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Impacts Associated With the Use of MMT as an Octane Enhancing Additive In Unleaded Gasolines - A Critical Review

prepared for:

**Canadian Vehicle Manufacturers
Association**

**Association of International Automobile
Manufacturers of Canada**

July 2002

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July 24, 2002

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EXECUTIVE SUMMARY

To achieve air quality goals, new motor vehicles have been, and will continue to be, required to comply with increasingly stringent emission standards, both in the U.S. and in Canada. Harmonized standards allow for the harmonized use of sophisticated emission control technologies which in turn provides large environmental benefits at lower costs. To comply with existing emission standards, manufacturers have developed sophisticated systems to control engine operation and advanced catalysts that can reduce pollutant levels by more than 90% relative to engine-out levels over 100,000 miles or more of operation. Overall, current new vehicles have emissions that are 95 to 98% lower than those from pre emission control vehicles. In addition, manufacturers have developed on-board diagnostic (OBD) systems capable of identifying emission-related defects, alerting vehicle owners that defects exist, and facilitating the repair of those defects. Compliance with adopted and proposed future standards will require the use of increasingly sophisticated and advanced emission control technologies and reduce the allowable tolerances with respect to increases in emissions over the lifetime of the vehicles. Commensurate improvements in OBD systems will also be required. As a result, factors that could be ignored or tolerated in the past, even though they were known to increase emissions or impair OBD system performance, particularly on vehicles in customer service, are now of critical importance. In addition, these new technologies may be even more sensitive than older technologies to these types of factors. The continued use of methylcyclopentadienyl manganese tricarbonyl (MMT) as an octane-enhancing additive in unleaded gasoline in Canada is one of these factors.

MMT is used by refiners for economic reasons as an additive for unleaded gasolines to improve the octane rating, which is related to the propensity of a gasoline to cause engine knock. The primary combustion products of MMT are small particles of manganese oxides that are deposited in the combustion chamber of the engine and on spark plugs, as well as on oxygen sensors and catalysts in the exhaust system. While MMT use in unleaded gasoline has been widespread in Canada since 1977, it was banned in the U.S. from the late 1970s through the end of 1995 for environmental reasons; MMT use continues to be banned in California and those areas of the U.S. with the most severe air quality problems where reformulated (i.e., cleaner burning) gasolines are required. Despite the lifting of the ban on MMT use in conventional gasolines sold in the U.S., surveys of the properties of commercial gasolines sold in the U.S. show that MMT use in urban areas of the U.S. is virtually nonexistent.

Because of the ongoing concerns regarding the impact of MMT use on vehicle performance and emissions, Sierra Research, at the request of the Canadian Vehicle Manufacturers Association (CVMA) and the Association of International Automobile Manufacturers of Canada (AIAMC), performed a critical review of the information available in the technical literature related to the impact of the use of MMT in gasoline

on vehicle technology and performance. In performing this review, the primary focus was on the information available in the peer-reviewed technical literature, not on the voluminous information submitted during the various regulatory proceedings and litigations related to MMT use. The studies identified were categorized as being performed by the following groups:

1. Ethyl Corporation;
2. The automotive industry;
3. The petroleum industry;
4. Governmental organizations; and
5. Non-governmental organizations including academic researchers.

The following issues were addressed in the review:

1. MMT and the history of its use as an additive for use in unleaded gasolines.
2. MMT effects on vehicle operation and emissions including:
 - formation of combustion chamber and spark plug deposits,
 - plugging of catalytic converters,
 - performance of catalytic converters and oxygen sensors,
 - changes in tailpipe emissions, and
 - effects on OBD II system operation and performance.
3. The health effects associated with MMT and its combustion products.

The results of the review are summarized below and presented in tabular form at the end of this Executive Summary.

With respect to the impacts on engines, emission control systems, and emissions resulting from MMT's use as a gasoline additive, it is clear that the manganese oxides resulting from the combustion of MMT deposit in the engine combustion chamber, on spark plugs, and in the exhaust system, including on catalytic converters and oxygen sensors. It is also clear that these deposits lead to increases in engine-out HC emissions, which in turn lead to higher tailpipe HC emissions. Deposits on spark plugs can lead to engine-out HC emission increases for the same reasons as combustion chamber deposits; in later model vehicles, these deposits can cause spark plug misfire under certain conditions, which again leads to increased engine-out HC emissions. In addition, manganese oxide particles formed from MMT combustion can, under some conditions, result in the plugging of catalytic converters and, in general, result in higher tailpipe PM emissions. Other negative effects of manganese oxide deposits on catalysts include changes in oxygen storage properties that could render OBD monitoring systems incapable of detecting degraded catalysts.

The only positive effects reported to result from manganese oxides are small improvements in catalytic converter efficiency, which are attributed to the preferential

adsorption of catalyst poisons by the oxides, and moderate reductions in tailpipe NO_x emissions observed in two Ethyl test programs involving late 1980s and early 1990s vehicles. While the reduced NO_x tailpipe emissions may be attributed at least in part to improved catalyst activity, other factors appear to be involved—these may include changes in the nature of the chemical reactions occurring in catalytic converters due to the presence of manganese oxides and changes in engine-out emission levels. In addition, there are issues associated with these test programs that raise questions regarding the relevance of the data to vehicles operated in Canada; these include the MMT levels of the test fuels being less than half that allowed in Canada and the vehicles upon which MMT impacts were evaluated being driven on MMT-free gasoline for a substantial period of time when new.

Public exposure to MMT, manganese compounds and particulates that result from MMT combustion is of concern with respect to public health. MMT itself is a highly toxic compound for which no detailed study of public exposure has been performed. The issue of whether public exposure to manganese compounds resulting from MMT combustion poses a significant threat to public health is somewhat complicated. Manganese oxide particles emitted from vehicles using MMT have been shown to be less than 2.5 µm in diameter. As evidenced by the promulgation of new air quality standards for PM in this size range specifically to protect public health, the manganese oxide particles emitted due to MMT use are of general concern. In addition, there are concerns stemming from the toxicity of manganese compounds in particular. Although the Canadian government concluded in 1994 that public exposure to manganese particles from MMT use is not of concern, a significantly different conclusion has been reached in the U.S., where significant concerns still exist and new studies are ongoing. In addition, the possibility that MMT will lead to increased emissions of particulate matter and toxic air contaminants has also been described in the literature.

MMT Issues and Studies Matrix					
Issue	Auto Industry	Ethyl	Oil Industry	Government	Non-Gov. Organizations
Health Effects	N/A	N/A	N/A	Canada - No Concern U.S. - Still Being Studied	Concern
Exhaust Emissions Impacts	MMT increases HC, PM and Toxic Air Contaminant emissions	MMT generally increases HC emissions and decreases NOx emissions	N/A	MMT increases HC emissions in older vehicles	N/A
Catalyst Impacts	Manganese oxide deposits can plug catalytic converter and lead to slight increases in observed catalyst efficiency	Manganese oxide deposits can plug catalytic converters and lead to slight increases in observed catalyst efficiency	N/A	N/A	N/A
Combustion Chamber Deposits	Manganese deposits form leading to higher engine-out HC emissions	Manganese deposits form and higher engine-out HC emissions are observed	N/A	N/A	N/A
Ignition Misfire	Manganese deposits form on spark plugs and cause misfire	Manganese deposits form on spark plugs but do not cause misfire	N/A	N/A	N/A
OBD System Performance	Suggests that OBD catalyst monitoring may be impaired	Suggests that OBD catalyst monitoring is not impaired	N/A	N/A	N/A
Oxygen Sensor Impacts	MMT may affect oxygen sensor performance even at concentrations	MMT damages sensors at higher levels but not at lower levels	N/A	N/A	N/A

Section 1

MMT – Overview

MMT - OVERVIEW

Summary

Methylcyclopentadienyl manganese tricarbonyl (MMT) is a highly toxic organo-metallic compound used by refiners for economic reasons as an additive in unleaded gasolines to improve the octane rating, which is related to the propensity of a gasoline to cause engine knock. The primary combustion products of MMT are small particles of manganese oxides that are deposited in the combustion chamber of the engine and on spark plugs, as well as on oxygen sensors and catalysts in the exhaust system. While MMT use in unleaded gasoline has been widespread in Canada since 1977, it was banned in the U.S. from the late 1970s through the end of 1995 for environmental reasons; MMT use continues to be banned in California and those areas of the U.S. where reformulated (i.e., cleaner burning) gasolines are required. Despite the lifting of the ban on MMT use in conventional gasolines sold in the U.S., surveys of the properties of commercial gasolines sold in the U.S. show that MMT use in urban areas of the U.S. is virtually nonexistent.

MMT - OVERVIEW

Technical Background

MMT is the acronym for methylcyclopentadienyl manganese tricarbonyl, a manganese-based organo-metallic compound. Chemical property data for MMT are provided in Table 1. MMT is a yellow to dark orange liquid under normal conditions. It is quite toxic and decomposes when exposed to light.

Chemical Formula	$\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$
Molecular Weight	218.1
Melting Point (°C)	1.5
Boiling Point (°C)	233
Density (g/cm ³)	1.4
Vapor Pressure (mm Hg @ 21°C)	0.052
Toxicity	High

MMT is produced by the Ethyl Corporation and is added to gasoline in Canada and some other countries to improve the octane rating. The octane rating is a measure of the propensity of the gasoline to cause engine “knock” and related driveability problems that can lead to engine damage. The use of MMT in gasoline at levels up to the limit set in Canada by the Canadian General Standards Board (CGSB), 18 milligrams of Mn per liter of gasoline, can increase the octane rating of regular unleaded gasoline by as much as 1.25 octane numbers and that of premium gasolines by as much as 0.75 octane numbers.¹ MMT is used in gasoline to increase octane because gasoline producers have found it to be more economical than other methods of increasing gasoline octane ratings.

Up until the mid-1980’s in Canada, tetraethyl lead (TEL - $\text{Pb}(\text{C}_2\text{H}_5)_4$) was widely used as a gasoline additive for purposes of improving the octane ratings of gasoline. However, concerns regarding the environmental and health impacts of automotive emissions of lead and regulations requiring the use of catalytic converters that would be poisoned by lead resulted in requirements mandating the production of unleaded gasolines in the mid-1970s in the United States and Canada. Although MMT was first introduced into

gasoline in the U.S. in 1957 as a supplement for TEL, the perceived need for a lead-free, octane-enhancing additive to replace TEL led to the introduction of MMT into unleaded gasolines as such a replacement beginning in the mid-1970s.²

When MMT-containing gasoline is introduced into the engine of a gasoline-powered vehicle, most of the MMT is converted to manganese oxides as a result of the combustion process. These oxides take the form of small particles with diameters of less than 1 μm . The most prevalent oxide is trimanganic tetroxide (Mn_3O_4), with some manganese sesquioxide (Mn_2O_3) also being reported. The MMT that passes through the engine and exhaust system in an unreacted form quickly undergoes photolysis in the atmosphere when exposed to light. The half-life of MMT in the atmosphere has been reported to be on the order of 15 seconds. Early development work performed by Ethyl regarding MMT indicates that the formation of very small metal oxide particles is critical to the anti-knock characteristics of MMT because these particles interrupt chemical reactions leading to engine knock.³ These small particles of manganese oxides deposit in the combustion chamber, on spark plugs, and in the exhaust system (including on oxygen sensors and catalyst converters) of gasoline-powered vehicles.^{4,5}

History of MMT Use in Gasoline in the U.S. and Canada

As noted above, MMT was first introduced into leaded gasolines in U.S. in the late 1950s as a supplement for TEL. Beginning in the mid-1970s, MMT was introduced into unleaded gasolines in the U.S. by refiners at levels varying up to 33 mg Mn per liter, the maximum level recommended by Ethyl. This upper limit on MMT use was recommended by Ethyl to prevent problems such as shortened spark plug life and because the effect of increased MMT concentration begins to have smaller effects on gasoline octane ratings beyond that range. In 1977, Ethyl reduced its maximum recommended level to 16.5 mg Mn per liter based on concerns expressed by auto manufacturers regarding the impacts of MMT on vehicle emissions and emission control systems.⁶ Despite the reduction in recommended MMT levels in unleaded gasoline, the introduction of MMT into unleaded gasoline sold in California was banned in California in September 1977.^{7,8} That ban, which was recently reviewed by CARB, remains in place.⁹

Amendments in 1977 to the U.S. Clean Air Act resulted in a ban on the use of MMT in unleaded gasoline throughout the rest of the U.S. that took effect on September 15, 1978.¹⁰ However, the 1977 Amendments also include provisions that would allow the U.S. EPA to grant waivers allowing the use of MMT and other fuel additives in gasoline provided that applicants for such waivers demonstrate that the use of the additive does not cause or contribute to the failure of any emission control device or cause vehicles to exceed the emissions standards to which they were certified. Ethyl Corporation applied for such a waiver in 1978 for MMT in gasoline at concentrations equivalent to 16.5 and 8.3 mg Mn per liter. This application was denied by the U.S. EPA in September 1978 because of concerns regarding increases in HC emissions.¹¹ Ethyl Corporation submitted another waiver application in 1981 for MMT at concentrations equivalent to 4.1 mg Mn per liter, which was again rejected by the U.S. EPA for similar reasons.¹² A third waiver application was submitted by Ethyl for MMT at the 8.3 mg Mn per liter level in 1990;

Ethyl later withdrew that application but submitted a similar application in 1991. This fourth application was ultimately denied by the U.S. EPA based on concerns that the methodology used to assess the impact of MMT on vehicle emissions was obsolete and because of concerns regarding the impact of public exposure to the combustion products of MMT.¹³ The denial of Ethyl's fourth waiver application was overturned by the U.S. Court of Appeals and MMT has been allowed for use in conventional unleaded gasolines in the U.S. at levels of up to 8.3 mg of Mn per liter since the end of 1995. Despite this fact, MMT use does not appear to be widespread in the U.S., as evidenced by the fact that nationwide fuel surveys conducted by the American Automobile Manufacturers Association (AAMA) in the summer of 1997¹⁴ found no manganese in any of the samples taken of U.S. unleaded gasolines and a similar survey performed in the summer of 1998¹⁵ found manganese at measurable levels in only one U.S. sample out of a total of 428 U.S. samples. The manganese level in this one fuel was 0.3 mg Mn per liter, far below the level normally associated with MMT treatment, and this result would not appear to be indicative of MMT use.

While MMT has not been used to any significant degree in unleaded gasolines marketed in the U.S. since the mid-1970s, the additive has been widely used in unleaded gasoline marketed in Canada since 1977. As noted above, the CGSB National Standard of Canada for Unleaded Automotive Gasoline allows for the use of MMT at levels up to 18 mg Mn per liter, more than twice the maximum level currently allowed in conventional gasolines in the U.S. Samples of gasoline taken from Canadian service stations during the summers of 1997 and 1998 as part of the AAMA surveys showed MMT to be in widespread use in certain areas of Canada at levels approaching the CGSB maximum. The Canadian federal government attempted to restrict the use of MMT by enacting the Manganese-based Fuel Additives Act in April of 1997. However, the provisions of the Act limiting the movement of MMT were rescinded in July 1998. At this time, the use of MMT in Canadian unleaded gasolines up to the levels allowed by the CGSB is unrestricted in those jurisdictions that have adopted the CGSB gasoline standards.

Prohibitions on MMT Use in U.S. Reformulated Gasolines

Regulations requiring the reformulation of gasolines to reduce emissions of HC, NO_x, and toxic air contaminants in those areas of the U.S. with the worst air quality problems have been enacted by the U.S. EPA and the California Air Resources Board. The use of MMT is prohibited in reformulated gasolines sold in the United States under both U.S. EPA and CARB regulations. On the federal level, heavy-metal additives, including MMT, are also prohibited in the reformulated gasolines, notwithstanding the general EPA waiver regarding MMT.¹⁶ Since reformulated gasoline is required on a statewide basis in California, MMT use is effectively banned by the 1977 statute banning its use in unleaded gasolines in general.

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11. Federal Register, 43: 41424, September 18, 1978.
12. Federal Register, 46: 58630, December 1, 1981.
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Section 2

Vehicle Exhaust Emission Control Systems

VEHICLE EXHAUST EMISSION CONTROL SYSTEMS

Summary

Gasoline-powered motor vehicles have been required to comply with the increasingly stringent standards imposed by governmental agencies in the U.S. and Canada over the past 30 years.

The pollutants of primary concern in the engine exhaust from gasoline-powered vehicles are the following:

- **HC** (hydrocarbons) attributable to unburned or partially burned fuel (most so-called toxic air contaminants such as benzene, formaldehyde, and 1,3 butadiene are considered to be hydrocarbons);
- **CO** (carbon monoxide) resulting from the incomplete combustion of hydrocarbons;
- **NO_x** (oxides of nitrogen), which are formed from the nitrogen and oxygen present in air as a result of high temperature and pressure conditions that occur in the engine cylinders during combustion; and, to a somewhat lesser extent,
- **PM** (particulate matter), which can arise from a number of sources including incomplete vaporization of fuel droplets, incomplete combustion, sulfur and other inorganic compounds present in gasoline and lube oil, and metals such as lead and manganese that are introduced as fuel additives.

To comply with existing emission standards, manufacturers have developed sophisticated computer controlled systems that rely on input from a number of different sensors to precisely control engine operation. Key among these sensors is the oxygen or air/fuel ratio sensor (or sensors) used to maintain precise control the relative amounts of fuel and air delivered to the cylinders of the engine. These computerized engine control systems both reduce the levels of emissions coming directly out of the engine and facilitate the use of highly effective exhaust aftertreatment devices to further lower pollutant levels before they reach the tailpipe. At present, three-way catalytic converters (which oxidize HC and CO and reduce NO_x) are the primary aftertreatment device. These catalysts are required to reduce engine-out emission levels by more than 90% for 100,000 miles or more of operation. In addition, manufacturers have developed on-board diagnostic (OBD) systems capable of identifying emission-related defects, alerting vehicle owners that defects exist, and facilitating the repair of those defects.

Compliance with the recently adopted Tier 2 emission standards will require the use of increasingly sophisticated and advanced emission control technologies and reduce the allowable tolerances with respect to increases in emissions over the lifetime of the vehicles. Commensurate improvements in OBD systems will also be required. Some of these advanced technologies will require modifications to gasoline properties if they are to perform properly.

VEHICLE EXHAUST EMISSION CONTROL SYSTEMS

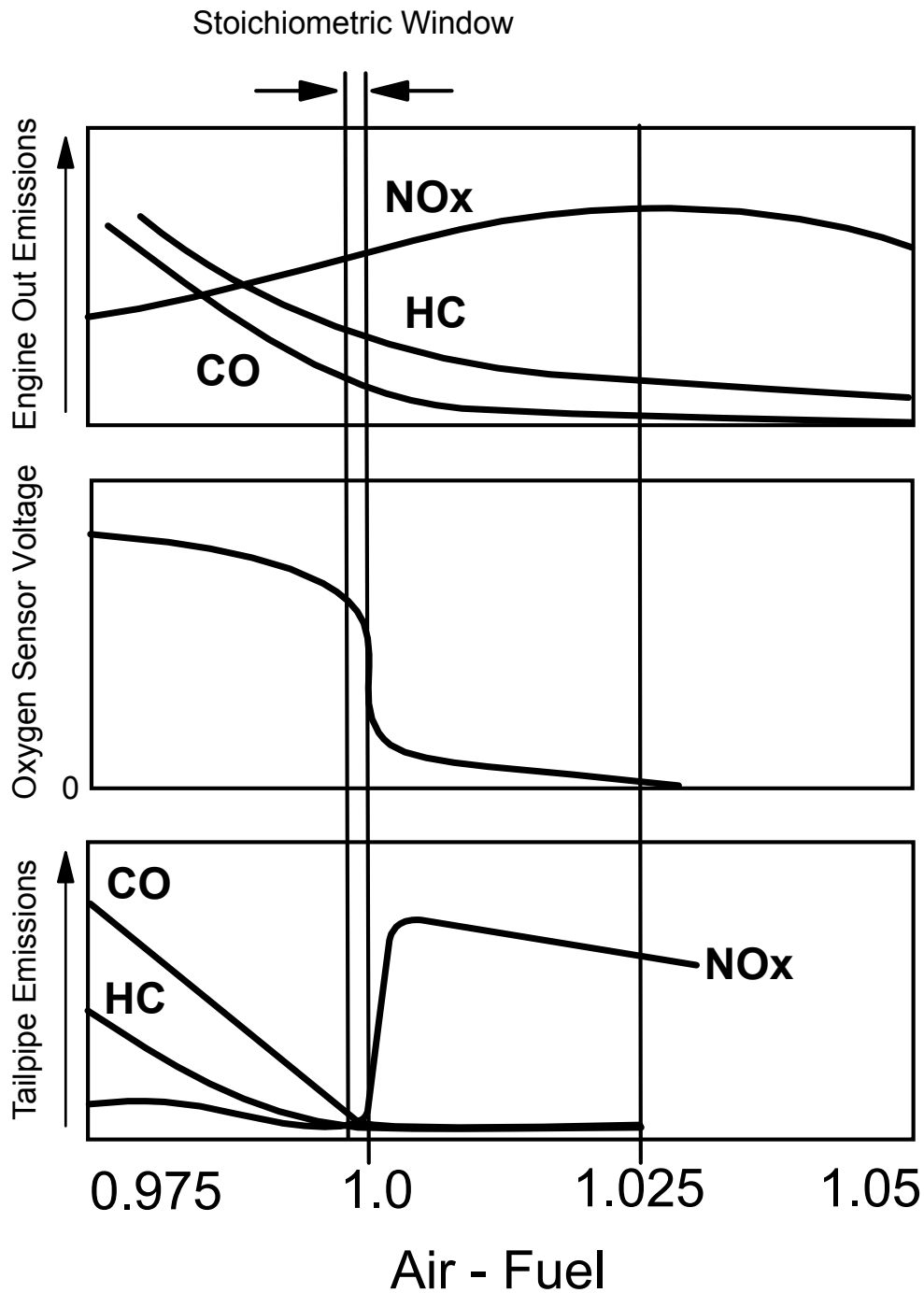
The system designed to reduce exhaust emissions from gasoline-powered vehicles essentially consists of two basic components: (1) the engine and its fuel management system, which are designed to reduce emission levels coming directly from the engine and provide control over the composition of exhaust gases; and (2) aftertreatment devices, which are used to further reduce pollutant concentrations in the exhaust gases. In addition, as noted above, the emission control system on more recent vehicles also includes the OBD II system, which monitors the engine, fuel management system, and aftertreatment devices for proper performance.

Basic Engine Operation - The first step in the operation of a gasoline-fueled engine begins with a mixture of fuel and air being drawn into an engine cylinder through the intake valve (or valves) as a result of the downward motion of the piston on the intake stroke. This mixture of fuel and air is referred to as the “charge.” At some point at the end of the intake or the beginning of the compression stroke, the intake valve closes and the charge is compressed as the piston moves back up in the cylinder. As a result of this compression, there is an increase in both the pressure and temperature of the charge. At a predetermined point during the compression stroke, the ignition system causes the spark plug to fire, which results in the ignition of the charge. Combustion then takes place towards the end of the compression stroke and into the beginning of the power stroke, which is the downward stroke following combustion. The contents of the cylinder are then discharged into the exhaust system through the exhaust valve (or valves) during the final upward movement of the piston on the exhaust stroke.

The chemical composition of the exhaust gases is determined by a number of factors, the most important of which are the ratio of air to fuel in the charge and whether the charge has been properly ignited. Assuming that proper ignition has occurred, engine-out emissions of HC and CO will be high and NO_x emissions will tend to be low if there was excess fuel present in the charge (rich operation); NO_x emissions will tend to be high and HC and CO emissions will tend to be low if there was excess air present in the charge (lean operation). A conceptual representation of engine-out emission levels for HC, CO, and NO_x as a function of air fuel ratio is shown in the top graph in Figure 1.

If proper ignition does not occur, HC emissions will tend to be high and CO and NO_x emissions will tend to be lower; however, the degree to which emissions are affected will depend on the specific circumstances surrounding the event. Improper ignition is also referred to as misfire.

Figure 1

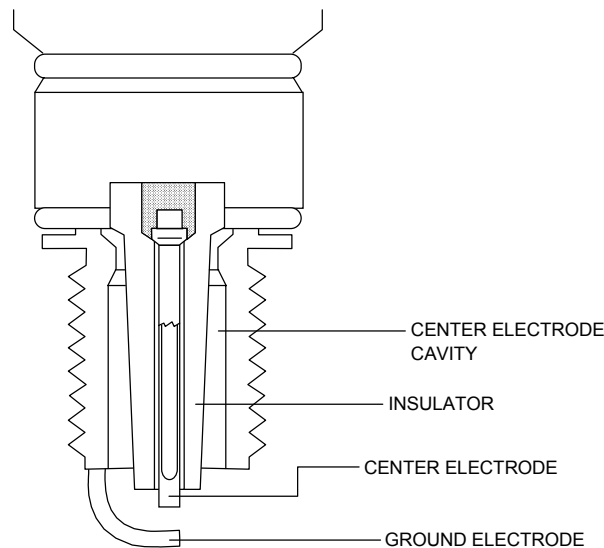


There are a number of other factors associated with engine design that can affect emissions. These include the surface to volume ratio of the combustion chamber, where larger surface areas tend to lead to higher HC emissions; and the compression ratio,

where higher ratios tend to lead to higher NO_x emissions. In cylinder deposits can also affect emissions.

Spark Plugs - As discussed above, the firing of the spark plug initiates the combustion of the cylinder charge under normal conditions. Figure 2 shows a schematic of a standard spark plug. As shown, the center electrode is surrounded by a ceramic insulator and is opposite the curved ground electrode. Spark is caused by the creation of a large voltage difference between the center electrode of the spark plug and the ground electrode. The spark originates at the center electrode and then arcs across the “gap” to the ground electrode. In general, the greater the gap the greater the required voltage difference and the greater the amount of the cylinder charge that is ignited.

Figure 2
Diagram of Spark Plug



Fuel Management Systems - On older vehicles, carburetors were used to add fuel to the air being drawn into the engine. Usually, a single carburetor located on the top of the intake manifold prepared the air-fuel mixture that was introduced into all cylinders of the engine. On newer vehicles, fuel injection systems are used. While there are many different variants, fuel injection systems can be broken down into two basic types: single-point (or throttle-body) and multi-point. In single-point systems, a single large fuel injector is used to replace the carburetor and is located at the top of the intake manifold. As is the case with a carburetor, this single injector is used to prepare the air-fuel mixture that is introduced into all cylinders of the engine. With multi-point systems, an individual fuel injector is provided for each cylinder of the engine. The injectors are located in the runners of the intake manifold leading to each cylinder. In general, multi-point systems provide much more precise control of air fuel ratio than do carburetors or

single-point systems. Therefore, they are found on virtually all new vehicles produced today.

In addition to the type of fuel metering device that is used on a vehicle, the other important factor with respect to air-fuel ratio is whether there is a control system associated with the fuel metering device. On most 1981 and later model year vehicles, fuel metering devices are controlled by what is known as a “closed-loop, feed-back control system.” In general, this system uses output signals from one or more oxygen sensors placed in the exhaust stream along with signals from other sensors to maintain a near stoichiometric* air/fuel ratio. As is discussed below, in order to improve the efficiency of catalytic converters, the feedback control system rapidly switches the air/fuel ratio of the vehicle back and forth between slightly rich (excess fuel) and slightly lean (excess air) operation in a narrow window about the stoichiometric point, relying primarily on the output signal from the oxygen sensor(s).

Despite the name, what an oxygen sensor actually measures is the amount of oxygen remaining in the exhaust after all of the HC, CO, and other reducing species have been oxidized. The sensor consists of a small, highly efficient catalyst that performs the oxidation function and a detector that measures the oxygen content of the gas sample after it has passed through the sensor catalyst. A generalized representation of the output voltage of an oxygen sensor is shown in the second graph of Figure 1. The very steep portion of the response curve shown in Figure 1 is referred to as the switch point of the sensor.

Oxidation Catalysts - The first type of catalytic converter developed for motor vehicle applications was the oxidation catalyst. As noted previously, oxidation catalysts oxidize HC and CO in vehicle exhaust under conditions where there is excess oxygen in the exhaust gas stream. Catalysts of this type were introduced with the 1975 model year in the U.S. and to a lesser degree in Canada. They were found on most passenger cars and light-duty trucks through the 1980 model year in the U.S. and until somewhat later in Canada. In addition, they continued to be used on some applications in both the U.S. and Canada for a considerably longer period of time, particularly on heavier gasoline-powered trucks.

The primary catalytic materials in oxidation catalysts were the noble metals, platinum (Pt) and/or palladium (Pd), which were supported on a ceramic monolith substrate or in some cases on ceramic beads. A high surface area coating, usually alumina (Al_2O_3), was applied to the substrate. The high surface area coating is used to provide a large number of sites at which reactions can take place. The noble metals were applied to the high surface area coating using wet methods. The available surface area of a typical automotive converter (which has a volume on the order of 1 to 2 liters) is on the order of 45,000 square meters or about 500,000 square feet.¹ This area equates to that of about ten football fields. In addition to the noble metals and high surface area coating, other compounds are also incorporated into the catalyst formulation for a variety of reasons,

* At the stoichiometric point, there is just enough air present to provide enough oxygen to completely combust the fuel.

including to enhance (or promote) the activity of the noble metals, to stabilize the noble metals, or to reduce the sensitivity of the catalyst to poisons such as lead.

With respect to stabilization, it is the available noble metal surface area that is important in automotive catalysts, rather than simply the total mass of the noble metals.*

Therefore, in catalyst preparation, great attention is paid to assure that the noble metals are present in the smallest particle sizes possible (i.e., dispersed to the greatest possible extent) in order to maximize surface area. Larger noble metal particle sizes are more thermodynamically favoured; as a result, when catalysts are exposed to high temperatures, the noble metals can “sinter” into larger particles and thus reduce the available surface area and the efficiency of the catalyst. Stabilizers are therefore used to minimize sintering.

Three-Way Catalysts - In contrast to oxidation catalysts, three-way catalysts are designed to oxidize HC and CO and reduce NO_x. High efficiency for both of these processes is achieved by rapidly switching the air/fuel ratio of the vehicle back and forth between rich (excess fuel) and lean (excess air) operation in a narrow window about the stoichiometric point using the closed-loop feedback fuel control system described above. The impact of three-way catalysts used in combination with closed-loop feedback control can be seen in the bottom graph shown in Figure 1. This graph depicts a generalized representation of tailpipe emissions of HC, CO, and NO_x from a three-way catalyst, closed-loop vehicle as a function of air:fuel ratio. As shown, at near stoichiometric air:fuel ratios, emissions of all three pollutants are low; excessive deviations from stoichiometry toward lean air fuel ratios result in low emissions of HC and CO, but high emissions of NO_x. This is due primarily to the fact that catalyst conversion efficiency remains high for HC and CO under lean conditions, but becomes very low for NO_x reduction. Conversely, rich deviations lead to high NO_x reduction efficiency but poor efficiency for HC and CO oxidation and, therefore, relatively low NO_x emissions but high HC and CO emissions. As this figure illustrates, proper management of the air:fuel ratio is a critical factor in assuring that three-way catalysts operate at a high efficiency level for all three pollutants.

Three-way catalysts are formulated using one or a combination of three “noble” metals: Pt, Pd, or rhodium (Rh). In the past, the first two of these metals were used to provide good oxidation properties while the latter was used to provide good reduction properties.

Some advanced catalysts continue to rely on the use of Pt and Rh while others use only Pd to perform both the oxidative and reductive functions associated with three-way catalysts. Most three-way catalysts employ a ceramic monolith substrate to support the catalyst although some catalysts use metallic substrates. Again, a high surface area coating is used and other compounds are included in the catalyst formulation to improve efficiency, stabilize the noble metals, and reduce the sensitivity of the catalyst to poisons.

One such compound is ceria (CeO₂). Ceria stores oxygen during lean conditions (excess air) and releases it during rich conditions (excess fuel), allowing for the oxidation of HC and CO. The storage of oxygen during lean conditions also facilitates the reduction of

* While it is surface area rather than total mass that is important, it must be noted that for a given size of metal particle, the total surface area will increase as the number of metal particles, and hence the total mass or “loading,” of precious metals, is increased.

NOx.² As is discussed below, the oxygen storage properties of ceria are also of critical importance to operation of OBD II catalyst efficiency monitors.

OBD II Systems - OBD II systems are in widespread use on later-model vehicles sold in Canada and the United States. The purpose of these systems is to identify emission control system defects and malfunctions leading to high emissions, to inform the motorist that such defects exist, and then to facilitate the repair of the vehicle. Focusing in more detail on the CARB OBD II regulations, the general requirement is that the MIL be illuminated whenever a malfunction occurs that causes the emissions of any pollutant to exceed a level equal to 1.5 times the applicable emission standard. Given that the exhaust emission standards for different certification levels vary, this means that, on a gram per mile basis, the actual exceedance of the emissions standard that constitutes a “malfunction” under the CARB OBD II regulations also varies and compliance with both the OBD II regulations as well as the exhaust emission standards becomes more difficult as one moves from vehicles certified to less stringent standards to those certified to more stringent standards.

From the perspective of exhaust emissions, the two most important monitoring requirements are probably those associated with catalyst efficiency and oxygen sensor performance. CARB staff has long recognized that catalyst monitoring is very challenging and has provided some relief with respect to catalyst monitoring requirements for LEV program vehicles. At present, the catalyst monitoring criterion for TLEVs requires that the MIL be illuminated once emissions exceed a level equal to the sum of 2.0 times the applicable standard plus the emissions level of the vehicle when it was new.* Similar requirements apply for LEVs and ULEVs, with the respective multiplier values being 2.5 and 3.0 times the applicable standard. Beginning with the 2002 model year, the catalyst monitoring malfunction criterion is 1.75 times the applicable standard for all LEV program vehicles without any addition of new vehicle emission levels. Catalyst monitoring requirements for LEV II vehicles also generally specify a malfunction criterion of 1.75 times the applicable standard for HC as well as requirements that catalyst efficiency for NOx conversion also be monitored using a similar malfunction criterion.

Although the OBD II regulations call for the monitoring of “catalyst efficiency,” the actual property being monitored is a somewhat related property known as the “oxygen storage capacity” of the catalyst. Again, oxygen storage capacity in automotive catalytic converters is provided mainly by ceria.² Catalyst monitoring strategies are based on the concept that high levels of oxygen storage capacity correlate with high HC conversion efficiencies. However, the relationship between oxygen storage and efficiency can vary dramatically and catalysts with good conversion efficiencies can exhibit low oxygen storage.^{2,3} Given this, automakers and their suppliers have reengineered catalysts in order to provide a better relationship between oxygen storage and efficiency.

* Because new-vehicle emissions can be highly variable, CARB defines “new” in this case as a vehicle that has accumulated 4,000 miles.

As noted above, the OBD II catalyst monitoring strategies currently being employed by manufacturers rely on a linkage between the oxygen storage capacity of the catalyst and the HC conversion efficiency of the catalyst. The monitoring system usually involves two oxygen sensors: one placed upstream of the monitored catalyst, and the second placed either somewhere within* or behind the monitored catalyst. The primary function of the front oxygen sensor is to facilitate the rapid switching of the air/fuel ratio necessary for stoichiometric operation and high conversion efficiencies of HC, CO, and NOx. In performing this function, the sensor's output voltage switches rapidly between its rich and lean limits in a cyclic pattern. This cyclic pattern is caused by the variations in the oxygen content of the exhaust gas created with the shifting of the air fuel ratio. Oxygen is alternatively adsorbed (during lean conditions) and released (during rich conditions) as the exhaust gas passes through the catalyst; this results in a change in the oxygen content of the exhaust. Therefore, the response pattern of a sensor in or downstream of a catalyst with high oxygen storage is considerably different than that of the front sensor. Conversely, if the catalyst has little or no oxygen storage capacity, the downstream sensor response pattern is similar to that of the upstream sensor. This approach to catalyst monitoring is generally known as the dual oxygen sensor method.⁴

Another approach to monitoring catalyst efficiency based on oxygen storage involves the use of calibrated excursions to rich and lean conditions specifically for monitoring purposes. The delay period between the time at which an excursion is ordered or observed at the front oxygen sensor and the time at which it is observed at the rear oxygen sensor can be used to infer catalyst oxygen storage capacity. High oxygen storage capacity causes the delay period to be longer than it would be if there were little or no oxygen storage capacity. This approach to monitoring is generally known as the titration method.⁴

The other provisions of the CARB OBD II regulations that are of concern here are those applying to oxygen sensors. For oxygen sensors, the malfunction criteria require MIL illumination if the operating characteristics of the sensor have been degraded such that emissions of any pollutant exceed 1.5 times the applicable standard or if the sensor can no longer function adequately enough to be used for monitoring catalyst efficiency.

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* Because of the relatively small changes in catalyst efficiency associated with the OBD II malfunction criterion for LEVs, manufacturers may have to monitor efficiency using a small volume of catalyst at the front catalyst. Therefore, the second oxygen sensor has to be located within the actual catalyst bed.

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Section 3

Ignition Misfire Due to MMT

IGNITION MISFIRE DUE TO MMT

Summary

To assure proper engine operation in a gasoline engine, it is necessary for the spark plug to create in a predetermined location a spark of precisely controlled intensity and duration under specific conditions. If for some reason the spark plug is altered such that the intensity or duration of the spark is changed, then improper combustion will occur. This phenomenon, commonly referred to as ignition misfire, can result in poor driveability and, in general, increased engine out emissions of hydrocarbons in combination with degraded fuel economy. In addition, engine out emissions of NO_x may be reduced to some degree.

It is well known that the formation of deposits on spark plugs can affect spark intensity and duration. In fact, spark plugs are designed specifically to prevent the accumulation of carbon deposits on the plugs for this very reason. It is also well known, based on studies performed by Ethyl Corporation and the auto industry, that the use of MMT in gasoline causes deposits of manganese oxides to form on spark plugs. While Ethyl claims that these deposits do not cause misfire, auto industry studies show that the manganese oxide deposits cause misfire by altering the electrical characteristics of spark plugs, which leads to weaker spark or no spark at all.

MMT Issues and Studies Matrix					
Issue	Auto Industry	Ethyl	Oil Industry	Government	Non-Gov. Organizations
Ignition Misfire	Manganese deposits form on spark plugs and cause misfire	Manganese deposits form on spark plugs but do not cause misfire	N/A	N/A	N/A

IGNITION MISFIRE DUE TO MMT

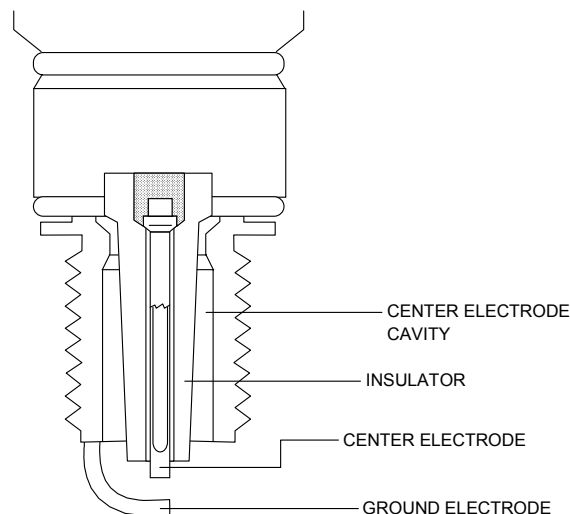
Technical Background

To provide a background for understanding how MMT can affect ignition misfire, the pertinent features of normal combustion, spark plug operation, and causes of misfire are discussed below.

Normal Combustion - Operation of a gasoline-fueled engine begins with a mixture of fuel and air* being drawn into an engine cylinder through the intake valve (or valves) as a result of the downward motion of the piston. This mixture of fuel and air is commonly referred to as the “charge.” During the next step in operation, the charge is compressed by the upward movement of the piston. This compression causes an increase in both the pressure and temperature of the charge. Once compression of the charge has occurred, the charge is ignited by the spark plug and combustion takes place in the cylinder.

Spark Plugs - As noted above, the spark plug is the key component that causes combustion to occur in an engine. A schematic of the tip of a standard spark plug is shown in Figure 1. As shown, the primary structures of importance are the center and ground electrodes, the ceramic insulator for the center electrode, and the center electrode

Figure 1



* In some cases, the “air” drawn into the cylinder contains some percentage of exhaust gas supplied by the exhaust gas recirculation (EGR) system, which lowers the peak temperature and pressure in the cylinder during combustion, thereby reducing the formation of oxides of nitrogen.

cavity. The location of the spark plug in the cylinder is also an important design consideration in achieving optimum combustion. To create a spark in a short period of time, a large voltage difference is created between the center electrode and the ground electrode. Usually, the plug is designed such that the spark originates at the center electrode and then arcs across the “gap” to the ground electrode. In general, the greater the gap, the greater the required voltage difference and the greater the amount of the cylinder charge that is ignited.

Misfire - To obtain optimum combustion, it is essential that the charge be properly ignited by the spark plug. Improper ignition leading to incomplete combustion or a complete lack of combustion is referred to as “misfire.” One effect of misfire is that the fuel (hydrocarbons) in the cylinder is not completely burned, which can lead to poor driveability, reduced power output, increased fuel consumption, and higher engine-out hydrocarbon emission levels. Improper combustion may also lead to higher engine-out carbon monoxide (CO) emissions and lower peak cylinder temperatures and pressures, with resultant reductions in engine-out NO_x emissions. Of course, if combustion fails to occur, the original air-fuel mixture is exhausted from the cylinder into the exhaust stream. Misfire can also lead to observed increases in tailpipe hydrocarbon and CO emissions, and reductions in NO_x emissions.¹

Misfire can occur for a number of reasons, including (1) the formation of deposits between the center and ground electrodes of the spark plug, and (2) the formation of deposits on the center electrode and insulator of the spark plug. Formation of conductive deposits in the “gap” between the center and ground electrodes can provide a pathway for the spark energy to pass between the electrodes without the development of the voltage difference required to create a spark. This results in a “fouled” spark plug and either a weak spark or no spark. The formation of deposits along the center electrode and insulator can create conductive “pathways” that allow some of the spark energy to be lost from the center electrode, resulting in a reduction in the voltage difference between the center and ground electrodes. This in turn leads to a weaker spark or, in some cases, no spark at all and improper combustion. To prevent the formation of carbon deposits on the center electrode, spark plugs are designed so that the temperature of the central electrode is maintained above 350° C. However, the same phenomenon can occur if deposits of other conductive materials form on the center electrode and insulator.

Development of Spark Plug Technology - During the early 1970s, when attention was first focused on the use of MMT as a gasoline additive, spark plugs were designed to be compatible with relatively low-voltage ignition systems and to be replaced at relatively short mileage intervals (around 15,000 miles). Since that time, there have been substantial changes in spark plug design to accommodate higher voltage ignition systems, improve combustion to reduce emissions, and increase spark plug life. These changes include the use of precious metals such as platinum for electrode surfaces and improved temperature control to minimize formation of carbon deposits. At present, most spark plugs are designed to last for 100,000 miles of vehicle operation. As a result of these advancements, current spark plugs are likely to be more sensitive to factors not considered during their design, such as operation on fuels containing MMT.

Misfire Due to MMT Use in Gasoline

The combustion of gasoline containing MMT in spark-ignited engines leads to the formation of small particles of manganese oxides. Possible fates of these particles in the combustion chamber, per se, include deposition on surfaces inside the chamber, including on the crown of the piston and spark plugs and on exhaust valve surfaces. As a result, the potential exists for manganese deposits from MMT used in gasoline to cause ignition misfire by affecting spark plug performance. This section reviews the data on the impact of MMT use on misfire available from studies performed by Ethyl Corporation and the auto industry.

Ethyl Studies - With the enactment of regulations eliminating the use of lead in gasoline and the opportunity for using MMT in unleaded gasoline in the mid-1970s, Ethyl Corporation published several papers that addressed, at least to some degree, the impact of MMT use on combustion chamber deposits and spark plug performance. The first of these papers² examined two fleets of different early-1970s model year vehicles produced by different manufacturers and found that MMT use in gasoline at levels equivalent to 33 mg of Mn per liter led to misfire on at least some of the vehicles due to the accumulation of MMT combustion products in the spark plug gap. A second study published by Ethyl³ again investigated the use of MMT at levels equivalent to 33 mg Mn per liter, but this time focused exclusively on 1972 to 1977 model year vehicles. With respect to spark plugs, the study, which presented no real data, acknowledged “substantial deposits” of MMT combustion products on the plugs, but claimed that MMT use did not result in any “unusual spark plug problems.” Other Ethyl studies of MMT impacts on On-Board Diagnostic (OBD) system operation are also used to infer that MMT use does not lead to spark plug misfire.⁴

Auto Industry Studies - The first auto industry study addressing misfire was published by General Motors.⁵ In this study, it was observed that an increase in engine-out emissions occurred as a result of the use of MMT at the 33 mg Mn per liter level for 80,000 km in a 1976 model year vehicle. It was also found that this increase in emissions could be reversed to some degree by the replacement of spark plugs. Given the heavy deposit formation on the spark plugs, however, it was not clear whether it was the elimination of deposits via plug replacement or differences in the firing characteristics of new and MMT-exposed plugs that led to the observed emission reductions.

Since that time, there have been several auto industry studies examining the effects of MMT use on spark plug deposits and performance.^{6,7,8,9} The results of these studies show that MMT use at levels down to 8.3 mg Mn per liter still leads to heavy deposits of manganese oxides on spark plugs. In addition, they document that these deposits can lead to significant occurrences of misfire, which is detected by OBD systems. The proposed mechanism regarding misfire involves a transition of the Mn_3O_4 deposits from a nonelectrically conducting form to a conducting form under the high-temperature, high-pressure conditions experienced in the combustion chamber during the compression and power strokes. Available data indicate that this transition begins at around 450° C,¹⁰ which is well within the normal temperature window for spark plug operation. As noted above, this same basic mechanism leads to misfire when carbon deposits form on spark

plugs and has also been reported to occur as a result of lead deposits in areas where high concentrations of lead were used in gasoline.¹¹

In both cases, instead of arcing across the gap from the center electrode to the ground electrode, the current in this case travels from the center electrode down the body of the insulator surrounding the electrode and spark occurs somewhere in the cavity between the center electrode and the ground side (inside the threaded portion) of the spark plug. That this phenomenon occurs is supported by “tracking” marks through the manganese oxide deposits on the central electrode insulator created by the flow of current through the material and resultant melting and glazing due to resistive heating. Further, the development of high-energy ignition systems that generally result in greater electrical potentials between the center and ground electrodes and changes in spark plug design may explain why this effect is more prevalent in recent studies.

Conclusions

Based on the available information, it is clear that MMT use leads to manganese oxide deposits on the spark plugs and that these deposits can cause ignition misfire by affecting spark plug performance. The effects of misfire include poor drivability, reduced power output and fuel economy, and increased engine out emissions of hydrocarbons. Ignition misfire can also decrease engine out emissions of NO_x. Further, the mechanism of manganese oxide deposit effects on spark plug performance has been documented to occur in essentially the same manner as deposits of other conductive materials.

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Section 4

Combustion Chamber Deposits Due to MMT

COMBUSTION CHAMBER DEPOSITS DUE TO MMT

Summary

Combustion chamber deposits form due to the presence of heavy hydrocarbon molecules and gums in fuels, lubricating oils, as well as oil and fuel additives including MMT. Combustion chamber deposits may lead to higher hydrocarbon emissions and/or higher NOx emission levels depending on their chemical nature.

It is well known that MMT use in gasoline leads to the formation of manganese oxide particles that deposit in the combustion chamber and exhaust system. That these deposits form in the combustion chamber is confirmed by studies performed by both the Ethyl Corporation as well as the auto industry. Data from all studies shows that use of MMT leads to higher engine-out HC emissions. Data from an auto industry study of impacts on older vehicles indicate that engine-out HC emissions decrease once MMT related combustion chamber deposits are removed.

MMT Issues and Studies Matrix					
Issue	Auto Industry	Ethyl	Oil Industry	Government	Non-Gov. Organizations
Combustion Chamber Deposits	Manganese deposits form leading to higher engine-out HC emissions	Manganese deposits form and higher engine-out HC emissions are observed	N/A	N/A	N/A

COMBUSTION CHAMBER DEPOSITS DUE TO MMT

Technical Background

In this section, the formation and effects of combustion chamber deposits due to MMT use are discussed. While combustion chamber deposits that form on spark plugs can also lead to misfire, that issue is addressed in a separate section.

Formation of Combustion Chamber Deposits - In vehicles running on unleaded gasoline that does not contain MMT, deposits form in the combustion chamber due to the presence of heavy hydrocarbon molecules and gums in fuels as well as the presence of lubricating oils in the combustion chamber. In addition, certain types of fuel and oil additives may lead to more combustion chamber deposits. Other factors in deposit formation include engine design and operating characteristics. Deposits may be mainly carbonaceous or inorganic depending on the mechanism of formation.

The general impacts of combustion chamber deposits on emissions are two-fold. First, they may lead to higher hydrocarbon emissions due to the adsorption and desorption of fuel molecules on the deposits. Second, they may lead to higher NO_x emission levels due to higher peak cylinder temperatures and increased effective compression ratios. The higher peak cylinder temperatures result from the insulating effect the deposits have on cylinder surfaces, which reduces the effectiveness of the engine cooling system. Deposits, depending on their chemical nature, may have other effects on emissions if they have an effect on the chemistry of the combustion process.

Combustion Chamber Deposits Due to MMT Use

Early development work performed by Ethyl regarding MMT indicates that the formation of very small metal oxide particles is critical to the anti-knock characteristics of MMT as these particles interrupt chemical reactions leading to engine knock.¹ These small particles of manganese oxides deposit in on the surfaces of the combustion chamber including the spark plug. As discussed above, it is well known that the presence of combustion chamber deposits can affect emissions. In this section, data regarding the use of MMT on combustion chamber deposits from studies performed by Ethyl Corporation and the auto industry are summarized.

Ethyl Studies - A study published by Ethyl² focused exclusively on 1972 to 1977 model year vehicles using MMT at levels equivalent to 33 mg Mn per liter. Heavy deposits of MMT combustion products were reported in the combustion chambers of 1975 model year engines produced by two manufacturers. However, the emissions impact of the

manganese deposits observed on spark plugs and other surfaces in the combustion chamber on engine-out emissions was not assessed.

While the effects of combustion chamber deposits were not explicitly studied, data collected in another Ethyl study, again involving 1972 to 1977 model year vehicles,³ indicate that MMT use at levels equivalent to 16.5 (less than the current Canadian limit) and to 8.3 mg of Mn per liter increased engine-out HC emissions from 1977 model year vehicles. Ethyl again presented data in a later study⁴ that clearly indicated that engine-out HC emissions increase substantially and linearly as a function of fuel MMT level over a range from about 4 mg Mn per liter to 33 mg Mn per liter for a fixed period of MMT use. In addition, this study showed that engine-out HC emissions increase with the duration of operation on MMT-containing fuels over time during the first 30,000 miles of vehicle operation. While not conclusive, these increases in engine-out HC emissions could have been related to combustion chamber deposits.

Auto Industry Studies - Concerns regarding the effect of MMT on engine life, component life, and emissions also led to the performance of several studies by auto companies and the Coordinating Research Council (CRC). The results of these studies clearly established increases in engine-out HC emissions resulting from MMT impacts on spark plugs and combustion chamber deposits. The first study, published by General Motors,⁵ found that the increase in engine-out emissions associated with MMT use at 33 mg Mn per liter for 80,000 km in a 1976 model year vehicle could be reversed to some degree by the replacement of spark plugs and to a much greater degree by the elimination of combustion chamber deposits. However, given that heavy deposit formation occurred on the spark plugs, it was not clear whether it was the elimination of deposits via plug replacement or differences in the firing characteristics of new and MMT-exposed plugs that led to the observed emission reductions. Increased engine-out HC emissions attributed primarily to combustion chamber deposits were also reported in another General Motors study where MMT impacts at the 33 mg Mn per liter level were evaluated.⁶ Finally, a CRC-sponsored study that evaluated MMT impacts at levels of 33, 16.5, and 8.3 mg Mn per liter on older vehicles also found increases in engine-out HC emissions, with higher MMT levels leading to greater increases relative to MMT-free fuels.⁷ Again this suggests but does not demonstrate that MMT-related combustion chamber deposits were the cause of the observed increase in emissions.

There have been auto industry studies of the impacts of MMT-related combustion deposits on emissions from late model vehicles. However, during the early 1990s Ford published⁸ the results of a study of MMT impacts at the 8.3 mg Mn per liter level that included emissions data. This study involved four 1991 Escort vehicles and four 1991 Bronco vehicles equipped with prototype engines being evaluated for use in 1993 model year vehicles and operated over 100,000 miles. For each vehicle type, two vehicles were operated on fuel with MMT and two were operated on MMT-free fuel. As was observed in older studies, the results of this study showed that MMT use, even at 8.3 mg Mn per liter, caused a substantial increase in engine-out HC emissions. The magnitude of this emissions increase was observed to increase with increasing vehicle mileage (i.e., greater accumulation of manganese oxides resulting from MMT combustion), which again suggests that MMT-derived combustion chamber deposits could be responsible.

Conclusions

Based on studies conducted on MMT in the mid- to late 1970s, MMT use at levels down to 8.3 mg Mn per liter (less than half the CGSB limit for MMT use in Canada) was shown to result in increased emissions of HC. This result appears to be linked to combustion chamber and spark plug deposits, which increased engine-out HC emissions. Studies of more recent vehicles continue to find that the use of MMT leads to the same effect—higher HC emissions—and strongly suggest a link to combustion chamber deposits.

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Section 5

Impacts of MMT on Catalytic Converters

IMPACTS OF MMT ON CATALYTIC CONVERTERS

Summary

Manganese oxide particles formed as a result of the presence of MMT in gasoline are deposited throughout the engine and the exhaust system. On catalyst-equipped vehicles, one potential deposition site is the catalytic converter. The available data indicate that the use of MMT in gasoline can result in the deposit of manganese oxide particles on the inlet sections of catalytic converters and that these deposits can plug catalyst passages. The results of this include increased exhaust system back pressure and problems with vehicle operability as well as potential increases in exhaust emissions due to the reduction in the effective volume of the catalytic converter. In addition, the general deposition of manganese oxide particles on catalytic converters as a result of MMT use appears to lead to slight increases in catalytic converter effectiveness. It is not clear, however, if this result occurs because the manganese oxides shield the catalyst from poisons or because they alter the chemistry occurring in the catalyst.

MMT Issues and Studies Matrix					
Issue	Auto Industry	Ethyl	Oil Industry	Government	Non-Gov. Organizations
Catalyst Impacts	Manganese oxide deposits can plug catalytic converter and lead to slight increases in observed catalyst efficiency	Manganese oxide deposits can plug catalytic converters and lead to slight increases in observed catalyst efficiency	N/A	N/A	N/A

IMPACTS OF MMT ON CATALYTIC CONVERTERS

Technical Background

Catalytic Converter Design - The first type of catalytic converter developed for motor vehicle applications was the oxidation catalyst. Oxidation catalysts oxidize hydrocarbon (HC) and carbon monoxide (CO) in vehicle exhaust under conditions where there is excess oxygen in the exhaust gas stream. Catalysts of this type were introduced with the 1975 model year and were found on most passenger cars and light-duty trucks through the 1980 model year in the U.S. and to a lesser degree in Canada. However, they continued to be used in some applications for a considerably longer period of time, particularly on heavier gasoline-powered trucks.

The second and dominant type of catalytic converter is a three-way catalyst. In contrast to oxidation catalysts, three-way catalysts are designed to oxidize HC and CO and reduce NOx. High efficiency for both of these processes is achieved by rapidly switching the air/fuel ratio of the vehicle back and forth between rich (excess fuel) and lean (excess air) operation in a narrow window about the stoichiometric point using the closed-loop feedback fuel control system.

Although oxidation catalysts use different formulations of noble metals [platinum (Pt), palladium (Pd), and rhodium (Rh)], as well as promoters and stabilizers, their basic construction and principles of operation are similar. The catalytic materials, including promoters and stabilizers and a high surface area coating, usually alumina (Al_2O_3), are commonly applied in several steps to a ceramic monolith substrate or in some cases on ceramic beads. The high surface area coating is used to provide a large number of sites at which reactions can take place. The available surface area of a typical automotive converter (which has a volume on the order of 1 to 2 liters) is on the order of 45,000 square meters or about 500,000 square feet.¹ This area equates to that of about ten football fields. In addition, as noted above, other compounds besides the noble metals are also incorporated into the catalyst formulation for a variety of reasons, including to enhance (or promote) the activity of the noble metals, to stabilize the noble metals, or to reduce the sensitivity of the catalyst to poisons such as lead or even reversible poisons such as sulfur.

With respect to stabilization, it is the available noble metal surface area that is important in automotive catalysts, rather than simply the total mass of the noble metals.* Therefore,

* While it is surface area rather than total mass that is important, it must be noted that for a given size of metal particles, the total surface area will increase as the number of metal particles, and hence the total mass, or "loading," of precious metals, is increased.

in catalyst preparation, great attention is paid to assure that the noble metals are present in the smallest particle sizes possible (i.e., dispersed to the greatest possible extent) in order to maximize surface area. Larger noble metal particle sizes are more thermodynamically favored; as a result, when catalysts are exposed to high temperatures, the noble metals can “sinter” into larger particles and thus reduce the available surface area and the efficiency of the catalyst. Stabilizers are therefore used to minimize sintering.

Current automotive catalysts are required to maintain extremely high pollutant conversion efficiencies for very long periods of time and factors that result in even small reductions in that efficiency can cause vehicles to exceed applicable emission standards.

Catalytic Converter Damage Due to MMT Use in Gasoline

Manganese oxide particles formed as a result of the presence of MMT in gasoline are deposited throughout the engine and the exhaust system. On catalyst-equipped vehicles, one potential deposition site is the catalytic converter. While there are several reasons to be concerned about the deposition of manganese oxide particles on catalysts, the most basic concern is that they will plug the passageways through which exhaust gases flow through the catalyst. Such plugging can increase engine backpressure, leading to operational problems that would require catalyst replacement to correct. In addition, plugging results in higher catalyst space velocities and decreased residence times for exhaust in the catalytic converter (i.e., forcing the same volume of exhaust gas through a reduced volume of catalyst), which in turn could lead to lower overall conversion efficiencies and higher tailpipe emissions. Concerns regarding catalyst plugging have grown more acute as monolithic catalysts with higher cell densities (i.e., smaller passages) have come into more widespread use in order to meet more stringent emission standards.

The other concern with respect to the use of MMT in gasoline is whether it will lead to reductions in catalyst efficiency due to reactions with noble metals or promoters or by physically blocking the pores of the high surface area coatings.

Catalyst Plugging

Ethyl Studies - Studies conducted by Ethyl during the mid-1970s examined the issue of catalyst plugging due to the use of MMT in unleaded gasoline. In the first study,² plugging was reported on the inlet ends of monolith-type catalysts with gasolines containing MMT at the 33 mg Mn per liter level under conditions where exhaust temperatures were on the order of 1500°F. Catalysts located away from the exhaust manifold (e.g., underfloor catalysts) were reported to be exposed to exhaust temperatures in this range under severe driving conditions, while catalysts that were close-coupled to the exhaust manifold experienced high temperatures under normal operating conditions. On-road testing indicated that catalyst plugging could occur after as few as 10,000 miles of operation. Plugging was not reported for pelleted converters.

Two later studies^{3,4} reported that plugging of monolith-type converters could be reduced by lowering the MMT content of gasoline from 33 mg Mn per liter to 16.5 mg Mn per liter, eliminating the use of close-coupled catalysts, and eliminating the use of expansion chambers upstream of converters (use of expansion chambers is a relatively common practice). Some problems were also reported with respect to plugging of converters based on ceramic beads.

The issue of catalyst plugging has been addressed with respect to newer vehicles in two additional Ethyl studies. The first of these⁵ examined changes in catalyst backpressure over 35,000 miles of rapidly accumulated “high speed” operation on a test track using gasoline containing MMT at the 8.3 mg Mn per liter level, testing one vehicle with the MMT-containing fuel and another with MMT-free fuel. These vehicles were equipped with close-coupled catalysts. While no plugging was reported, no data were provided regarding catalyst temperatures and it is not clear whether catalyst temperatures reached the levels that earlier studies reported were necessary to observe plugging.

Catalyst backpressure data were also presented for 42 vehicles that had accumulated 74,000 miles of operation on either gasoline with MMT at 8.3 mg Mn per liter or MMT-free fuel. These vehicles had also been subjected to rapid mileage accumulation using the standard certification mileage accumulation cycle, which does not involve severe operation. The reported results were characterized as supporting a conclusion that no catalyst plugging had occurred.

No data were presented, however, for the six test vehicles representing the only model in the Ethyl test fleet that was reported to have close-coupled catalysts. As explained above, because of the use of close-coupled catalysts (which are exposed to higher exhaust temperature), this model would appear to have been the most likely of those tested by Ethyl to experience some degree of plugging. Interestingly, this was the same model used in the high-speed driving evaluation discussed above where backpressure measurements were made, but for some reason Ethyl used rental vehicles for the high-speed evaluation instead of the vehicles of that model from the test fleet that should have been readily available.

The second Ethyl study⁶ presented data from a laboratory reactor study where catalyst cores were cut from catalysts removed from vehicles operated for 23,000 to 74,000 miles on gasoline containing MMT at the 8.3 mg Mn per liter level. Again, mileage was accumulated on these vehicles using the standard certification mileage accumulation schedule. Strangely, the paper describing this study makes no mention of how the cores were taken (e.g., from the center of the catalyst or towards the edge), the diameter of the cores, nor of the precautions that were taken to prevent the dislodging of manganese oxide deposits from the inlet ends of the cores while they were being cut from the ceramic monoliths. The paper does conclude, however, that plugging did not occur based on the fact that catalyst conversion efficiencies did not generally differ between converters exposed to MMT-free fuel and those exposed to fuel with MMT at the 8.3 mg Mn per liter level.

No instances of catalyst plugging have been reported in any of the Ethyl studies on vehicles operating on MMT-free unleaded fuels.

Auto Industry Studies - Catalyst plugging due to MMT usage was a major concern to auto makers and catalyst suppliers, who addressed the issue when catalysts were first introduced in the mid-1970s in several studies.^{7,8,9,10} Problems with plugging of both ceramic bead and monolithic catalyst converters is reported at MMT levels in the range from 8 to more than 33 mg Mn per liter. In general, the results of these studies were similar to those reported in the Ethyl studies; however, problems with catalyst plugging were reported at somewhat lower exhaust temperatures and at lower MMT levels in auto industry studies.

Focusing on the more widely used monolith-type converters, the most definitive of the auto industry studies⁹ found that exhaust temperature and the gasoline MMT level were the most significant factors with respect to plugging, with both higher exhaust temperature and higher MMT levels leading to increased problems with monolith plugging. A mechanism for monolith plugging was also proposed, based on the fact that the melting point of pure Mn_3O_4 , the primary manganese oxide observed as a combustion product of MMT, could be lowered by mixing with other materials in the engine exhaust to the point where the particles in the exhaust could actually be liquid droplets under certain high-temperature conditions. These droplets would then impinge and stick to the surface (rather than tending to bounce off as they would if they were solid) at the inlet end of the catalyst inlet. Given sufficient time under these conditions, enough material would accumulate to block the cells of the monolithic converter.

Turning to on-road studies, no problems with catalyst plugging were reported in the CRC study of MMT effects⁸ at MMT levels of 8.3 and 16.5 mg Mn per liter. However, given the above and the fact that the study was based on the relatively modest EPA mileage accumulation driving schedule, plugging problems would not have been expected. Plugging problems were reported by the New York State Department of Environmental Conservation on several 1975 model year in-use police vehicles with monolithic catalysts that were operated on fuels containing as much as 55 mg Mn per liter for what appears to have been a relatively short period of time.¹¹

For newer vehicles, rather than performing additional laboratory studies regarding the physical plugging of catalytic converters operating on MMT-containing fuels, the auto industry has instead simply removed and examined catalysts from in-use Canadian vehicles. One study of nine catalysts removed from in-use Canadian vehicles reported light to severe blockage of monolith passageways on the inlet side.¹² Another evaluation of 400 in-use Canadian catalysts removed from vehicles and replaced under warranty by a vehicle manufacturer again reported physical plugging of the inlet ends of monoliths that ranged from minor to severe.¹³ Finally, evidence of catalyst plugging was observed on a 1991 model year vehicle after 100,000 miles of operation over an accelerated mileage accumulation schedule using gasoline containing MMT at the 8.3 mg Mn per liter level.¹⁴

As with the Ethyl studies, there have been no reports of catalyst plugging (other than due to the thermal destruction [i.e., melting] of the monolith or pellets) on MMT-free unleaded gasolines in any of the auto industry studies.

MMT Effects on Catalytic Converter Performance

Ethyl Studies - Three Ethyl studies addressed the issue of MMT effects on the performance of early catalytic converter designs,^{15,16,17} and all reported that the use of MMT in gasoline results in somewhat higher catalyst conversion efficiencies relative to those observed with the use of MMT-free unleaded gasolines.

Three additional Ethyl studies have addressed the effects of MMT use at the 8.3 mg Mn per liter on the performance of more recent catalytic converters.^{6,18,19} The first test program involved 48 1988 model year vehicles (six identical vehicles from eight different models). All vehicles first accumulated 1,000 miles of operation on MMT-free fuel, after which half of the vehicles (three from each model) used gasoline containing MMT at the 8.3 mg Mn per liter level for 74,000 miles of operation and the other half continued to use MMT-free gasoline. It should be noted that the use of MMT-free fuel for the first 1,000 miles of operation is not something that would generally occur under in-use conditions where MMT-containing gasolines are marketed because vehicles in those areas would use that fuel beginning when new.

In this test fleet, catalyst conversion efficiency was measured at odometer readings of 1,000 miles (i.e., at the end point of the period where all vehicles were using MMT-free fuel), 50,000 miles, and 75,000 miles. For HC conversion efficiency, there was no difference in the fleet-average conversion efficiency at 50,000 miles; there was only a slight difference at 75,000 miles, where a 0.7% higher conversion rate was observed for the vehicles using MMT. Higher fleet-average CO and NO_x conversion efficiencies were also observed at 50,000 and 75,000 miles for vehicles operating on gasoline with MMT, with the differences amounting to 1.1% and 3.7%, respectively. However, no data analysis was presented that examined whether these differences were statistically significant, simply indicative of normal variations in emissions levels, or due to changes in engine out emissions levels.

The second Ethyl study⁶ involved the laboratory evaluation of the conversion efficiencies of a number of catalytic converter samples taken from test vehicles representing five different 1988 to 1991 vehicle models operated on either MMT-free gasoline or gasoline containing MMT at the 8.3 mg Mn per liter level over accelerated mileage accumulation schedules for between about 20,000 and 75,000 miles. In general, this study found no statistically significant differences between the conversion efficiencies of catalysts exposed to MMT-free and MMT-containing gasoline. There was only one vehicle model for which catalyst efficiencies were found to be significantly higher for catalysts exposed to MMT, and there were only two test vehicles of that model type included in the study. Although the data presented in this paper are also purported to show that the use of MMT reduces catalyst exposure to oil-borne poisons, this assertion was not reconciled with the fact that, in most cases, the higher efficiencies that would be expected for catalysts exposed to MMT (and protected from poisons) were not observed.

A third Ethyl study¹⁹ involved 22 1992 and 1993 model year vehicles, again divided into two fleets: one operated on MMT-free gasoline, and the other operated on gasoline containing MMT at the 8.3 mg Mn per liter level. While not explicitly stated, it appears that these vehicles were operated for a period of 5,000 to 10,000 miles on MMT-free fuel before mileage accumulation began on fuel containing MMT.²⁰ Again, this type of exposure to MMT-free fuel is an artifact of the testing protocol and makes extrapolation of results to the vehicles using MMT fuel in-use tenuous at best. The reason for this conclusion is that manganese oxide deposition appears to be the main result of MMT use and the nature of that deposition could be altered by extended operation on MMT-free fuel in test vehicles, which would not occur on in-use vehicles in areas where MMT-containing gasoline is marketed. Higher catalyst conversion efficiencies were reported as the result of MMT use, but data were not presented for all of the different models included in the test fleet and no explanation for this was given.

Auto Industry Studies - Results generally similar to those of the Ethyl studies have been reported for older vehicles in studies performed by the auto industry and studies under cooperative auto and oil industry sponsorship regarding the issues of MMT effects on catalyst efficiency. These studies confirmed that MMT provides small but real improvements in catalyst efficiency.^{8,21} This effect was attributed to the scavenging of oil-derived catalyst poisons, particularly phosphorus and zinc, and residual Pb in unleaded gasoline by Mn₃O₄ deposits on the inlet ends of monolith converters. As was observed in the Ethyl studies, this effect did not increase with increasing MMT content and occurred at MMT levels as low as 4 mg Mn per liter.

The effects of MMT use on catalyst conversion efficiency from newer vehicles were evaluated in one auto industry study using catalytic converters taken from in-use Canadian vehicles.¹² In this laboratory study, in-use converters exposed to MMT exhibited reduced catalyst efficiency for HC, CO, and NO_x compared to a similar laboratory-aged catalyst that had not been exposed to MMT combustion products. However, it is not clear that in comparing the laboratory-aged, MMT-free catalyst with the in-use catalysts exposed to MMT that all relevant factors that could impact the results have been properly taken into account.

One interesting finding reported in this study was that ammonia formation was observed to be substantially greater for the catalysts that had been exposed to MMT. While ammonia is generated to some degree by normal catalysis and is not routinely measured during vehicle emissions tests, this finding is of some significance as ammonia is an important precursor with respect to the formation of secondary particulate matter in the atmosphere. In addition, the increased formation of ammonia by MMT-exposed catalysts suggests that a fundamental change in the chemical processes is occurring on the catalysts.

Only one auto industry study has directly addressed the impact of MMT use on more recent vehicles.^{14,22,23} This study involved four 1991 Ford Escort and four 1991 Explorer vehicles with 1993 prototype engines operated on either MMT-free fuel or fuel containing MMT at the 8.3 mg Mn per liter level for 100,000 miles of accelerated mileage accumulation. Two vehicles of each model were operated on each fuel. As with

the Ethyl studies, all vehicles were operated for a period of 5,000 miles of operation on MMT-free fuel, which again makes the extrapolation of results to in-use vehicles using MMT-containing gasolines difficult at best.

Although catalyst efficiency was not directly determined, tailpipe HC emissions were observed to increase on vehicles that accumulated mileage on MMT-free fuels when their catalysts were replaced by those from the vehicles that accumulated mileage on the fuel with MMT. Similarly, the reverse procedure (i.e., MMT vehicles with MMT-free catalysts) generally resulted in lower tailpipe HC emissions. While no statistical analysis was performed, this result suggests that use of MMT impaired the HC conversion efficiency of these catalysts. Results for CO were varied, but there was a trend toward lower tailpipe NO_x emissions with the MMT-exposed catalysts. These results are inconsistent with the theory that MMT enhances catalyst activity by reducing the exposure of the catalyst to poisons because lower emissions of all three pollutants would be expected when MMT-exposed catalysts were placed on MMT-free vehicles, and vice versa. Instead, the results again suggest that MMT causes changes in the chemical reactions taking place on the catalyst, as was suggested by the increased ammonia formation observed in the study discussed above.

Conclusions

The use of MMT in unleaded gasoline can cause the deposition of manganese oxides on catalytic converters, particularly on the inlet end of monolith-type substrates. The magnitude of manganese deposition increases with increasing gasoline MMT content and with higher exhaust temperature. Deposition of manganese oxides can lead to the plugging of catalyst channels. Plugged catalysts increase exhaust system backpressure, leading to problems with vehicle operation, and could also lead to increased emissions as a result of higher space velocities and decreased residence times. Catalyst plugging has not been reported to be an issue on vehicles using MMT-free unleaded gasolines.

The available data have shown small increases in catalyst conversion efficiencies resulting from the use of MMT in gasoline. One proposed explanation is that the manganese oxides deposited on the converter protect the catalyst to some degree from poisons present in the oil and fuel. Other data do not support this explanation, however, and suggest that the presence of manganese oxides alters the chemistry occurring in the converter.

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Section 6

Impacts of MMT on Oxygen Sensors

IMPACTS OF MMT ON OXYGEN SENSORS

Summary

On most 1981 and later model year vehicles, fuel control is achieved with what is known as a “closed-loop, feed-back control system.” In general, this system uses output signals from one or more oxygen sensors placed in the exhaust stream along with signals from other sensors to maintain a near stoichiometric air/fuel ratio. In addition, on 1996 and later model year vehicles, at least two oxygen sensors are used to monitor catalyst efficiency in addition to performing their primary role of fuel control.

Because proper oxygen sensor performance is key to both air-fuel ratio control and catalyst monitoring on later model vehicles, potential adverse impacts due to the deposition of manganese oxides resulting from MMT use is of considerable concern. MMT impacts on oxygen sensor performance could lead to higher emissions because of imprecise air-fuel ratio control and failure of the OBD II system to detect damaged catalysts.

Only limited studies exist regarding MMT impacts on oxygen sensor performance. An early study by Ethyl showed that MMT had adverse impacts on sensor performance. Later studies reported no adverse impacts at lower MMT levels; the results of these studies, however, are far from conclusive. The one available auto industry study suggests that MMT may affect sensor performance, leading to a rich bias in air-fuel ratio and higher HC emissions. Overall, the available data regarding MMT impacts on oxygen sensor performance indicate that MMT has the potential to adversely affect sensors, but do not prove that low-level MMT use adversely impacts the performance of current sensors.

MMT Issues and Studies Matrix					
Issue	Auto Industry	Ethyl	Oil Industry	Government	Non-Gov. Organizations
Oxygen Sensor Impacts	MMT may affect oxygen sensor performance even at low concentrations	MMT damages sensors at higher levels but not at lower levels	N/A	N/A	N/A

IMPACTS OF MMT ON OXYGEN SENSORS

Technical Background

Despite the name, what an oxygen sensor actually measures is the amount of oxygen remaining in the exhaust after all of the hydrocarbon (HC), carbon monoxide (CO), and other reducing species have been oxidized. The sensor consists of a small, highly efficient catalyst that performs the oxidation function and a detector that measures the oxygen content of the gas sample after it has passed through the sensor catalyst.

On most 1981 and later model year vehicles, fuel control is achieved with what is known as a closed-loop, feed-back control system. In general, this system uses output signals from one or more oxygen sensors placed in the exhaust stream, along with signals from other sensors to maintain a near stoichiometric* air/fuel ratio. As is discussed below, in order to improve the efficiency of catalytic converters, the feedback control system rapidly switches the air/fuel ratio of the vehicle back and forth between slightly rich (excess fuel) and slightly lean (excess air) operation in a narrow window about the stoichiometric point, relying primarily on the output signal from the oxygen sensor(s). In addition, on 1996 and later model-year vehicles, at least two oxygen sensors are used to monitor catalyst efficiency in addition to the performing their primary role of fuel control.

Because proper oxygen sensor performance is key to both air-fuel ratio control and catalyst monitoring on later model vehicles, potential adverse impacts due to the deposition of manganese oxides resulting from MMT use is of considerable concern. MMT impacts on oxygen sensor performance could lead to higher emissions because of imprecise air-fuel ratio control and failure of the OBD II system to detect damaged catalysts.

Ethyl Studies - The first Ethyl study that evaluated MMT impacts on oxygen sensor performance¹ involved MMT use at 16.5 and 8.3 mg Mn per liter. This study indicated that the use of MMT at the 16.5 mg Mn per liter level had an impact on the performance of early oxygen sensors after as few as 5,000 miles of operation. Ethyl has performed three additional studies^{2,3,4} that include assessments of MMT impacts on oxygen sensor performance.

The first of these test programs involved 48 1988 model year vehicles (six identical vehicles from eight different models). All vehicles first accumulated 1,000 miles of operation on MMT-free fuel, after which half of the vehicles (three from each model)

* At the stoichiometric point, there is just enough air present to provide enough oxygen to completely combust the fuel.

used gasoline containing MMT at the 8.3 mg Mn per liter level for 74,000 miles of operation and the other half continued to use MMT-free gasoline. It should be noted that the use of MMT-free fuel for the first 1,000 miles of operation is not something that would generally occur under in-use conditions where MMT-containing gasolines are marketed because vehicles in those areas would use that fuel beginning when new. With respect to oxygen sensors, proper function was purported to be demonstrated by conducting emissions tests after replacing the sensor in the most stable vehicle operated on MMT-free fuel with sensors from each of the other five vehicles. Testing was performed on MMT-free fuel, and the results showed no statistically significant difference in tailpipe emissions when comparing oxygen sensors from the MMT vehicles with those from the MMT-free vehicles. While these results indicate that oxygen sensor function was not severely impaired, it would have been more conclusive, however, if sensor performance had also been evaluated based on changes in engine-out, rather than tailpipe, emissions. Furthermore, it is difficult to understand why such data were not collected and presented since Ethyl measured engine-out emissions to compute catalyst efficiency estimates.

The second Ethyl study³ involved 22 1992 and 1993 model year vehicles, again divided into two fleets: one operated on MMT-free gasoline, and the other operated on gasoline containing MMT at the 8.3 mg Mn per liter level. While not explicitly stated, it appears that these vehicles were operated for a period of 5,000 to 10,000 miles on MMT-free fuel before mileage accumulation began on fuel containing MMT.⁵ Again, this type of exposure to MMT-free fuel is an artifact of the testing protocol and makes extrapolation of results to the vehicles using MMT fuel in-use tenuous at best. The reason for this conclusion is that manganese oxide deposition appears to be the main result of MMT use and the nature of that deposition could be altered by extended operation on MMT-free fuel in test vehicles, which would not occur on in-use vehicles in areas where MMT-containing gasoline is marketed. In this study, the fact that oxygen sensors are not adversely impacted by MMT use was again purported to be demonstrated by comparing tailpipe emissions results from MMT-exposed sensors to those from sensors exposed only to MMT-free fuel on vehicles otherwise operated exclusively on MMT-free fuel. Again, it would have been more instructive to include comparisons of engine-out and tailpipe emissions.

Finally, Ethyl claimed in another study⁴ that, based on static response testing, MMT use does not alter the operation of the oxygen sensor because the switch point of the sensor was the same on aged sensors regardless of exposure to MMT. However, static response testing is only one way in which oxygen sensor performance can be evaluated; the result would be more relevant had other types of testing, including dynamic response testing and an evaluation of sensor response rates, been performed.

Auto Industry Studies - Only one auto industry study has directly addressed the impact of MMT use on late-model vehicles.^{6,7,8} This study involved four 1991 Ford Escort and four 1991 Explorer vehicles with 1993 prototype engines operated on either MMT-free fuel or fuel containing MMT at the 8.3 mg Mn per liter level for 100,000 miles of accelerated mileage accumulation. Two vehicles of each model were operated on each fuel. As with the Ethyl studies, all vehicles were operated for a period of 5,000 miles of

operation on MMT-free fuel, which again makes the extrapolation of results to in-use vehicles using MMT-containing gasolines difficult at best.

The impact of MMT on oxygen storage performance was also evaluated by performing component switching. Oxygen sensor exchange led to inconsistent changes in both engine-out and tailpipe emission levels. This study showed that MMT use led to increases in tailpipe HC emissions and that the magnitude of these increases was greater as more mileage, and hence more manganese oxide, was accumulated. This increase in emissions could be attributed to higher engine-out HC emissions with MMT and, as noted above, an apparent decrease in the conversion efficiency of MMT-exposed catalysts. One possible explanation for these results would be MMT impacts on oxygen sensor performance that led to a rich air-fuel ratio bias.

Conclusions

The limited available data regarding MMT impacts on oxygen sensor performance indicate that MMT has the potential to adversely affect sensors, but do not prove that low level (8.3 mg Mn per liter) MMT use adversely impacts the performance of current sensors.

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Section 7

Effects of MMT on OBD System Performance

EFFECTS OF MMT ON OBD SYSTEM PERFORMANCE

Summary

To comply with existing emission standards, manufacturers have developed sophisticated systems to control engine operation and advanced catalysts that can reduce pollutant levels by more than 90% relative to engine-out levels over 100,000 miles or more of operation. In addition, manufacturers have been required to develop on-board diagnostic (OBD) systems capable of identifying emission-related defects, alerting vehicle owners that defects exist, and facilitating the repair of those defects. From the perspective of potential MMT impacts on OBD systems, the two most important monitoring requirements are probably those associated with catalyst efficiency and oxygen sensor performance. The concern is that manganese oxide deposits will alter the oxygen storage properties of the catalyst and response of the oxygen sensors that are used to both control the air-fuel ratio for the engine perform OBD catalyst monitoring.

Limited studies regarding the impact of MMT on OBD system performance have been performed by Ethyl and the auto industry. The OBD studies conducted by Ethyl do little to address the real issues associated with the impacts of MMT use on OBD system performance. In contrast, the two auto industry studies, although limited, do suggest that increased oxygen storage attributable to deposited manganese oxides could result in the failure of OBD monitors to detect truly degraded catalysts. Although there have been no data published from studies of the more advanced catalyst monitoring systems on current vehicles, it would appear that manganese-related oxygen storage would still present a potential problem.

MMT Issues and Studies Matrix					
Issue	Auto Industry	Ethyl	Oil Industry	Government	Non-Gov. Organizations
OBD System Performance	Suggests that OBD catalyst monitoring may be impaired	Suggests that OBD catalyst monitoring is not impaired	N/A	N/A	N/A

EFFECTS OF MMT ON OBD SYSTEM PERFORMANCE

Technical Background

To comply with existing emission standards, manufacturers have developed sophisticated systems to control engine operation and advanced catalysts that can reduce pollutant levels by more than 90% relative to engine-out levels over 100,000 miles or more of operation. In addition, manufacturers have been required to develop on-board diagnostic (OBD) systems capable of identifying emission-related defects, alerting vehicle owners that defects exist, and facilitating the repair of those defects. Compliance with adopted and proposed future standards will require the use of increasingly sophisticated and advanced emission control technologies and reduce the allowable tolerances with respect to increases in emissions over the lifetime of the vehicles. Commensurate improvements in OBD systems will also be required. As a result, factors that could be ignored or tolerated in the past, even though they were known to increase emissions or impair OBD system performance, particularly from vehicles in customer service, are now of critical importance. In addition, these new technologies may be even more sensitive than older technologies to these types of factors.

OBD II systems are found on all 1996 and later model vehicles sold in Canada and the United States as well as some earlier models. The purpose of these systems is to identify emission control system defects and malfunctions leading to high emissions, to inform the motorist that such defects exist, and then to facilitate the repair of the vehicle. Although other agencies also have OBD regulations, virtually all vehicles are designed to comply with OBD II regulations developed by the California Air Resources Board. Under the CARB OBD II regulations, the general requirement is that the MIL be illuminated whenever a malfunction occurs that causes the emissions of any pollutant to exceed a level equal to 1.5 times the applicable emission standard. Given that the exhaust emission standards for different certification levels vary, this means that, on a gram per mile basis, the actual exceedance of the emissions standard that constitutes a “malfunction” under the CARB OBD II regulations also varies and compliance with both the OBD II regulations as well as the exhaust emission standards becomes more difficult as one moves from vehicles certified to less stringent standards to those certified to more stringent standards.

From the perspective of potential MMT impacts on OBD II systems, the two most important monitoring requirements are probably those associated with catalyst efficiency and oxygen sensor performance. Catalyst monitoring is among the most challenging of the OBD II requirements and CARB has provided some relief with respect to catalyst monitoring requirements for LEV program vehicles relative to the general 1.5 times the standard malfunction criteria. However, CARB staff has proposed catalyst monitoring requirements for LEV II vehicles (which will be similar to those for Tier II vehicles) that

will generally require MIL illumination at 1.5 times the applicable standard for both HC and NOx.

Although the OBD II regulations call for the monitoring of “catalyst efficiency,” the actual property being monitored is a somewhat related property known as the “oxygen storage capacity” of the catalyst. Oxygen storage capacity in automotive catalytic converters is provided mainly by ceria.¹ Catalyst monitoring strategies are based on the concept that high levels of oxygen storage capacity correlate with high conversion efficiencies. However, the relationship between oxygen storage and efficiency can vary dramatically and catalysts with good conversion efficiencies can exhibit low oxygen storage.^{1,2} Given this, automakers and their suppliers have reengineered catalysts in order to provide a better relationship between oxygen storage and efficiency.

As noted above, the OBD II catalyst monitoring strategies currently being employed by manufacturers rely on a linkage between the oxygen storage capacity of the catalyst and the HC conversion efficiency of the catalyst. The monitoring system usually involves two oxygen sensors: one placed upstream of the monitored catalyst, and the second placed either somewhere within* or behind the monitored catalyst. The primary function of the front oxygen sensor is to facilitate the rapid switching of the air/fuel ratio necessary for stoichiometric operation and high conversion efficiencies of HC, CO, and NOx. In performing this function, the sensor’s output voltage switches rapidly between its rich and lean limits in a cyclic pattern. This cyclic pattern is caused by the variations in the oxygen content of the exhaust gas created with the shifting of the air fuel ratio. Oxygen is alternatively adsorbed (during lean conditions) and released (during rich conditions) as the exhaust gas passes through the catalyst; this results in a change in the oxygen content of the exhaust. Therefore, the response pattern of a sensor in or downstream of a catalyst with high oxygen storage is considerably different than that of the front sensor. Conversely, if the catalyst has little or no oxygen storage capacity, the downstream sensor response pattern is similar to that of the upstream sensor. This approach to catalyst monitoring is generally known as the dual oxygen sensor method.³

Another approach to monitoring catalyst efficiency based on oxygen storage involves the use of calibrated excursions to rich and lean conditions specifically for monitoring purposes. The delay period between the time at which an excursion is ordered or observed at the front oxygen sensor and the time at which it is observed at the rear oxygen sensor can be used to infer catalyst oxygen storage capacity. High oxygen storage capacity causes the delay period to be longer than it would be if there were little or no oxygen storage capacity. This approach to monitoring is generally known as the titration method.³

The other provisions of the CARB OBD II regulations that are of concern here are those applying to oxygen sensors. For oxygen sensors, the malfunction criteria require MIL illumination if the operating characteristics of the sensor have been degraded such that

* Because of the relatively small changes in catalyst efficiency associated with the OBD II malfunction criterion for LEVs, manufacturers may have to monitor efficiency using a small volume of catalyst at the front catalyst. Therefore, the second oxygen sensor has to be located within the actual catalyst bed.

emissions of any pollutant exceed 1.5 times the applicable standard or if the sensor can no longer function adequately enough to be used for monitoring catalyst efficiency.

Effects of MMT Use in Gasoline on On-Board Diagnostic (OBD) System Performance

Ethyl Studies - Ethyl has performed two laboratory studies related to the impact of MMT use on OBD II system performance, both of which were apparently conducted in direct response to the two auto industry studies discussed below. The first of these studies⁴ investigated the impact of manganese oxide deposits on catalyst oxygen storage properties; the second⁵ appeared to respond directly to the results of the Ford study discussed below that found MMT use to result in an OBD-equipped vehicle failing to properly identify a significantly degraded catalyst.

In the first Ethyl study, the results were purported to show that manganese oxides deposited on catalytic converters have no impact on either the oxygen storage properties of the catalysts or the ability of OBD catalyst monitors to identify degraded catalysts; the data, however, are rather unconvincing. First, the HC conversion efficiencies of all of the catalyst samples subjected to detailed analysis were still high, on the order of 80% or more, and generally would not have been identified as being degraded by the then-current OBD catalyst monitoring systems. Therefore, since the non-manganese-related oxygen storage capacity of the converters was never in fact degraded, this study did not address the basic issue of whether manganese oxide deposits on degraded catalysts can alter oxygen storage such that OBD monitors fail to detect the loss in conversion efficiency. In addition, while reduced data purporting to show oxygen sensor response to the tested catalysts were presented, the actual sensor data themselves, which would have been more instructive, were not presented.

In the second Ethyl study, a somewhat different approach was used, but the results are again purported to demonstrate that manganese oxides do not alter catalyst oxygen storage properties or the ability of the OBD monitor to detect degraded catalysts. The results are again unconvincing. The first issue is that the “degraded” catalysts used in this study again had high conversion efficiencies and should not have been identified as being defective by the OBD II system. Further, the laboratory aging process used by Ethyl to degrade catalysts did not appear to be representative of in-use aging because the laboratory-aged catalysts had far lower oxygen storage capacities at a given level of conversion efficiency than did catalysts from in-use vehicles examined by Ethyl. Therefore, the relevance of the study to the normal operation of OBD systems is suspect.

Finally, the only truly “degraded” catalysts examined by Ethyl were “dummy” catalysts without washcoats or noble metals, which means that the efficiency and oxygen storage capacity of the catalysts were either zero or very near zero. There are no circumstances under which this type of “dummy” catalyst represents a condition that could occur on an in-use vehicle since all in-use catalysts will possess both a washcoat and noble metals. In addition, in order for the OBD II system to be “fooled” by MMT in this case, the amount

of oxygen storage resulting from the accumulation of MMT combustion products on the catalyst supports would have to equal that of a fully formulated catalyst (i.e., with washcoat and noble metals) with a high HC conversion efficiency. Therefore, MMT use would result in a “failure” of the Ethyl test only if there were a large increase in oxygen storage capacity.

As noted with respect to the first Ethyl study, the concern in the real world will be whether MMT use will add sufficient oxygen storage capacity to a partially deactivated catalyst with some remaining oxygen storage capacity, such that the OBD II system will incorrectly diagnosis the catalyst as “good” instead of “bad.” This is a fundamentally different situation than those studied by Ethyl in either study.

Auto Industry Studies - Auto industry studies of MMT impacts on OBD system performance have been focused on the impact that deposited manganese oxides have on the oxygen storage properties of catalytic converters and the performance of the oxygen sensors used to perform catalyst system monitoring. As noted above, OBD catalyst monitors correlate changes in catalyst oxygen storage properties with changes in catalyst efficiency. Therefore, anything that affects this correlation will impact the accuracy of the monitoring system.

One laboratory study performed by Ford⁶ showed that Mn_3O_4 could be reduced under conditions commonly encountered in automotive exhaust streams and that the additional oxygen storage capacity provided by Mn_3O_4 could lead to a situation where the substantially degraded catalysts were not detected by the monitoring system. Oxygen sensor response data were also presented to confirm that manganese oxides were in fact providing additional oxygen storage capacity.

A similar result was obtained for a 1994 model year vehicle equipped with a steady-state catalyst monitoring system (in contrast to more sophisticated systems designed to comply with current requirements that are linked to catalyst performance over the FTP driving cycle). In this study,⁷ again conducted by Ford, a degraded catalyst was placed on a test vehicle that was then operated on gasoline containing MMT at the 8.3 mg Mn per liter level. The OBD system initially detected the degraded catalyst, but could no longer do so after 40,000 miles of steady-state operation on a chassis dynamometer at speeds between 40 and 55 miles per hour.

Although there have been no auto industry studies showing that MMT use will result in the failure of OBD systems to identify malfunctioning oxygen sensors, one General Motors study has reported that MMT-related spark plug misfire has been detected by an OBD system.

Conclusions

As discussed above, the OBD studies conducted by Ethyl do little to address the real issues associated with the impacts of MMT use on OBD system performance. In contrast, the two auto industry studies, although limited, do suggest that increased oxygen storage attributable to deposited manganese oxides could result in the failure of OBD monitors to detect truly degraded catalysts. Although there have been no data published from studies of the more advanced FTP-based catalyst monitoring systems on current vehicles, it would appear that manganese-related oxygen storage would still present a potential problem.

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Section 8

MMT Impacts on Exhaust Emissions

MMT IMPACTS ON EXHAUST EMISSIONS

Summary

The basic approach to regulating emissions from motor vehicles has been to ensure that emissions from new vehicles meet applicable standards when they are first introduced into commerce. Emission standards for motor vehicles were first adopted beginning in the 1960s and have become much more stringent over time. To comply with these emission standards, vehicle manufacturers have been required to develop increasingly sophisticated systems to control exhaust emissions. In order to comply with exhaust emission standards, modern vehicles are equipped with sophisticated computer and sensor controlled systems for managing the operation of the engine, advanced catalytic converters and in some cases other specialized componentry.

The effects of MMT on exhaust emissions are important for two reasons. The first of these is that increases in exhaust emissions could lead to adverse impacts on air quality and public health. The second is that the use of MMT could lead to situations where vehicles exceed applicable emission standards when they would not otherwise. This second issue is of particular importance with respect to current and future vehicles that must meet extremely stringent emission standards. These vehicles will use advanced control technologies that may be more sensitive to inorganic compounds (such as sulfur and manganese) present in gasoline and what are slight increases in emissions on current vehicles may be sufficient to cause these vehicles to exceed their standards.

The available studies regarding MMT impacts on tailpipe emissions of both older and newer vehicles late-model vehicles show that the use of MMT leads to higher tailpipe emissions of HC and PM. Also, although data are limited, the increase in HC emissions also results, as one would expect, in an increase in emissions of gaseous air toxics. Lower tailpipe NOx emissions were observed on later model vehicles exposed to MMT in the Ethyl test programs but not in the auto industry testing nor in the test data from older vehicles.

MMT Issues and Studies Matrix					
Issue	Auto Industry	Ethyl	Oil Industry	Government	Non-Gov. Organizations
Exhaust Emissions Impacts	MMT increases HC, PM and Toxic Air Contaminant emissions	MMT generally increases HC emissions and decreases NOx emissions	N/A	MMT increases HC emissions in older vehicles	N/A

MMT IMPACTS ON EXHAUST EMISSIONS

Technical Background

The basic approach to regulating emissions from motor vehicles has been to ensure that emissions from new vehicles meet applicable standards when they are first introduced into commerce. This process, known as new vehicle or new engine “certification,” requires manufacturers to demonstrate that their products meet applicable emission standards when new and that they can reasonably be expected to continue to do so for a specified period of time or usage in the hands of the purchaser. In general, today this period is based on mileage and is described as the “useful life” of the vehicle. For most vehicles produced since the mid-1990s the useful life period is 100,000 miles, and even longer periods will apply to future vehicles. Regulatory agencies confirm compliance on in-use vehicles through testing programs and other means. Manufacturers whose vehicles fail to comply with emission standards in-use could be forced to recall and repair those vehicles.

Emission standards for motor vehicles were first adopted beginning in the 1960s and have become much more stringent over time. To comply with these emission standards, vehicle manufacturers have been required to develop increasingly sophisticated systems to control exhaust emissions. In order to comply with exhaust emission standards, modern vehicles are equipped with sophisticated computer- and sensor-controlled systems for managing the operation of the engine, advanced catalytic converters, and in some cases other specialized componentry. At present, these systems can reduce pollutant levels by more than 90% relative to engine-out levels over 100,000 miles or more of operation. Overall, current new vehicles have emissions that are 95 to 98% lower than those from pre-emission control vehicles from the 1960s.

In addition to emissions of hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NO_x), particulate matter (PM) emissions from gasoline-powered vehicles have recently become an issue of some concern given studies published regarding the health effects of exposure to very fine PM emissions.

In order to comply with the most stringent emission standards, substantial advances in emission control technology relative to even current vehicles will be required. These changes will require further reductions in engine-out emissions of all pollutants; more precise air-fuel ratio control; and catalysts with higher cell densities (e.g., smaller, more easily plugged channels), improved conversion efficiencies for all pollutants, and greater durability. In addition, the need to improve fuel economy may lead to the widespread introduction of lean-burn direct-injection gasoline engines. Current three-way catalysts, which require stoichiometric air-fuel ratios to reduce NO_x emissions, are not viable in

this application and new technologies are being evaluated. These technologies, which include selective catalytic reduction and NO_x adsorbers, are fundamentally different than current catalytic converters.

Many of the advanced emission control technologies that will be used to comply with future emission standards are very sensitive to the presence of inorganic compounds in gasoline. For example, the presence of sulfur in gasoline, which acts as a reversible or partially reversible catalyst poison (depending on a number of factors), will be dramatically reduced in the next few years. Given this, the question is not only whether MMT is adversely affecting exhaust emissions from vehicles currently in operation, but also whether it will damage or even destroy these advanced emission control devices.

In addition to the potential impacts of MMT on vehicle emissions as they relate to manufacturers' obligations, it is obvious that any increases in emissions associated with MMT use could have an adverse impact on air quality and public health.

The impacts of MMT use on exhaust emissions have been evaluated in a number of studies conducted principally by Ethyl Corporation and the auto industry over the course of the last 25 years or more. These studies were essentially conducted in two phases: the first phase occurred during the mid- to late 1970s when MMT was first introduced into unleaded gasoline; the second phase, which is still ongoing, began in the late 1980s with the renewal of Ethyl's efforts to obtain permission from the U.S. EPA to use MMT in unleaded gasoline.

MMT Effects on Tailpipe Emissions Levels

Ethyl Studies - The effects of MMT on tailpipe emission levels were examined in three Ethyl studies^{1,2,3} and a fourth study presents the results of a statistical analysis of the impact of MMT levels on tailpipe HC emission levels from older vehicles.⁴ The Ethyl studies generally conclude that use of MMT at the 33 mg Mn per liter level results in higher exhaust HC emissions than MMT-free gasoline, but that there is no impact on tailpipe emissions associated with use of MMT at 16.5 mg Mn per liter or lower concentrations. The assertion that tailpipe HC emissions do not increase with MMT use at these levels, despite engine-out HC emissions being higher, is explained in the Ethyl studies by the higher conversion efficiency of catalysts on vehicles that used MMT-containing fuels. However, the Ethyl studies also noted that enhancement of catalyst conversion efficiency by MMT did not appear to increase with increasing MMT levels, as similar results were obtained at both the 8.3 and 16.5 mg Mn per liter levels.

The Ethyl studies reported mixed results with respect to the impact of MMT on tailpipe emissions of CO and NO_x, although improvements in catalytic converter efficiency for CO were noted and reductions in CO emissions observed on some vehicles were attributed to that effect. The Ethyl studies involved only one limited attempt to assess the impact of MMT use on PM emissions.¹ Higher PM emissions were observed with MMT at 33 mg Mn per liter relative to MMT-free fuel, but the differences were reported to be within the variability of the measurement procedure.

There have been two Ethyl studies focused on later model vehicles that address the effects on tailpipe emissions as a result of the use of MMT at the 8.3 mg Mn per liter level.^{5,6} The first test program involved 48 1988 model year vehicles (six identical vehicles from eight different models). All vehicles first accumulated 1,000 miles of operation on MMT-free fuel, after which half of the vehicles (three from each model) used gasoline containing MMT at the 8.3 mg Mn per liter level for 74,000 miles of operation and the other half continued to use MMT-free gasoline. It should be noted that the use of MMT-free fuel for the first 1,000 miles of operation is not something that would generally occur under in-use conditions where MMT-containing gasolines are marketed because vehicles in those areas would use that fuel beginning when new.

This study showed that, for the fleet of 48 vehicles tested, there was a statistically significant increase in HC emissions and a statistically significant decrease in NOx emissions due to the use of MMT at the 8.3 mg Mn per liter level. The reduced NOx emissions were attributed to the ability of manganese deposits to protect the catalytic converter from oil-borne poisons. However, based on other data related to the study, this mechanism could not be responsible for the observed reduction in NOx emissions. Tailpipe CO emissions were somewhat lower for the MMT vehicles, but the difference in emissions was apparently not statistically significant. Particulate emissions were reported to be about 50% lower from vehicles using MMT-containing gasoline relative to MMT-free gasoline.

The second Ethyl study⁴ involved 22 1992 and 1993 model year vehicles, again divided into two fleets: one operated on MMT-free gasoline, and the other operated on gasoline containing MMT at the 8.3 mg Mn per liter level. While not explicitly stated, it appears that these vehicles were operated for a period of 5,000 to 10,000 miles on MMT-free fuel before mileage accumulation began on fuel containing MMT.⁷ Again, this type of exposure to MMT-free fuel is an artifact of the testing protocol and makes extrapolation of results to the vehicles using MMT fuel in-use tenuous at best. The reason for this conclusion is that manganese oxide deposition appears to be the main result of MMT use and the nature of that deposition could be altered by extended operation on MMT-free fuel in test vehicles, which would not occur on in-use vehicles in areas where MMT-containing gasoline is marketed. Although no results from any statistical analyses of the data were presented, the reported tailpipe emissions results were similar to those of the first Ethyl study wherein higher tailpipe emissions of HC and lower tailpipe emissions of CO and NOx were observed for the vehicles using gasoline with MMT.

Auto Industry Studies - Results generally similar to those of the Ethyl studies have been reported in studies performed by the auto industry and studies under cooperative auto and oil industry sponsorship regarding the issues of MMT effects on tailpipe emissions from older vehicles. With respect to tailpipe emissions, studies investigating the issue reported higher tailpipe HC emissions^{8,9,10,11} in response to the use of MMT-containing gasolines. The magnitude of the emissions increase was generally observed to increase as MMT levels increased from 8.3 to 33 mg Mn per liter. There were no discernable impacts of MMT use on tailpipe CO and NOx emissions. Finally, limited data showed that MMT use at 33 mg Mn per liter resulted in PM emissions that were approximately double those observed with MMT-free fuel.

Only one auto industry study has directly addressed the impact of MMT use on late-model vehicles.^{12,13,14} This study involved four 1991 Ford Escort and four 1991 Explorer vehicles with 1993 prototype engines operated on either MMT-free fuel or fuel containing MMT at the 8.3 mg Mn per liter level for 100,000 miles of accelerated mileage accumulation. Two vehicles of each model were operated on each fuel. As with the Ethyl studies, all vehicles were operated for a period of 5,000 miles of operation on MMT-free fuel, which again makes the extrapolation of results to in-use vehicles using MMT-containing gasolines difficult at best. Tailpipe HC emissions were substantially higher for the vehicles that were operated on MMT-containing fuels. The impact of MMT use on tailpipe CO and NOx emissions was more variable, with NOx emissions being higher for the MMT vehicles at 50,000 miles but equivalent to the MMT-free vehicles at 100,000 miles. Particulate emissions were about two times higher from the vehicles using gasoline with MMT, and emissions of manganese particles increased with increasing mileage accumulation on MMT-containing fuel. In addition, tailpipe emissions of toxic air contaminants (benzene, 1,3 butadiene, formaldehyde and acetaldehyde) were generally observed to be higher from the vehicles operating on MMT containing fuels. This result is consistent with the higher observed HC emissions from vehicles operating on MMT containing fuel.

Government Studies - An analysis of the then-available data regarding MMT impacts on vehicles was performed by the U.S. EPA in 1978. The published results of that analysis¹⁵ indicated that MMT use did have an adverse impact on HC emissions at levels down to 8.3 mg Mn per liter. Based on this, the U.S. EPA concluded that MMT use would result in, or contribute to, motor vehicles failing to comply with the HC emission standards to which they were certified. This analysis, like the others noted above, did not identify any effects of MMT on CO or NOx emissions and did not consider PM emissions. A study by the Canadian General Standards Board in 1986 performed for Environment Canada also concluded that there were adverse impacts of HC emissions due to MMT use at levels up to 18 mg Mn per liter.¹⁶

Conclusions

The available studies regarding MMT impacts on tailpipe emissions of both older and newer vehicles late-model vehicles show that the use of MMT leads to higher tailpipe emissions of HC and PM. Also, although data are limited, the increase in HC emissions also results in an increase in emissions of gaseous air toxics as one would expect. Lower tailpipe NOx emissions were observed on later model vehicles exposed to MMT in the Ethyl test programs but not in the auto industry testing nor in the test data from older vehicles although this later fact is not surprising given that most 1970s vehicles were not equipped with either three-way catalysts or closed-loop feedback control systems.

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Section 9

Health Effects of MMT Use

HEALTH EFFECTS OF MMT USE

Summary

Public exposure to MMT and the manganese compounds that result from its combustion is a public health concern. MMT itself is a highly toxic compound for which no detailed study of public exposure has been performed. The issue of whether public exposure to manganese compounds resulting from MMT combustion poses a significant threat to public health is somewhat complicated. Manganese oxide particles emitted from vehicles using MMT have been shown to be less than 2.5 µm in diameter. As evidenced by the promulgation of new air quality standards for PM in this size range specifically to protect public health, the manganese oxide particles emitted due to MMT use are of general concern. In addition, there are concerns stemming from the toxicity of manganese compounds in particular. Vehicle operated on MMT containing fuels both emit manganese oxide particles and have higher overall levels of particulate emissions. Although the Canadian government has concluded that public exposure to manganese particles from MMT use is not of concern, a significantly different conclusion has been reached in the U.S., where significant concerns still exist and new studies are ongoing.

MMT Issues and Studies Matrix					
Issue	Auto Industry	Ethyl	Oil Industry	Government	Non-Gov. Organizations
Health Effects Associated with MMT and Its Combustion Products	N/A	N/A	N/A	Canada - No Concern U.S. - Still Being Studied	Concern

HEALTH EFFECTS OF MMT USE

Technical Background

Public exposure to MMT and the manganese compounds that result from its combustion represents a public health concern. MMT itself is a highly toxic compound for which no extensive study of public exposure has been performed. Another issue is whether public exposure to manganese compounds resulting from MMT combustion poses a significant threat to public health. Manganese-containing particles emitted from vehicles using MMT have been shown to be less than 2.5 μm in diameter. As evidenced by the promulgation of new air quality standards for PM in this size range specifically to protect public health, the manganese-containing particles emitted due to MMT use are of general concern. In addition, there are concerns stemming from the toxicity of manganese compounds in particular. Vehicle operated on MMT containing fuels both emit manganese oxide particles and have higher overall levels of particulate emissions. Although the Canadian government has concluded that public exposure to manganese particles from MMT use is not of concern, a significantly different conclusion has been reached in the U.S., where significant concerns still exist and studies focused on this issue are ongoing.

Health Concerns with MMT

It is well known that MMT is a highly toxic compound that also causes genetic changes.^{1,2} Only a small percentage of the MMT added to gasoline is directly emitted in the exhaust of motor vehicles and, because of its relatively low vapor pressure, concentrations of MMT in the vapors emitted by MMT-containing gasolines are low. Therefore, emissions of MMT per se are expected to be small; in addition, because it undergoes rapid photolysis, MMT emitted to the atmosphere is not expected to persist for more than a minute or two during daylight hours. However, measurable amounts of MMT in ambient air have been reported at service stations and other outdoor locations.³ In addition, while there appear to be no data regarding the persistence of MMT in the atmosphere under conditions of darkness, MMT has been detected at measurable levels in underground parking garages.¹ MMT has also been detected at measurable levels in rain water and storm runoff water collected along highways in Canada.⁴ Overall, it appears that there is a lack of data on public exposure to MMT in ambient air in areas where MMT is used and, consequently, no detailed assessments of the public health implications of such exposure.

Health Concerns with MMT Combustion Products

Increased Emissions of Fine Particulate Matter - As a result of the concerns regarding the impact of small particles on human health, the U.S. EPA has promulgated National Ambient Air Quality Standards (NAAQS) for particulate matter less than 2.5 μm in diameter. In doing so, the agency indicated that particles in this size range pose a particular health risk in and of themselves, regardless of their chemical composition. Particles in this size region penetrate deep into the pulmonary tract where they can be deposited.

When MMT-containing gasoline is introduced into the engine of a gasoline-powered vehicle, most of the MMT is thought to be converted to manganese oxides as a result of the combustion process. Early development work performed by Ethyl regarding MMT indicates that the formation of very small metal oxide particles is critical to the anti-knock characteristics of MMT because these particles interrupt chemical reactions leading to engine knock.⁵ These oxides take the form of small particles with diameters of less than 1 μm and the presence of very small manganese particles as a result of MMT use has been observed in the ambient air of urban areas.⁶ In contrast, manganese-containing particles resulting from the suspension of soil dust or brake wear will have much larger diameters, generally greater than 10 μm .

The most prevalent manganese oxide found in automotive exhaust is trimanganic tetroxide (Mn_3O_4), with some manganese sesquioxide (Mn_2O_3) also being reported. More recent work, however, indicates that MMT combustion products include particles consisting of manganese sulfates and phosphates in addition to manganese oxides.^{7,8}

Another interesting finding reported in an auto industry study⁹ was that ammonia formation was observed to be substantially greater for the catalysts that had been exposed to MMT. This finding is of some significance as ammonia is an important precursor with respect to the formation of fine secondary particulate matter (ammonium sulfate and ammonium nitrate) in the atmosphere.

Based on the increased emissions of fine PM resulting from MMT use and the health risks posed by public exposure to fine PM, use of MMT poses a public health risk, regardless of whether the chemical composition of the manganese oxide particles is a concern, because it increases exposure to fine PM.

Toxicity of MMT Combustion Products - Manganese compounds are ubiquitous in the environment and manganese is an essential trace element required for life. Despite this, exposure to manganese and manganese compounds can pose a health threat. In the United States, manganese compounds in general are listed as hazardous air pollutants by the federal government¹⁰ and as toxic air contaminants by the State of California.¹¹ As noted in reference 1,

Exposure to excess manganese has been observed to affect various organ systems, including the respiratory, cardiac, reproductive, and central nervous systems.

Based on this, there is no question as to whether manganese compounds emitted from vehicles as a result of MMT use can be toxic: they can. In addition, as noted above, given the size of the manganese oxide particles, there is no question that they can penetrate and be deposited deep into the lung region. Therefore, the issue is whether the level of public exposure to the manganese oxides and other possible combustion products resulting from MMT use is great enough to be of concern from the perspective of public health. As with most issues related to public health risks, this issue is complicated by the fact that some individuals may be much more sensitive than others to exposure; for example, it is well known that asthmatics are more sensitive to ambient ozone levels than the general population. The issue of sensitive individuals has been reported with respect to exposure to manganese compounds,¹² and infants have also been identified as being particularly sensitive.¹

As with the impacts of MMT use on vehicle operation and emissions, the issue of whether MMT use in unleaded gasoline will lead to ambient levels of MMT combustion products high enough to warrant concern was first addressed in the mid-1970s when the widespread use of MMT in unleaded gasoline was first considered. In addressing this concern, there are two basic questions to be answered: (1) what is or would be the level of public exposure to MMT combustion products, and (2) what level of exposure to these combustion products can be deemed to be “safe.” The answer to the first question is relatively straightforward. Because the public exposure level is affected by the level of manganese used in unleaded gasoline, the amount of gasoline used in the area, and the fraction of gasoline that is treated, it can either be estimated or, in areas where MMT is already being used, be determined through measurements of ambient levels of manganese compounds. Such measurements have reported elevated levels of manganese containing particles near roadway sampling sites in Canada.³

Unfortunately, the answer to the second question, regarding safe exposure levels, is not as straightforward. In 1994, Health Canada performed a study¹ addressing this issue and determined that exposure to manganese oxides resulting from MMT use and other factors did not represent a threat to public health. In contrast, in 1994, prior to being ordered to allow the use of MMT in gasoline in the U.S., the U.S. EPA rejected Ethyl Corporation’s waiver request, with U.S. EPA Administrator Carol Browner stating:¹³

EPA recently completed a risk assessment on manganese emissions associated with the use of MMT and determined that there are important unanswered questions about potential public health risks and that health effects and exposure studies are needed.

These studies include those required under the U.S. EPA’s Fuels and Fuel Additives Registration Regulations.¹⁴ Under these regulations, the Ethyl Corporation is required to characterize emissions resulting from MMT usage and to conduct tests on the carcinogenicity, mutagenicity, teratogenicity, reproductive toxicity, and neurotoxicity of MMT combustion products. In addition, the U.S. EPA recently published a notice of proposed alternative requirements regarding this testing specifically for MMT.¹⁵

Other Issues

It is generally recognized that the use of MMT in gasoline leads to higher exhaust emissions levels of hydrocarbons. Given that the most important toxic air contaminants emitted by gasoline vehicles (benzene, 1,3 butadiene, formaldehyde, and acetaldehyde) are hydrocarbons, one might expect that the use of MMT would increase emissions of these compounds. Although data are limited, this effect has been observed in one auto industry study where benzene, 1,3 butadiene, and to a lesser extent formaldehyde emissions (as well as total hydrocarbon emissions) were higher for vehicles using MMT.¹⁶ This study also showed higher overall particulate emission rates for vehicles operating on MMT and that the increase in emissions was greater than could be accounted for by manganese oxide particles.

Conclusions

Based on the available information, it is clear that MMT is a toxic compound and that the use of MMT leads to public exposure to the compound. In addition, MMT use as a gasoline additive leads to higher emissions of fine particulate matter and that particulate matter contains various manganese-containing compounds. However, the risk that MMT use as a gasoline additive poses to public health is still being studied. In addition to the risk posed by MMT and MMT combustion products, the limited data available suggest that MMT increases emissions of benzene, 1,3 butadiene, and formaldehyde from gasoline-powered vehicles as a result of the general increase in hydrocarbon emissions observed from MMT use.

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