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TECHNICAL REPORT

A Review of the Compatibility of Methanol/Gasoline Blends with Motor Vehicle Fuel Systems

by

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Scope and Emphasis

This literature review of the compatibility effects of methanol/gasoline blends on vehicle systems has been undertaken as part of a larger effort by EPA to evaluate the request for a waiver of the Section 211(f) fuel additive regulations submitted by Anafuel Unlimited on February 20, 1981. This waiver has been requested by Anafuel for Petrocoal, an oxygenated, unleaded gasoline blend containing up to 12% methanol, up to 6% C-4 alcohols (not identified) and up to 0.033 g/gal but not less than 0.023 g/gal of a proprietary compound claimed by Anafuel to be a corrosion inhibitor.

Within the two week time period allowed for the preparation of this report, it has been impossible to obtain copies of literature which were not immediately available. Fortunately, a fairly comprehensive collection of references was located in-house and few important references are missing from this review. Another limitation to this report is that no compatibility information is available on the specific composition for which a waiver is requested, other than what has been supplied by the requestor. It is known that several interested parties are or will soon be conducting bench or fleet scale compatibility tests of Petrocoal,(1,2)* and the results of these tests may be important. However, since the results from these or other tests are not yet available, they are not included in this review. Other general limitations have been applied to this review to simplify and streamline this report. Only methanol/gasoline blends containing 10-15% methanol are included in this review. Special emphasis has been given to the effects of inhibitors and C-4 alcohols on the compatibility of methanol /gasoline blends in motor vehicles.

In order to best fit the specific purpose of this report and yet provide a sufficient amount of general information for background, this report is structured to fulfill two objectives. The first objective is to review in general terms the overall information on compatibility of

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* Numbers in parentheses indicate references listed in back of this report.

methanol/gasoline blends. The second objective is to apply the existing pieces of information to the Petrocoal blend in order to provide an estimate of the most likely problem/benefit areas of this blend. A related part of this objective will be a discussion of the data gaps which need to be filled in order to evaluate more fully the compatibility of Petrocoal as a motor fuel.

Conclusions

- Bench tests on typical automotive fuel systems materials of construction have indicated a number of sensitive materials in both metal and non-metal categories.

- Presence of inhibitors and/or C_4 alcohols may have a beneficial effect on automotive metals compatibility as measured in bench tests. Inhibitors have not shown any beneficial effects on non-metals.

- The bench tests have generally not shown good correlation with vehicle tests, which have appeared to indicate less problems than expected based on the bench tests.

- A wide variation in experience is evident between different researchers on the gross effects (performance, not emission) of continued use of methanol/gasoline blends. The extent of fuel related vehicle problems has varied for fleet tests over 1 year of duration.

- Very little data are available on the emissions durability of vehicles using methanol/gasoline blends. What data there are, are generally favorable, but are too sparse to support a conclusion.

- Relative to the Petrocoal blend, it is apparent that this blend has compositional characteristics (according to manufacturers' specs) preferable from a vehicle compatibility viewpoint, to a blend using only methanol. However, there appears to be no available data, either in the published literature or supplied by Anafuel, which would conclusively demonstrate that Petrocoal would be safe (from a emission control standpoint) to operate in currently available motor vehicles over long time periods.

- Relative to the Petrocoal blend several data gaps must be filled before the compatibility issue is resolved.

  1) Emissions durability to 50,000 miles should be demonstrated.

  2) Long term observed and controlled vehicle tests are probably needed.

  3) Bench data on water separation sensitivity and the corrosive effects of water contaminated blends are needed.

  4) More complete data are needed on non-metals such as nitrile for Petrocoal blends.

Review of Compatibility Literature

This section of the report provides a general overview of the compatibility information on methanol/gasoline blends. The effect of automotive fuel in general and methanol in particular on automotive fuel systems can be broken into two areas depending on the materials of interest; metals or non-metals. Further stratifications of the data are presented to pertain to the particular characteristics of Petrocoal. These categories are concerned with inhibitors and higher alcohols relative to how their presence impacts the compatibility of methanol/gasoline blends. Finally, there is a brief section on emissions durability over extended mileage. Since the Anafuel waiver request is discussed in later sections of this report, and since the data submitted by Anafuel have not been published, it will not be reviewed in this part of the report.

Several general reviews have been written which deal with the compatibility of methanol/gasoline blends (3,4,5,6,7). These studies indicate that a wide variation exists in the results of compatibility studies on methanol blends. Many different types of automotive materials have been tested under a variety of conditions. The following sections will discuss the results of these investigations on the different automotive materials of construction.

Metals

A variety of metallic parts have been identified as potentially sensitive to degradation by methanol/gasoline blends in the range of 10-15% methanol. The most frequently referred to metals are (a) terne steel or terne plate, which is used in fuel tanks, (b) magnesium and (c) aluminum, which are used in carburetors and fuel pump bodies (4).

Terne steel, which is sheet steel that is hot dipped in a tin-lead solution to retard corrosion, is almost exclusively used in current automotive fuel tanks except for some foreign models, where zinc coatings are used (1,2,4). Bench scale tests by Leng (8) on pure methanol have shown severe degradation or dissolution of the lead/tin coating of terne plated steel. A report by Poteat (9) showed accelerated corrosion of terne plate when a 10% methanol blend was compared to Indolene as a base. But both Indolene and the methanol blend corroded terne steel at a small fraction of the rate of pure methanol(See Table 1).

Table 1

Uniform Corrosion of Terne Steel in Various Fuels

Fuel	Corrosion (mg/decemeter^2)
Indolene	0.031
10% Methanol/90% Indolene (Dry)	0.173
10% Methanol/90% Indolene (Water Saturated)	0.261
Methanol	4.34

Uniform corrosion leads eventually to a removal of the protective terne lining the fuel tank, which in turn leads to accelerated corrosion of the fuel tank steel itself. Presence of water contamination leads not only to more uniform corrosion but tends to increase the tendency toward pitting corrosion which can lead to perforation of a fuel tank in a short period of time (9). Keller (6) presented data indicating that little corrosion of terne plate occurred except with dry pure methanol.

Fleet test results using terne metal in the gas tanks have not shown any catastrophic failure of the tanks due to corrosion by gasoline/methanol blends under 15% methanol (10,11,12,13,14). However, Lindquist, et al. (13) indicated that the conduction of spurious galvanic currents by rear mounted fuel pumps can lead to rapid fuel tank failure. No other instances of this type of failure in fleet tests have been found in the literature on this failure mode but the acceleration of corrosion due to the presence of electrical currents in methanol/gasoline blends has been reported from bench scale experiments by other investigators (6,9).

To expand on the issue of galvanic corrosion in methanol/gasoline blends, gasoline is known to be a relatively good electrically insulating liquid due to the general non-polar nature of the constituent hydrocarbons. Methanol on the other hand is very polar and conducts electricity much better (9). Therefore, the presence of methanol in a fuel blend would be expected to increase the tendency and extent of galvanic corrosion (6,9).

Magnesium and aluminum have also been identified as potential problem metals with respect to use of methanol/gasoline blends. Both of these materials have exhibited extensive corrosion potential in bench scale tests (6,8,9). Poteat (9) reported specific corrosion problems (pits) with aluminum at the interface of separated, water contaminated methanol/gasoline blends. Magnesium tended to dissolve in pure methanol and was significantly corroded in methanol/gasoline blends (6). Recommendations for metals to be <u>avoided</u> when methanol is used as a motor fuel (pure or in blends) include magnesium, cadmium, antimony, lead and alloys rich in these metals (8,10).

Non-Metals

The non-metals used in fuel systems consist of a large number of different polymers, elastomers, rubbers, etc. which have been responsible for the most reported failures of vehicles fueled with methanol/gasoline blends (10,13). Other investigators have shown no problems in operation of methanol/gasoline blends (8). Bench scale testing of non metals has uncovered a large nunber of sensitive non-metals which are used in automotive fuel systems. Some materials have shown consistent adverse reactions to methanol/gasoline blends. The materials which are particularly sensitive have been identified as natural rubber (not used in current motor vehicles), polyurethane (used as fuel lines in some vehicles), cork gasket material, leather, polyester bonded fiberglass laminate, PVC, and certain other plastics (polyamides and methylmethacrylate) (6,8,15,16). Other materials have shown esentially complete resistance to degradation in methanol/gasoline blends. These resistant materials are Buna N and Neoprene rubber, polyethylene, nylon and polypropylene (6,8,15,16). A very large class of non-metals appear to be affected inconsistently in various literature references. Nitrile was found to be resistant to methanol/gasoline blends by Leng (8) but to be highly sensitive in bench scale tests by Abu-Isa (15) and Cheng (16). Viton, a fluorocarbon elastomer used widely in fuel systems, shows a great variation in effects, which has been at least partially attributed to slight variations in the composition of the Viton itself (13).

It is very important to note that some non-metals such as epichlorohydrin, fluorocarbon elastomers and nitrile appear to be most sensitive to intermediate blends of methanol/gasoline and less sensitive to pure gasoline or pure methanol (15,16). The reason for this behavior can be explained by an examination of the solvent or solubility parameter for different solutions. For some elastomers the solubility parameters are closest to the solubility parameter of the mixed fuel and "like dissolves like" in the jargon of the chemist (15).

In-service failures of methanol/gasoline blends due to non metals have been caused by a variety of problems. Duncan et al. (13) reported very few problems in 3 years of operation on methanol/gasoline blends. Among the problems reported were the failure of polyurethane fuel lines, swelling of an expanded foam carburetor float, softening and swelling of needle valve tips, disintegration of in-line fuel filters and failure of one acceleration pump diaphragm. However, it is not known whether vehicles used in this program are sufficiently similar to current U.S. vehicles to extrapolate the results. Nierhauve (10) indicated that 13 cars in a fleet test exhibited numerous problems that illustrate that these cars are not suited to run on methanol blends (15% methanol) without modifications. This fleet test showed problems similar but more wide spread than the New Zealand tests (13).

Based on informal contacts with investigators at domestic automobile manufacturers, it was learned that there is widespread concern about the possible negative impact of methanol/gasoline blends in current U.S. vehicles. Acceleration pump cup diaphragms were identified as a particular concern in addition to other elastomeric materials and sensitive metals.

Inhibitors and Higher Alcohols

Corrosion inhibitors and higher alcohols have been investigated as a partial or total means of addressing the negative effects of methanol/gasoline blends as automotive fuel (6,17,18). Corrosion inhibitors are used in conventional gasolines to retard corrosion in metal fuel systems components. Higher alcohols, especially C4 iso or tertbutyl alcohol, have been tried as a way to prevent or minimize phase separation in water contaminated blends. The prevention of phase separation would have definite benefits for overall driveability as well as in corrosion of water sensitive components such as aluminum (6). There are very little data on the overall effect of using both of these methods at the same time on gasoline/methanol blends. Codling (17) reports favorable results using a proprietary blend of inhibitors (PROMAX 8027 and PROAL) to eliminate pure ethanol corrosion when used at the refinery gate in amounts of approximately 0.5 g/gallon. It is not known what effect this formulation would have on methanol/gasoline blends. Bench scale tests performed by Keller (6) using a methanol/higher alcohol/gasoline blend with and without corrosion inhibitors showed essentially no benefits due to the inhibitors. Inhibitors are not known to exert any effects on non-metals, due to methanol/gasoline blends (6). Higher alcohols have been well investigated for their effects on the water sensitivity of methanol/gasoline blends (18). Data generated by Svahn (18) showed that 1% isobutanol added to a 15% methanol/gasoline blend provided a stable blend up to 0.4% water at +5°C. Data generated by Keller (6) confirmed Svahn's data above and concluded that a non-specific blend of C_2-C_4 alcohols, as would be produced by certain methanol production processes, would be effective as a co-solvent to minimize water separation in methanol/gasoline blends.

Emissions Durability

A prime consideration in evaluating the overall compatibility of a fuel additive or fuel blend is the effects the blend will have on total emissions over the vehicles' useful life compared to operation with gasoline. The currently accepted way to gauge this effect is to operate the vehicle for 50,000 miles according to federal specifications contained in CFR 40 Part 86. However, this type of test specification is designed to provide an accelerated view of a vehicle's emission durability over a 50,000 mile period. Normally, this type of program may take only 6 months to complete rather than the 5 or so years in consumer use. Thus, if a fuel blend has long term effects on a vehicle (taking place after first 6 months) different than gasoline, a program of this type may not uncover it. Therefore, other information on long term vehicle operation and bench scale tests are important to the overall evaluation of a new gasoline additive or blend.

Very little data on methanol/gasoline blends are available on the emissions durability using the federal test procedures for 50,000 miles of operation. Stamper et al. (14) presented data for seven 1977 and 1978 vehicles for 50,000 miles of operation. These data did not indicate any emissions increases which could be attributed to compatibility problems with the methanol/gasoline blends. Crowley et al. (19) reported on a 4 vehicle fleet test (1975 vehicles) operated under similar but not identical conditions to that of Stamper. This program used a blend of 9% methanol, 1% isopropanol and a dispersant additive package in unleaded gasoline. The results of this program agreed with the previous program, showing no compatibility related emissions increases over 50,000 miles of operation over a 5 month time period.

Observations on Petrocoal

With the information presented in the previous sections of this report and with the information presently available on the composition of Petrocoal, some estimates can be made about the compatibility of Petrocoal. The composition of Petrocoal has been given as up to 12% methanol, up to 6% of unidentified C4 alcohols and up to 0.033 g/gal of a proprietary inhibitor. The C4 alcohols included in the Petrocoal additive may be sufficient to minimize phase separation in the field if appropriate caution is used in its distribution. The inhibitor in the Petrocoal blend, although unidentified, may decrease the corrosion potential of the blend, but other than a possible beneficial effect on sensitive metals which has not been indicated in the literature for inhibitors in general, no other beneficial effects are expected. In particular, the Petrocoal blend should have essentially the same degradative effects on elastomers that other 10%-15% methanol gasoline blends do. The investigators at automobile manufacturers which were informally contacted view the potential elastomer compatibility problems as a key concern in this waiver evaluation.

Observations on Anafuel Waiver Request

Up to this point in the report, the compatibility data presented by Anafuel have not been discussed. This section of this report intends to discuss the compatibility data that Anafuel presented in light of the overall literature, and to highlight data gaps which may be important to the overall evaluation of Petrocoal.

The Anafuel submissions consist of the main February 20 request to the EPA Administrator and a supplementary report prepared by Geoff J. Germaine PhD. It has been assumed that the compatibility information contained in the February 20 request is a summary of the data in the supplementary report. Therefore, only the supplementary report will be reviewed.

As a general comment, the compatibility report submitted by Anafuel seemed to be of high quality and the experiments were reported in a professional manner. The data presented indicate no significant or even noticeable problems with the Petrocoal blends in the metals and elastomers tested. However, these results appear to conflict with the published literature and also have several omissions and inaccuracies that should be pointed out.

With respect to metals, the existing literature do not support the possibility of an inhibitor that can eliminate the corrosive and degradative effects of a 10% methanol/gasoline blend on metals. However, since the corrosive effects of a low percentage methanol/gasoline blend have not been shown to be a major problem with metals tested in the Anafuel compatibility tests, it is possible that metal corrosion may not be a negative factor with Petrocoal. Some success has been shown with ethanol in developing inhibitors and thus it may be possible to have some effect on methanol/gasoline blends with a proprietary inhibitor.

The brief statement in the Anafuel report on the possible presence of galvanic corrosion is strongly supported by the literature. Methanol and methanol/gasoline blends do conduct electricity much better than gasoline. The impact of this tendency on actual vehicle operation is not known, but results from current fleet tests have not identified galvanic corrosion as a problem.

The report points out that zinc is now used to plate gasoline tanks in current vehicles (since 1975). This statement is incorrect as terne plate is still used exclusively in domestic and most foreign vehicles. In fact, the samples tested in the Anafuel report would actually be terne plate if they came from an American vehicle (such as the GM Monza). Magnesium should have been tested as a particularly susceptible metal which, because of its light weight, is being used in more vehicle applications. It is possible that the carburetor metal tested in the Anafuel report is some magnesium alloy but no definite information could be obtained from the manufacturers (according to Anafuel). Water has been indicated as both a bad and good actor in metal corrosion studies with methanol, and the presence of at least some water in the gasoline distribution network is endemic. Also, water condenses in motor vehicle gasoline tanks. However, Anafuel submitted no data on water-contaminated blends. The metal compatibility results with the pure additive (60-70 methanol) are suspect based on existing literature and should be verified. Most references indicated at least some noticable corrosion of these metals with methanol at this percentage regardless of inhibitors.

With respect to non-metals, there is little existing literature that would collaborate the data presented in the Anafuel waiver request. The elastomers tested by Anafuel were noted in the existing literature as being the most resistant to attack by methanol but even these materials tended to show some effects with methanol/gasoline blends. Many more elastomers must be examined before conclusions on Petrocoal and elastomers are made. Nitrile rubber, as the report indicates, should be tested with Petrocoal as well as fluorocarbon elastomers. Specific problem parts should be tested also including accelerator pump plungers and in-line fuel filters. Water contaminated blends were not tested and should be tested. It is important to have a complete picture on the compatibility of Petrocoal with vehicle systems before a waiver is granted. Controlled fleet studies should perhaps be run, such as is being done in California for pure methanol vehicles. In this way, the extent of compatibility related vehicle emissions increases and operational difficulties can be ascertained.

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