A comparison of the detailed hydrocarbon speciation data from the five fuels indicated some emission differences resulting from the specific components in each fuel. Table 25 lists the hydrocarbon emissions from each fuel. When the total hydrocarbon emissions from the two additive blends were compared to the first batch of M85, the average total hydrocarbons were about 28 percent higher for T&I and about 17 percent higher for I&C. The hydrocarbon emissions for both additive blends when compared to the second batch of M85 were less than 10 percent lower for this batch of fuel.

A comparison with M100 yielded opposite results for the two additive blends compared to M85. Both batches of M100 yielded similar results for the total hydrocarbons. When compared to the results from the additive blends, the blend with T&I produced average total hydrocarbons about 25 percent lower than M100, and the blend with I&C was about 30 percent lower than M100.

When the average total hydrocarbons from the two additive blends were compared to the industry average gasoline, the total hydrocarbons were about 44 percent higher for T&I and about 31 percent higher for I&C. The NMOG emissions were about 69 percent higher for T&I and about 54 percent higher for I&C. In general, the total hydrocarbons were higher for the two additive blends than for the M85 and RF-A fuels and lower than for the M100 fuel.

c. Individual Hydrocarbons

To determine the effect that the luminosity additives have on the exhaust emissions, a comparison of the individual hydrocarbons from the hydrocarbon speciation of the five test fuels was made. In general, the components in the test fuels were reflected in the hydrocarbon speciation results. Appendix F lists the detailed results of the hydrocarbon speciations.

As expected, the cold-start emissions constituted the majority of the hydrocarbon emissions for each fuel. Methanol was present at the highest concentrations for all fuels except the industry average gasoline. The other components varied depending on the concentration of the additives in the fuel. M100 had about one third more methanol and much less of the other constituents than the

TABLE 25. SUMMARY OF HYDROCARBON EMISSIONS FOR VOLKSWAGEN JETTA

Test No.	Run No.	Total Speciated HC, g/mi ^a	NMOG, g/mi	Ozone Formation, g/mi	Ozone Formation Potential ^b	Toxics, mg/mi ^c
T&I	1	0.22	0.21	0.24	1.14	12.8
	2	0.24	0.23	0.27	1.17	18.0
	avg.	0.23	0.22	0.26	1.16	15.4
I&C	1	0.19	0.19	0.27	1.42	12.8
	2	0.22	0.20	0.26	1.30	13.6
	avg.	0.21	0.20	0.27	1.36	13.2
M85 (EM-1369-F)	1	0.18	0.16	0.23	1.44	12.6
	2	0.18	0.16	0.20	1.25	12.3
	avg.	0.18	0.16	0.22	1.35	12.5
M85 (EM-1403-F)	3	0.22	0.20	0.31	1.55	16.8 ^d
	4	0.24	0.22	0.28	1.27	15.1 ^d
	avg.	0.23	0.21	0.30	1.41	16.0 ^d
M100 (EM-850-F)	1	0.31	0.30	0.27	0.90	13.5
	2	0.28	0.28	0.25	0.89	14.0
	avg.	0.30	0.29	0.26	0.90	13.8
M100 (EM-1386-F)	3	ND ^e	ND	ND	ND	16.1 ^d
	4	0.31	0.30	0.28	0.93	14.8 ^d
	avg.	ND	ND	ND	ND	15.5 ^d
G	1	0.17	0.14	0.50	3.57	26.0
	2	0.14	0.11	0.40	3.64	28.4
	avg.	0.16	0.13	0.45	3.61	27.2

^aHC results based on speciated gas chromatograph results.

^bRatio of g/mi ozone to g/mi NMOG.

^cSummation of toxics - benzene, 1,3-butadiene, three isomers of xylene, formaldehyde, acrolein, and acetaldehyde.

^dData does not agree with previous tests indicating a possible change in the vehicle which prevents a direct comparison of the data.

^eNot determined because of problem with methanol analysis during the cold-start test.

other fuel blends. Corresponding quantities of the various additives were detected in the exhaust, and no cyclopentene or indan were detected in M85 or gasoline. M85 and gasoline yielded the most diverse group of hydrocarbons, while the alcohol-containing fuels produced the most aldehydes (mostly formaldehyde). Other comparisons were possible, but each comparison reflected the constituent in the fuel.

d. Ozone Formation

One criterion for the fuel additives was to have reactive vehicle exhaust emissions no more than 50 percent of the levels for M85 without the additive. When the five fuels were compared on the basis of the total ozone formation in g/mi, the two fuel additive blends, M85, and M100 formed similar amounts of ozone per mile. When these four fuels were compared against the industry average gasoline, the gasoline produced over 60 percent more ozone per mile emitted by the vehicle than the alcohol-containing fuels.

When the MIR factors were applied to the hydrocarbon speciation data from vehicle tests conducted using the five fuels in this study, the fuels were ranked on the basis of ozone formation potential. The blend with T&I was about 14 percent lower and the blend with I&C was equivalent to the first batch of M85. The second batch of M85 produced a higher ozone formation potential than the first batch, so the ozone formation potential for both additive blends were lower than that from the second batch of M85.

As mentioned earlier, olefins typically have higher reactivity factors than paraffins, so fuels containing higher concentrations of olefins would be expected to have a higher potential for ozone formation. When the two blends were compared to the first batch of M100, T&I was about 30 percent higher and I&C was about 50 percent higher than M100. The second batch of M100 yielded similar results for the ozone formation potential. The ranking of these five fuels from the best to the worst in terms of the lowest ozone formation potential are:

1. M100 (average of both batches)
2. 4% toluene + 2% indan
3. 5% indan + 5% cyclopentene
4. M85 blended from RF-A (average of both batches)
5. RF-A gasoline.

These data indicated that the additive blends resulted in a lower ozone formation potential than M85; however, the criterion of no more than 50 percent of the reactive hydrocarbons when compared to M85 was not met for the additive blends in this vehicle. All four methanol fuels were significantly better in terms of ozone formation potential than the industry average gasoline.

e. Toxic Emissions

Another comparison based on the hydrocarbon speciation data is the toxic emissions. The toxic emissions for the two additive blends when compared to the first batch of M85 (EM-1369-F) were about 20 percent higher for T&I and about 6 percent higher for I&C. With the second batch of M85 (EM-1403-F), the results were much different. The toxic emissions from T&I were 4 percent lower and about 18 percent lower for I&C. When compared to the first batch of M100 (EM-850-F), the

toxic emissions were about 12 percent higher for T&I and about 4 percent lower for I&C. With the second batch of M85 (EM-1386-F), the toxic emissions from T&I were less than 1 percent lower and about 15 percent lower for I&C. In the case of T&I, the negative impact on the toxic emissions as compared to M100 resulted primarily due to an increase from benzene in the exhaust for this blend. The higher benzene concentration was probably caused by the toluene in the additive.

The most significant difference in toxic emissions was observed between the alcohol-containing fuels and RF-A. Each alcohol fuel had between 41 and 54 percent lower toxic emissions when compared to RF-A. T&I yielded 43 percent lower toxics and I&C resulted in 51 percent lower toxics in the exhaust compared to RF-A. These data indicated that all four methanol fuels gave significantly lower toxic emissions than the industry average gasoline.