

Technical Support for Regulatory Action

A summary of Industry Comments
Received on Manganese Fuel
Additive (MMT)

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Notice

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Technology Assessment and Evaluation Branch
Emission Control Technology Division
Office of Mobile Source Air Pollution Control
U.S. Environmental Protection Agency

Manganese Fuel Additive (MMT)

The recent Supreme Court decision affirming the legality of the lead phase down has renewed interest in using the octane-improving fuel additive Methylcyclopentadienyl Manganese Tricarbonyl (MMT). The industrial segments most interested in use of MMT appear to be the manufacturers of it and the oil companies that are using it. According to the principal manufacturer of MMT (Ethyl Corporation) crude oil savings with MMT would amount to 1% of the crude run if all gasoline in the run were unleaded. It is apparent that the principal motivating force for the use of MMT is to improve the octane rating of the gasoline with MMT rather than with additional refining steps. The cost of MMT is traded off against a savings in crude required for the additional refining as well as refinery capital and operating costs.

MMT is currently in use as an octane "trimming" agent. The Environmental Monitoring and Support Laboratory (EMSL) of EPA is currently monitoring manganese (Mn) levels of gasolines sampled from service stations throughout the United States. The results of this survey have shown that an increasing percentage of the samples taken contain sufficient Mn to indicate MMT has been used to "trim" the octane of that sample. The latest sampling report (September, 1976) indicated 10% of the samples taken during the first half of 1976 contained significant Mn levels. This coupled with predictions of much greater use by the oil companies necessitated EPA requiring MMT be present in Certification service accumulation fuel beginning with the 1979 model year.

I. Summary of Submissions

EPA has been very interested in the MMT developments, especially because of the results of a number of EPA and industry studies that have recently been completed or are currently in progress. Some of the results from these studies show a potential negative influence of MMT on exhaust emissions. In order to more fully evaluate the research results of these industry studies, the Emission Control Technology Division of the EPA Office of Mobile Source Air Pollution Control invited the submission of MMT/emission control related data that has been developed by various companies. These following firms were contacted and supplied information to EPA.

<u>Company</u>	<u>Date Information Received</u>	<u>Comments</u>
American Motors Corp.	July 9, 1976	No data to report
Ford Motor Company	July 21, 1976	
Chrysler Corporation	July 26, 1976	
Shell Oil Company	August 10, 1976	
Gulf Oil Company	August 16, 1976	
	September 9, 1976	
British Leyland UK Ltd.	August 19, 1976	No data to report
Saab-Scania AB	August 25, 1976	No data to report
Ethyl Corporation	August 27, 1976	Main comments
	September 15, 1976	Additional data
General Motors Corp.	August 31, 1976	
Exxon Research & Engin. Co.	September 9, 1976	

A summary of these comments, by issue, is given in the following sections:

A. Effect of MMT on Octane Ratings

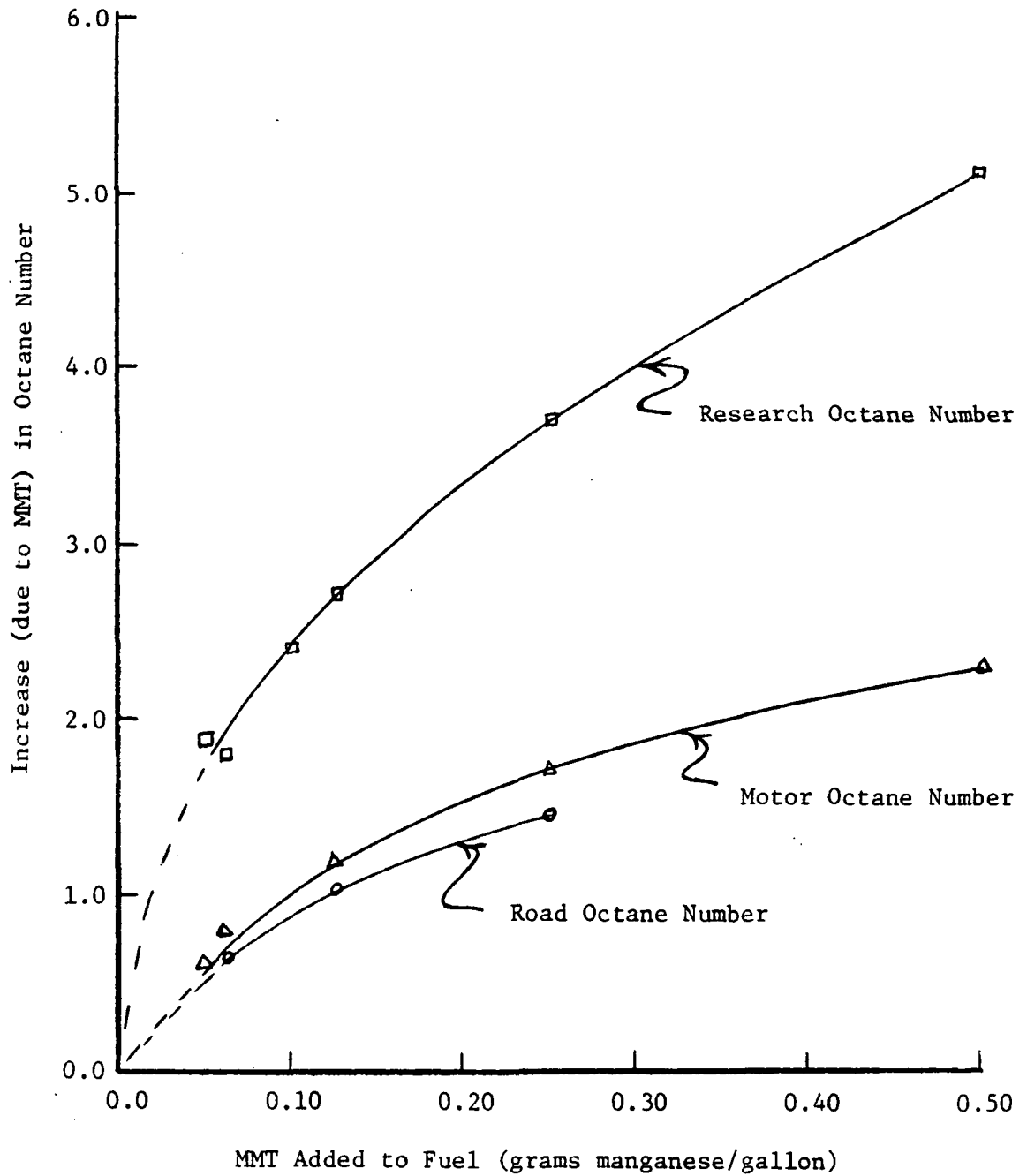
Gulf Research and Development submitted a set of data concerning the effect of MMT on octane ratings. A summary of this data is shown in Graph 1. This graph shows how octane numbers initially increase quite rapidly with the addition of MMT to gasoline. However, after the addition of about 0.125 gm Mn/gal the rate of increase in octane number is not as great.

The GM submission contained limited information concerning MMT effects on octane ratings. GM mentioned that the addition of 0.13 gm Mn/gal raised the Research Octane Number from 91.4 to 94.0 (an increase of 2.6) and raised the Motor Octane Number from 83.3 to 84.7 (an increase of 1.4).

Ethyl stated that "on the average 0.125 g Mn per gallon as MMT in unleaded gasoline gives an increase of about 2 road octane numbers". Ethyl has presented other data showing that the addition of 0.125 g Mn/gal increases RON by 2.4 and MON by 1.4. The data presented by GM and Ethyl tend to agree with that presented by Gulf, except that Gulf's Road Octane Number curve appears to be about one number low throughout its range relative to the data presented by Ethyl.

Graph 1

Effect of MMT on Octane Ratings -
Gulf Data (submitted to EPA Aug. 16, 1976)



With regards to expected usage levels and octane ratings, Shell stated the following: "It is our belief, after a review of all relevant data available to us, that the use of up to 0.1 gram of manganese per gallon (as MMT) in unleaded gasoline is a socially acceptable move which can be of benefit both to gasoline manufacturers and consumers. In general, this quantity of MMT in unleaded gasoline confers an octane improvement of 1.0 and 2.0 units (MON and RON respectively) thus permitting the production of a higher percentage of unleaded gasoline in a given refinery gasoline pool."

B. Effect on Gaseous Emissions

Shell Oil Company tested four 1975 vehicles designed to meet the 1975 Federal Standards (two Chevrolets 350 CID and two Fords 351 CID) at various intervals over 50,000 miles. The vehicles ran on lead-free gasoline containing 0.0625 gm Mn/gal. Shell concluded that HC, CO and NOx emissions did not deteriorate more rapidly than would be expected with MMT-free unleaded fuel.

Gulf Oil Company has reported the results of three studies that tested the effect of MMT on gaseous emissions. In the first study, three fuels were each run in the same three non-catalyst vehicles and the emissions were measured by the 1972 FTP. The fuels were 1) "base" fuel (without MMT or lead), 2) "base" fuel plus 0.125 gm Mn/gal, and 3) "base" fuel plus 0.125 gm Mn/gal plus 0.5 gm lead/gal. The results showed no significant difference in HC, CO and NOx emissions among the three fuels.

The second Gulf study involved operating four 1974 non-catalyst vehicles for 20,000 miles (91 RON unleaded gasoline) followed by operating the vehicle for another 20,000 miles with the same gasoline but with 0.125 gm Mn/gal added to it. The emissions were determined at various intervals. The results indicated that, whereas there was an appreciable fluctuation in the data, there was no significant deterioration in the emission levels for any of the vehicles.

The third Gulf study involves investigating the effect of MMT on catalyst activity and durability and at the time of the report was still an on-going study. Two pairs of comparison vehicles are accumulating 50,000 miles in normal customer service. These are 1975 vehicles, one pair of which are Chevrolets (350 CID engines, 2 barrel carburetors) and the others are Fords (351 CID engines, 2 barrel carburetors). One vehicle of each pair is using 91 RON unleaded gasoline whereas the other is using the same type fuel plus 0.125 gm Mn/gal. After 30,000 miles of operation, Gulf sees no significant differences in overall emissions between the two Chevrolets. However, the Ford operating on MMT is producing significantly lower CO emissions than the Ford operating on non-MMT fuel. This result may be due to vehicle variability rather than a direct effect of MMT use.

Chrysler tested a U.O.P. oxidation catalyst (70% Pt/30% Pd) in a tube furnace and on a single cylinder engine using both unleaded fuel and unleaded fuel with 0.12 gm Mn/gal. On a short-term basis, they found no significant reduction in catalyst efficiency.

Exxon reported an engine dynamometer test which was run under steady-state conditions simulating a 40 mph cruise, with catalyst temperatures of 1200-1250°F. Two fuel Mn levels of 0.0625 and 0.125 g/gal. were used. Under these conditions, no evidence of catalyst plugging was found after 700 hours or 28,000 miles of operation. No adverse effect of MMT was found on either catalyst conversions or engine HC emissions. Exxon also tested four 1975 California cars which were run for 30,000 miles under simulated urban driving conditions. Three of these vehicles used fuel containing 0.125 gm Mn/gal, while the fourth vehicle (the control) used Mn sterile fuel. Exxon's comparison of the emissions results indicated that MMT does not adversely affect either the gaseous exhaust emissions or sulfate emissions. However, non-sulfate particulates may have been increased by MMT usage.

Ford's laboratory tests of MMT on PTX catalysts showed no adverse effect under normal oxidizing conditions. Definite poisoning was noted under reducing conditions, the effects of which could be reversed by an oxidizing treatment above 500°C. Dynamometer testing with 0.25 gm Mn/gal over 96 hours (about 6,000 mi) showed no loss in catalyst efficiency. However, the test was terminated because of excessive back pressure caused by Mn deposits on the catalyst.

The GM submission reports some results from a program that was in progress wherein GM was evaluating 1) "current" (1976) and 2) "future" (1977) engine and emission control systems for compatibility with the MMT fuel additive. Two 1976 production Federal Oldsmobile Cutlasses with beaded underfloor converters and three 1977 prototype California Chevrolet Novas with monolithic manifold converters in addition to beaded underfloor converters were accumulating mileage on chassis dynamometers using a driving schedule which is considered more severe than the certification schedule. One Cutlass and one Nova were using Chevron UL77CQ unleaded gasoline which is normally used for mileage accumulation during exhaust emission certification tests. The other three cars were using Chevron UL77CQ fuel containing 0.13 grams of manganese per gallon. This program was planned to accumulate 50,000 miles on each car without changing spark plugs.

In evaluating the results from the "current" vehicle program, GM found that both Cutlasses completed 50,000 miles without any severe operational or emission control problems. Exhaust emissions from the tailpipe never exceeded the 1976 Federal standards for hydrocarbons, carbon monoxide, or nitrogen oxides. There was no apparent effect of MMT on tailpipe emissions. However, MMT appeared to increase the engine emissions of hydrocarbons. Engine back pressure increased by about 50% at full throttle on the car using MMT fuel, which probably indicates some plugging of the underfloor converter. However, emissions or performance with this car were not affected.

The "future" vehicle part of the GM program had not been completed at the time of the GM submission. The three Novas had accumulated mileages ranging from 20,000 to 40,000 miles. GM experienced many problems with one of the vehicles using MMT as the start catalyst plugged repeatedly. The other two vehicles (one with MMT fuel and one without) showed no significant deterioration in catalyst activity.

The first Ethyl Corporation submission (August 27) contained comments on the GM results showing higher engine-out HC emissions and stated that 1) this result was from one vehicle only, which could be atypical, and 2) regulated HC emissions were not adversely affected as the catalyst brought the emission down to within the applicable standards. Ethyl goes on to say "Our experience indicates that MMT actually helps in this regard by enhancing the activity of the catalyst."

Ethyl submissions described some work done with four non-catalyst cars. Two 1971 Plymouth 360-CID V-8 cars, a 1974 Buick 455-CID V-8 California car and a 1975 Ford 400-CID California car were operated for 50,000 miles of EPA-type durability driving. A 1972 Buick 350-CID V-8 was operated for 25,000 miles in continuous freeway service. Ethyl states that the data indicates some cars may show an increase in HC emission while others will show a decrease.

The CO data from the Ethyl experiments generally show a downward trend when manganese is added to the fuel. However, Ethyl did not report an improvement in CO emission except in cars equipped with catalysts where CO is generally lower with MMT than comparison cars which have not operated on MMT.

None of the Ethyl data showed any benefit for MMT in terms of NO_x control since, in nearly all Ethyl tests regardless of whether MMT is used, NO_x generally decreases with increasing mileage.

Ethyl also reported results of a fleet test of 22 vehicles operated on an EPA-type durability route for 50,000 miles (two vehicles failed to make the entire test). The fleet was paired such that one of the pair ran on 0.125 gm Mn/gal and the other ran on MMT sterile fuel. The overall conclusion was that the emissions at the end of the testing were essentially the same for both the MMT fueled vehicles and those run without MMT. Ethyl reports some other tests wherein plugging was observed on both dynamometer and road tests done on close-coupled monolithic catalysts run on MMT fuel. The testing employed a duty cycle that raises the catalyst temperatures in excess of 1500^oF.

C. Physical Effect (such as plugging) on Catalysts

In the Shell study of four 1975 vehicles (50,000 miles with unleaded fuel, 0.0625 gm Mn/gal), no plugging of either the pelletized or monolithic catalysts was observed. Gulf's study of two pairs of comparison vehicles (50,000 miles customer service, '75 Chevrolets 350 CID, '75 Fords 351 CID, one vehicle of each pair without and the other with 0.125 gm Mn/gal) includes testing exhaust pressures. As of 30,000 miles, Gulf found no evidence of catalyst plugging in any of the four vehicles. As mentioned in the previous section, Ford's engine dynamometer test showed PTX catalyst plugging at 96 hours (about 6,000 miles) using 0.25 gm Mn/gal. No temperatures were given for this data. Exxon's engine dynamometer testing showed no such plugging of the PTX catalyst after 700 hours (28,000 miles) of operation at lower MMT concentrations. They ran under steady state conditions (40 mph cruise simulation) with catalyst temperatures of 1200^o-1250^oF and used 0.0625 and 0.125 g Mn/gal.

The GM experiments have yielded information on the physical effects of MMT on catalysts. The GM program that was designed to evaluate MMT in 1976 production vehicles used two 1976 Oldsmobile Cutlasses with beaded

underfloor converters. They were tested at various intervals over 50,000 miles of heavy-duty chassis-dynamometer accumulation, one without and one with MMT in the fuel. The engine back pressure increased by about 50% at full throttle on the car using MMT fuel, which GM reports as indicative of some plugging of the underfloor converter. However, emissions or performance of this car were not affected.

The other GM program involved evaluations of 1977 California vehicles. GM used three Novas with monolithic manifold converters in addition to beaded underfloor converters, one of which used MMT sterile fuel and the other two used MMT fuel. The Nova that used MMT sterile fuel experienced no problems. One of the Novas using MMT fuel experienced very poor vehicle performance (it could not follow the driving cycle) at 8,000 miles. Upon removal of the monolithic converter, it was observed that the converter inlet was 80 to 90 percent plugged with deposits of manganese oxide, which had caused a doubling of engine back pressure. A new manifold converter was installed and the accumulation resumed. At 20,000 miles, HC emissions exceeded the standard and at 22,500 miles the second monolithic converter plugged. GM states that this plugging was probably due to higher exhaust gas temperatures, which exceed 1500°F by as much as 150°F during 70 mph cruising. The other Nova that used MMT fuel had no converter plugging in 40,000 miles, the probable principal reason being exhaust temperature slightly below the 1500°F "critical temperature" for catalyst plugging.

Ethyl commented on the Nova catalyst plugging problems in their first submission. Ethyl, too, states that the plugging is due to "the extraordinarily high temperature of the exhaust feed gas to the catalyst (1600°F+)". They also state that neither they nor GM can explain why the vehicle is operating at such high temperatures. One explanation that Ethyl gives as a possibility is that the higher test loading keeps the carburetor power jet open and the resultant rich mixture yields additional CO that is oxidized ahead of the catalyst thereby increasing

the temperature. Ethyl data show exhaust temperatures of vehicles operated on mileage accumulation dynamometers to be about 200°F higher than road operation temperatures.

With regard to the effect of MMT on catalysts, Ethyl states in their first submission that "We have accumulated many hundreds of thousands of test miles on monolithic and on pelleted exhaust catalysts with no adverse effects attributable to the use of MMT. There is good evidence from these tests that MMT enhances the conversion efficiency of exhaust catalysts". However, they later submitted to EPA a second letter detailing some plugging problems in an in-use fleet. Ethyl has "been operating a fleet of eight cars since about April of 1975 in field service using MMT in the gasoline. Four of these cars are General Motors, two are Fords and two are Chryslers. All were equipped with emission control systems designed to meet California emission standards. Four of these cars were assigned to personnel in Ethyl's Detroit Laboratories and four were assigned to field personnel in Ethyl's Petroleum Chemicals Division."

Ethyl made the following comments about these vehicles.

The four cars being operated by personnel in (the) Detroit Laboratories are being fueled by unleaded gasoline to which MMT has been added in an amount equal to 0.125 g Mn/gal of gasoline. All of these cars use monolithic catalysts and no problems have been encountered in their operation. However, in the case of the four General Motors cars operated by (Ethyl) field personnel the salesmen were to add, through small cans which they used to pour into the gas tank, MMT which was supposed to result in a concentration of MMT equivalent to 0.125 g Mn/gal gasoline. (Ethyl) now recognize(s) that the addition of MMT in this manner, if not done properly, could have resulted in some stratification and, in addition,

there is no way to know whether the amount of MMT was added to gasoline which may already have contained MMT when the gasoline was purchased. Much of the purchased gasoline was bought from oil companies who are MMT customers. If the particular purchased gasoline did in fact contain MMT, the Mn concentration in the tanks could have been as high as 0.25 g/gallon at times. Therefore, the exact concentration of MMT in the four field cars is now known.

Ethyl reported data indicating that two of these eight cars have developed some back pressure in the exhaust system at about 32,000 miles. A third car may have done so at 16,000 miles. All three were General Motors cars with pelletized catalysts. Ethyl's data indicate that this is caused by overheating of the catalyst to such an extent that the alumina in the pellets is converted from the usual gamma to the theta or alpha form, with concurrent shrinkage so that the shrunken pellets fall into the shallow depressions in which the exit louvers of the catalyst containers are located and partially block the louvers, thus reducing gas flow.

Ethyl also reported high back pressure problems on a police car after 25,000 miles of operation on 0.125 gm Mn/gal. They found a plugging situation similar to that discussed above. They go on to state that "We have been told that high back pressure is a problem in a high percentage of police cars equipped with pelleted catalysts using clear fuel".

Therefore, in summary, it appears that under many operating conditions MMT produces no measurable negative effects on either monolith or pelleted catalysts. However, there appear to be several operating conditions that could lead to temperatures high enough to not only destroy the catalyst's effectiveness but to also significantly impair the vehicle's performance. It is clear that the small amount of data presented does not resolve this issue.

D. Effect on Spark Plugs

The Shell submission reports that spark plug performance either measured directly in terms of misfire or indirectly in terms of emissions and fuel economy performance was not measurably affected by the presence of manganese, although distinct manganese deposits were very evident on used plugs.

Gulf notes that spark plug fouling has been encountered in two of the test cars. In the 1974 Mustang, fouling occurred at 15,000 miles. However, for this model car, the manufacturer recommends that spark plugs be changed at 12,000 mile intervals. In the 1975 Ford, fouling was also detected at 15,000 miles. This fouling occurred right at the recommended interval for spark plug change. There have been no spark plug failures in the other cars operating on manganese fuels.

General Motors data indicates MMT may cause plug fouling at high mileages.

Exxon reports vehicle tests of four 1975 California cars which were run for 30,000 miles under simulated urban driving conditions. Three of these cars used fuel containing 1/8 g Mn/gal., while the fourth car, which served as a control, used Mn sterile fuel. There were no adverse effects of MMT found on spark plug life in this service.

In general, it appears that at low mileages MMT has no effect (other than reddish deposits) on spark plugs. However, small amounts of data indicate a potential problem at higher mileages.

E. Effect on Octane Requirement Increase

Shell reported that octane requirement increase characteristics were similar to those determined during unleaded gasoline service. Gulf came

to essentially the same conclusion. No other data was reported on this subject.

F. Effect on Engine

Both Shell and Gulf tests indicated that engine wear rates are normal when the engine operates on MMT fuel. GM is studying this issue and has no results to report yet. Shell reported the observation that MMT "produced a very distinctive red-brown deposit layer covering the surfaces of the combustion chambers, spark plugs, and exhaust system including internal surfaces of the catalytic converter". They did not mention whether or not these deposits were harmful. Shell also studied the effect of MMT on lubricants and stated that "apart from an accumulation of manganese in the crankcase lubricant, there was no apparent effect on the lubricant and its ability to control sludge and varnish deposits". General Motors has stated that they are continuing to study some of these issues.

G. Effects on Gasoline Properties

Gulf reported that, except for octane ratings, no significant differences in fuel properties can be attributed to the addition of MMT to fuels.

H. Anticipated Future Usage

Shell has stated that their usage will be at concentrations up to 0.1 gm Mn/gal. They state that such levels will be needed initially by August, 1977 in some of their unleaded fuel production. This could grow to as much as 55% of their unleaded production over the next few years. In the remaining 45%, "it is questionable whether the use of MMT will ever prove desirable".

Gulf has commented on overall MMT usage stating that if all automotive gasoline is eventually unleaded, and if MMT is used at the maximum concentration recommended by Ethyl Corporation, then Gulf estimates that 14,000 tons of manganese per year will be consumed by the U.S. oil industry. Gulf also stated that in the foreseeable future, lead will be used in a significant portion of automotive gasoline, and the average concentration of manganese in unleaded gasoline will be lower than 0.125 gm/gal. Gulf forecasts that manganese consumption will reach 8,000 to 10,000 tons/year, and it should take about 10 years to reach that level of consumption.

With regard to industry and Exxon's MMT plans, Exxon stated the following:

We cannot, of course, speak for other gasoline producers with regard to usage of manganese. However, we could expect other companies also faced with octane capacity limitations resulting from the lead phasedown regulations to make use of as much MMT (up to the recommended maximum 0.125 g/gal.) as is available. Therefore, in the near term, its usage will probably be limited by the availability of raw materials and/or production capacity.

Exxon is currently using MMT at our Gulf/East Coast refineries and expect to begin its use at our California refinery in the near future. Initially, we expect our unleaded gasoline will average about 1/16 gram of manganese per gallon (0.0625 gm Mn/gal), with a maximum concentration of 1/8 gram per gallon (0.125 gm Mn/gal) on a continuing basis, subject to supply availability.

Preliminary Conclusions

The following preliminary conclusions can be drawn from the data submitted by the respondents:

1. Addition of about 0.125 gm Mn/gal of MMT increases the Research Octane Number by about 2.6 and the Motor Octane Number by about 1.3. The increase in Road Octane Number is uncertain as the data conflict.
2. Providing the catalyst does not plug or otherwise fail, the tailpipe emissions performance over time does not seem to deteriorate any more rapidly with MMT fuel than with MMT sterile fuel. Ethyl seems to think that catalyst HC efficiency may actually be improved by MMT because of limited data indicating increased engine-out HC emissions.
3. Limited testing indicates no adverse effects on sulfate emissions but a possible increase in non-sulfate particulate emissions.
4. Under many operating conditions (e.g. certification mileage accumulation), MMT appears to have no physical effect on catalysts other than coating the surface with a reddish-brown layer of manganese compound. However, operating conditions such as a heavy load cycle that elevate the catalyst to temperatures in excess of about 1500^oF appear to result in severe plugging of monolith catalysts. Also, limited data from GM indicate a plugging problem with pelleted, underfloor catalysts. The data presented are somewhat preliminary and more work is being done to confirm these findings.

5. Spark plug performance appears to be unaffected by MMT over the commonly recommended plug change intervals. However, some data indicate potential fouling problems at high mileages approaching 50,000 miles.
6. MMT appears to have no effect on octane requirement increase.
7. MMT appears to have no effect on engine wear rates, lubricant, or gasoline properties (other than octane number).
8. In the short term, MMT usage will be limited by the availability of raw materials and/or MMT production capability. During this short term, fuel concentrations of MMT will be at about 0.0625 gm Mn/gal and will be used in more than one half of the U.S. crude refining capacity.
9. In the long term, nearly all gasoline refiners and/or suppliers will probably be using MMT in much of their unleaded fuel frequently at concentrations of 0.125 gm Mn/gal. However, there are some companies (such as Shell) that indicate they will probably never use MMT in some portion of their fuels.
10. Projections of MMT usage appear to be generally independent of lead phase down. The oil companies that commented on this indicated that the lead phase down will tend to accelerate the introduction of MMT somewhat.
11. Projections of MMT usage were made implicitly assuming a lack of EPA regulation of MMT. Such regulation could markedly alter MMT usage patterns.