Petrol fuel additives effects on vehicle technology and the environment

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Summary

Regarding the changing fuel requirements, keeping pace with the vehicle and emission control technologies and with enviromental concerns, fuel additives play a special role, as there is a wider range in chemical composition of the fuel additives, and thus impact, compared with the fossil and renewable fuels themselves. In the previous report on worldwide use of different fuel quality and composition, *TNO 2020 R11950 Petrol fuel quality and its effects on vehicle technologies and the environment*, it was briefly remarked that metal-containing fuel additives in petrol, such as antiknock agents, were effectively banned for use in Europe. The Human Environment and Transport Inspectorate asked TNO a further clarification regarding the concerns about fuel additives, and antiknock agents in particular. There are many other fuel additives, for colorization, fuel stabilization, detergents, flow and lubricity improvers, and corrosion inhibitors, but these are considered not to have direct or indirect risks on health or the environment. This report will focus solely on antiknock additives for petrol fuels, also known as octane boosters, and the metallic fuel additives in particular.

In Europe, after the earlier ban of lead additives, an effective ban of other metal-contained additives (MFA, metallic fuel additives) was established in 2004 with a specific limit for MMT of 6 mg/litre from 2011, lowered to 2 mg/litre in 2014, based on a wider concern with metals in fuel. In recent years no use of MMT has been reported in the annual monitoring reports under the European fuel quality directive[1]. The more extensive studies, over a longer period of use of metal containing additives, are from USA, starting with alternatives for lead-containing additives (TEL and TML) to be phased out from the 1970's. Based on the precautionary principle, laid down in the USA and California Clean Air Acts, the supplier has to prove no harm to technology and environment as part of the request for a waiver for use, but failed to attain this waiver twice in 1978 and 1981. Concerns were raised on both elevated emission levels with MMT, in particular hydrocarbons, and observed manganese oxides deposits. In Canada, as comparison, the main metal-based antiknock agent, MMT, with manganese at levels of 8-18 mg Mn/liter petrol, was voluntarily removed from petrol as late as 2004. The seminal study by General Motors Research in 2006, with comparisons on the same vehicle models, between USA and Canada and the fuel composition transition in Canada raised concern on the effect of MMT on durability, with catalyst failures within the guarantee period. Similar concerns are for all metallic fuel additives, that can cause deposits at sensitive locations in the engine and emission control technology.

In 1991, a third waiver request to the USA EPA was denied on the ground of health risk associated with air-borne manganese, but the decision was successfully appealed on the ground that the EPA overstepped its jurisdiction. The main supplier, Ethyl Corporation, later Afton Chemical Ltd., also appealed successfully an earlier Canadian MMT ban from 1997. However, by this time North American refineries voluntary stopped the use of MMT in petrol, apart from the concerns because less contested antiknock additives and compounds, such as MTBE and ethanol, were available, which require much higher volumes admixtures.
In 2010, in Europe, Afton was not successful in appealing the 6 and 2 mg/litre limits.

[1] Quality of petrol and diesel fuel used for road transport in the European Union (Reporting year 2021) in pursuant to Article 7a of Directive 98/70/EC.

The European Court of Justice, in a decision ignoring the wealth of studies supplied from both sides, referred, simply and implicitly, to the precautionary principle. The legal encounters regarding MMT, before the ECJ decision, have been battles over the limitations and uncertainties of the scientific studies. The durability issues, these uncertainties concern, are known to be complex problems, with generally few truly significant conclusions. The impact of deterioration over the lifetime is known to be signifcant with new vehicles, with more complex and effective emission control technology. Therefore, any precautionary principle that existed twenty years ago applies doubly so for newer and cleaner vehicles. Any measure to reduce deterioration of emission control technology helps to reduce pollutant emissions.

The use of oxygenated components like MTBE and ethanol have been common in Europe and other developed regions for decennia. They do require good storage, transport, and fueling infrastructures, because of their hygroscopic nature, which attracts water, enhance corrosion, cause separation, and dissolve certain materials like rubber. For this reason developing countries, with poor infrastructure may be more hesitant with the use of oxygenated fuels.

Concerns in the literature with antiknock agents in general, but metallic fuel additives specifically, are manifold:

1. The inherent toxic nature of most of the the substances, with handling and unburned emissions from the tank and tailpipe.
2. The direct emissions of harmful substances into the air, such as heavy metals that affect the nervous system and accumulate in the body. Moreover, airborne metals, like iron, raise health concerns, despite its normal presence in the body.
3. Deposits on the cylinder walls may inhibit full combustion and lead to observed increases of hydrocarbon emissions.
4. Deposits on spark plugs may reduce their effectiveness for homogeneous ignition and combustion.
5. Deposits on sensors that control emission reduction technologies, such as lambda and NO_x sensors, that inhibit their function.
6. Deposits on valves and in catalyst channels that restrict flow or mechanical valve operation.
7. The deposits and interaction with the active catalytic surface, i.e., the washcoat, that reduce desired chemical conversion rates.

These technical concerns above may lead to direct environmental effects, but may also affect the vehicle emission performance, via the engine or aftertreatment, thus leading indirect and possibly delayed environmental effects.

All of these harmful effects are difficult to prove conclusively, as they require thousand of hours of controlled vehicle or engine operation, against a reference vehicle, but the abundant evident of manganese containing brown-reddish deposits, as lead deposits before in the 1970’s, raises ample concerns, of these effects. The organisations of vehicle and engine manufacturers, OICA and ACEA, requested a ban in 2002 in the UNECE GRPE session. The vehicle deterioration effect of the fuels used, especially with new and pending emission control technology, is not included in studies on Euro-2 and Euro-3 vehicles in the 1990’s, but they are likely to aggravate any observed problem and adding some new ones with new automotive technologies. The risks with new vehicle technology is likely greater than when the addititive use was still common and discussed extensively from 1978 to 2004.

Given these effects and concerns, before metallic fuel additives are allowed on the European market it must be proven that both the direct harm from the fuel and the exhaust gas is limited. In particular, it must be shown that the deterioration of both the engines and the advanced emission controls systems, as commonly used in Euro-5/6 from 2009, satisfy the same criteria as fuels within the legal specification, i.e., up to 160,000 kilometres.

Concerns for environmental effects of metallic fuel additives are clear, but the existence of hard and relevant evidence is often disputed. The older studies provide no proof for applicability for vehicles that entered the market in the last twenty years. Based on the precautionary principle, these additives were banned in Europe and since then limited new evidence emerged. However, much more important, the availability alternatives, such as MTBE, ethanol, and higher aromatics (BTEX) that also raise the octane number to the required level, are likely the reasons, why most stakeholders had no objections to or even welcomed the ban. With the required admixture of biofuels (E5 and E10), in combination with the allowed levels of aromatics, the need for special antiknock agents is limited. In 2005, the USA went as far as to phase out MTBE in favour of ethanol, due to the risk for ground water contamination by MTBE. In Europe, toxicity of MTBE is not considered to this extent. Costs are likely the main driver for the use of metallic fuel additives in developing regions, especially if market-ready petrol is imported from Europe.

In light of the many opposing studies and disputed evidence, and the particularly assertive stance of the fuel additive supplier, another evaluation of the scientific evidence seems superfluous at this stage. The precautionary principle should not allow outdated studies to be submitted as evidence for current vehicles, less than twenty years old. The EPA waiver stems from the 1990's. Before allowing the use of any metallic fuel additives in Europe, the direct and delayed effects on emission performance must be evaluated on modern vehicles. In the absence of such a complete study according to a carefully designed protocol, especially for vehicles from after 2005, which is now the majority of the fleet in almost all developed countries, the evidence of safe use is insufficient.

Contents

1 Introduction

In the previous report on worldwide use of different fuel qualities and compositions, *TNO 2020 R11950 Petrol fuel quality and its effects on vehicle technologies and the environment*, it was briefly remarked that metal-containing fuel additives, such as antiknock agents, were banned for use in Europe. The main focusses were, initially, lead-based TEL, and more recently manganese-based MMT. However, metal-based antiknock agents were more common, as the metal, when combined with the hydrocarbons, like ethyl groups when combusted, has a stabilizing effect on the combustion reducing the spontaneous ignition, known as knock. The known anti-knock fuel additives are summarized, but likely there are other combinations, molecules or complexes, especially of metals with methyl, ethyl, or aromatic hydrocarbon, known or investigated. The broad overview should be taken as an indication of the general risks associated with these types of additives.

Fuel additives are plentiful for many purposes. They are used for colorization. They stabilize the fuel against oxidation. There are detergents to reduce the formation of solids, i.e., gum. Some additives improve the physical properties, and improve flow and lubricity.
Other additives inhibit corrosion. And there are additives to improve the fuel properties at low temperatures. This report will focus solely on antiknock additives for petrol fuels, and the metallic additives in particular.

Risks of metallic fuel additives come in four main categories:

1. The toxic nature of the additives itself, as for the case for Tetra Ethyl Lead (TEL) and N-methylaniline (NMA), a risk for handling and spills, and evaporation, partial burned and unburned emissions.
2. The toxic nature of the combustion products, such as lead.
3. The deterioration of the engine and the combustion process.
4. The deterioration of the emission control technology and the functioning of the system as a whole.

Table 1: The protocol for testing metallic fuel additives under Euro-5/6, with typically 2-4 vehicles tested per technology type, like port-fuel and direct injection.

Fuel	Batch 1	Batch 2	Batch 3	Batch 4
“No-additive” fleet	Run-in, initial emission tests and aging up to 30000 km	30000 – 80000 km aging and periodic emission tests	80000 – 120000 km aging and periodic emission tests	120000 – 160000 km aging, periodic/final emission tests
“Additive fleet”	Run-in, initial emission tests and aging up to 30000 km	30000 – 80000 km aging and periodic emission tests	80000 – 120000 km aging and periodic emission tests	120000 – 160000 km aging and periodic/final emission tests

Antiknock agents or octane boosters may have all of these risks. However, the deterioration of engine and emission control technologies in normal use is difficult to prove definitively. It requires long and complex testing and the comparison with a reference deterioration. In laboratory tests, i.e., bench aging, some components can be tested, but due to the predefined gas composition and temperatures, thus not fully reflect normal use. Testing in the vehicle is the best, seemingly, only option. There has been a protocol developed, to allow metallic additives, by the European Commission, that requires the coverage of all common engine and aftertreatment technologies, and comparative testing up to 160,000 km. See Table 1.

Anti-knock fuel additives are often the more economical alternatives to improve the octane number of the fuel within the standards than tailoring the composition of the fuel in the refinery process, e.g., reformates. The amount of certain anti-knock agents is limited to a few grams per litre, while appropriate fuel composition, like aromatics and ethanol, require many volume percent of admixture to increase the octane number.

2 Changes in fuel quality standards

In report *TNO 2020 R11950 Petrol fuel quality and its effects on vehicle technologies and the environment*, an overview is given of the interplay between vehicle technology and fuel quality, showing that new vehicle technologies need better fuel quality. The legislator is the third party, next to fuel and car industries, stipulating further requirements on the fuel, mainly for environmental reasons. The reduction of the historically common components lead, sulphur, poly-aromatics, and benzene, are driven by the impact they have on health and environment.

The Worldwide Fuel Charter set the internal industrial fuel standards, set into law in the developed countries, to meet the requirements needed for the proper functioning of technologies, and reduce the environmental impact. Relevant items are set in legislation. Previous report exemplified this relation between emission standards, fuels, vehicles, and environmental impact.

Current report, which should be read in conjunction with the previous report, focusses on one aspect of this overall change in fuel quality, namely, petrol antiknock fuel additives. With the total phase out of lead-based TEL around 2000, in most countries, different alternatives came to the market, and their effects on vehicle and catalyst technologies was little known. Across the world there came bans on fuel additives like MMT, but eventually this culminated in a general, often voluntary, ban on metal and mineral-based additives in developed countries and regions. West-Africa (ECOWAS countries) will limit both Manganese and Iron in petrol in 2025.

As TEL, most metal-based additives are usually metals-hydrocarbons compounds, like iron with ethyl groups. With the combustion of the hydrocarbons and the oxidation of the metals, the additives have a stabilizing effect, partly due to the heat capacity, on the combustion process and the spontaneous combustion, known as “knock”, is reduced. For lead in TEL, it was known to stick to the surfaces, thus fouling spark plugs, cylinder walls, valves, and catalysts, if present. With TEL additives so-called scavenger compounds were used as additional additives to reduce this effect, e.g., toxic ethylene dibromide (EDB) and ethylene dichloride (EDC). Chlorine and bromide may affect negatively the fuel and engine systems, and a ban on its use agreed in the WWFC.

Direct injection technology, gasoline particle filters, high cell density (> 600 cpsi) three-way catalysts, EGR, turbo chargers, and possibly lean-NO_x traps, are new technologies emerged in the last years for petrol vehicles. Most historic fuel additives have not been fully tested in combination with most of these new technologies from Euro-4 (2005) onward.

With every new metal-based additive, similar but new effects were suspected and investigated. With the abandoned use of metal-based fuel additives these investigations were limited in scope from 2004 onwards.

At the same time, vehicle and emission control technologies evolved and shifted focus to allow for oxygen-based fuels, like ethanol, which has good antiknock characteristics, but due to the hydroscopic nature posed other problems that needed to be addressed.

Hence, apart from the more advanced aftertreatment, with, e.g., smaller channels in catalysts, the petrol fuels now used as reference for engine and emission control development are different from the pre-2000 fuels.

The current legislative restriction of metallic fuel additives, for MMT specifically lower than 2 mg/L, in Europe, voluntary restrictions in the USA and Canada, and the use of renewable fuels to meet antiknock requirements (octane number), the attention for metallic fuel additives has reduced.

3 Legislation development

The eventual worldwide ban in developed countries on metallic additives in fuels has been foremost a matter of the precautionary principle, albeit not explicit. Discussions on the development of special test procedures in Europe as late as 2007 have been overtaken by the phasing out of metallic additives from 2009, with Directive 98/70/EC. The studies of GM, Ford, and others and issues with catalyst failure within the guarantee period, with clear differences between the USA (petrol without MMT) and Canada (petrol with MMT), and differences in durability issues in the periods before and after the voluntary ban of MMT in Canada from 2004, provided enough circumstantial information to warrant a precautionary ban on metallic fuel additives.

Directive 2009/30/EC summarizes the official position:

The use of specific metallic additives, and in particular the use of methylcyclopentadienyl manganese tricarbonyl (MMT), might raise the risk of damage to human health and might cause damage to vehicle engines and emission control equipment. Many vehicle manufacturers advise against the use of fuel containing metallic additives and the use of such fuel may invalidate vehicle warranties. It is therefore appropriate to keep under constant review the effects of the use of the MMT in fuel in consultation with all relevant stakeholders. Pending further review it is necessary to take steps to limit the severity of any damage that may be caused. It is therefore appropriate to set an upper limit on the use of MMT in fuel, based upon currently available scientific knowledge.

The amount of MMT was restricted to maximum of 6 mg/litre manganese from 1 January 2011 and 2 mg/litre from 1 January 2014. The use of metallic additives shall be made available to the consumers at the fuel station with the label: “Contains metallic additives”.

Furthermore, by the directive any metallic fuel additives needed to be labelled as such. Many vehicle manufacturers threatened to void any vehicle warrantee if the vehicle owner uses such additives. The supplier Afton Chemical Ltd. appealed the UK implementation of this regulation, which made its way to the European Court of Justice. The court upheld the regulation, on the basis of what appears to be a form of the precautionary principle. Without definite proof that MMT was not harmful, in the face of the specific concerns raised, the regulation was right to limit the use of metallic fuel additives like MMT. In the light of the Court decision the promised further study seemed not necessary, but the Commission exemplified, apparently, the precautionary principle a few years later.

The Commission made no assessment as promised in aforementioned legislation.
A small document came to light with the court case. In 2013, a report by the Commission to European Parliament on “Concerning Article 8a of Directive 98/70/EC relating to the quality of petrol and diesel fuels and amending Council Directive 93/12/EEC” laid down the rules for assessing the harmful impact of metallic fuel additives, based on a test protocol and similar rules laid down by USA EPA:

It is apparent that there is a potential impact on health and the environment by the use of MFA [Metallic Fuel Additives]*. In order to assess this impact a methodology has been developed to be employed by any party interested in the establishment or revision of limit values for MFA in the Directive. The Commission will monitor the application of this methodology and will take all appropriate initiatives.*

The writers of this report are not aware that any party has taken up the action to establish that certain metallic fuel additives do not have impact on health and the environment, according to the guidelines given by the Commission. Based on the general concern this should be the appropriate action before starting the use of MFA. Referring to older reports, that do not consider the current vehicle technologies, do not compare with current fuel standards, or do not abide to current standards for protecting environment and general health.

The legislation Directive 2009/30 in force states in Article 8a the stipulations for metallic additives. This is an amendment from directive 98/70/EC:

'*Article 8a*

Metallic additives

1. The Commission shall conduct an assessment of the risks for health and the environment from the use of metallic additives in fuel and, for this purpose, develop a test methodology. It shall report its conclusions to the European Parliament and to the Council by 31 December 2012.

2. Pending the development of the test methodology referred to in paragraph 1, the presence of the metallic additive methylcyclopentadienyl manganese tricarbonyl (MMT) in fuel shall be limited to 6 mg of manganese per litre from 1 January 2011. The limit shall be 2 mg of manganese per litre from 1 January 2014.

3. The limit for the MMT content of fuel specified in paragraph 2 shall be revised on the basis of the results of the assessment carried out using the test methodology referred to in paragraph 1. It may be reduced to zero where justified by the risk assessment. It cannot be increased unless justified by the risk assessment. Such a measure, designed to amend non-essential elements of this Directive shall be adopted in accordance with the regulatory procedure with scrutiny referred to in Article 11(4).

4. Member States shall ensure that a label concerning the metallic additive content of fuel is displayed at any point where a fuel with metallic additives is made available to consumers.

5. The label shall contain the following text: "Contains metallic additives".

6. The label shall be attached to the place where information indicating the type of fuel is displayed, in a clearly visible position. The label shall be of a size and font that is clearly visible and easily legible.';

Article 8a (3) was replaced by directive 2015/1513:

3. In light of the assessment carried out using the test methodology referred to in paragraph 1, the European Parliament and the Council may revise the limit for the MMT content of fuel specified in paragraph 2, on the basis of a legislative proposal from the Commission.

Thus allowing for new evidence, that did not materialize so far. In the requirements themselves, below, the restriction of metallic additives are not listed. The test methodology gives the application scope: "*a candidate metallic additive in a fully formulated fuel*", thus including all metallic fuel additives, in principle. Manganese content, reflecting Article 8a, are part of EN228:2012 revision. Several countries, notably Germany, have a ban on the use as additive, typically above the detection limit of a few mg per litre.

European fuel quality standards for petrol in the legislation:

ENVIRONMENTAL SPECIFICATIONS FOR MARKET FUELS TO BE USED FOR VEHICLES EQUIPPED WITH POSITIVE-IGNITION ENGINES

Type: **Petrol**

Parameter (1)	Unit	Limits (2)	
		Minimum	Maximum
Research octane number		95 (3)	—
Motor octane number		85	—
Vapour pressure, summer period (4)	kPa	—	60,0 (5)
Distillation:			
— percentage evaporated at 100 °C	% v/v	46,0	—
— percentage evaporated at 150 °C	% v/v	75,0	—
Hydrocarbon analysis:			
— olefins	% v/v	—	18,0
— aromatics	% v/v	—	35,0
— benzene	% v/v	—	1,0
Oxygen content	% m/m		3,7
Oxygenates			
— Methanol	% v/v		3,0
— Ethanol (stabilising agents may be necessary)	% v/v		10,0
— Iso-propyl alcohol	% v/v	—	12,0
— Tert-butyl alcohol	% v/v	—	15,0
— Iso-butyl alcohol	% v/v	—	15,0
— Ethers containing five or more carbon atoms per molecule	% v/v	—	22,0
— Other oxygenates (6)	% v/v	—	15,0
Sulphur content	mg/kg	—	10,0
Lead content	g/l	—	0,005

(1) Test methods shall be those specified in EN 228:2004. Member States may adopt the analytical method specified in replacement EN 228:2004 standard if it can be shown to give at least the same accuracy and at least the same level of precision as the analytical method it replaces.

(2) The values quoted in the specification are 'true values'. In the establishment of their limit values, the terms of EN ISO 4259:2006 'Petroleum products — Determination and application of precision data in relation to methods of test' have been applied and in fixing a minimum value, a minimum difference of 2R above zero has been taken into account (R = reproducibility). The results of individual measurements shall be interpreted on the basis of the criteria described in EN ISO 4259:2006.

(3) Member States may decide to continue to permit the placing on the market of unleaded regular grade petrol with a minimum motor octane number (MON) of 81 and a minimum research octane number (RON) of 91.

(4) The summer period shall begin no later than 1 May and shall not end before 30 September. For Member States with low ambient summer temperatures the summer period shall begin no later than 1 June and shall not end before 31 August.

(5) In the case of Member States with low ambient summer temperatures and for which a derogation is in effect in accordance with Article 3(4) and (5), the maximum vapour pressure shall be 70 kPa. In the case of Member States for which a derogation is in effect in accordance with Article 3(4) and (5) for petrol containing ethanol, the maximum vapour pressure shall be 60 kPa plus the vapour pressure waiver specified in Annex III.

(6) Other mono-alcohols and ethers with a final boiling point no higher than that stated in EN 228:2004.

4 Petrol fuel additives

The list of antiknock agents is large, as many molecules have good combustion characteristics. The toxicity of the different substances is obtained from the European Chemical Agency. Compact, heavy “centralized” molecules with many methyl groups, or rings, have good antiknock characteristics, while long hydrocarbon chains, like alkanes, have already knock at low compression rates.

Knock is the uncontrolled autoignition, or explosive ignition, of parts of the unburned fuel as the pressure and temperature rises in the cylinder during the spark-ignited combustion. The knock characteristics are therefore determined, as octane number, based on one of two reference engine tests (RON, slower speed, early ignition, and MON, faster speed, late ignition) by comparing to a reference fuel mixture of iso-octane (three methyl groups attached to pentane) and the long molecule n-heptane. For many hydrocarbons the octane number are determined in the 1930’s. Notably, methane, propane, toluene, and ethanol, have RON well above 100. Therefore, a mixture of hydrocarbons and alcohols can be the basis of a fuel with proper antiknock characteristics.

The efficiency of an anti-knock agents is expressed in the raise of the octane number, from the base level around 85 RON. For a number of additives below, the number of points the fuel additive can raise the RON is given. Ten points raise, to 95 RON, brings the European regular fuel within required range.

4.1 TEL and TML (Tetra Ethyl/Methyl Lead)

The antiknock characteristics of tetraethyl lead (TEL) were known and used from the 1920’s. Health concerns were raised from the beginning, but only fifty years later cognitive health issues were linked to the use of TEL, and correlated to the lead accumulated in the body, like blood and bones. From the 1970’s, starting in the USA, TEL was being phased out and alternatives were sought. Only in the late 1990’s the use of TEL was banned in different countries and on 1 January 2000 in the whole of Europe, ending a seventy-year experiment with human health, especially with the cognitive development of children near traffic impeded by lead poisoning. The worldwide ban was only in 2011, thus including also developing nations, except for Yemen, Iraq, Afghanistan, Myanmar, and Algeria which banned lead in petrol late.

TEL itself harms the engine and brings damage to the three-way catalyst. This was the reason for its eventual demise as anti-knock additive, when catalyst technology was needed to meet emission standards from the 1980’s and 1990’s. The lead attached to the cylinder and valves, but also deactivated the catalyst. Special scavenger chemicals were added to reduce the deposit of lead, which in themselves were again toxic and harmful, like chlorine and bromide containing molecules. Chlorine-based additives are also banned nowadays with the metallic additives in developed countries, that follow the WWFC.

Later, tetramethyl lead (TML) and some other variants were also used as an antiknock additives. They raise the same concerns and were banned with the generic ban of lead in fuel.

4.1.1 Toxicity of TEL

According to the classification provided by companies to ECHA (European Chemical Agency) in REACH (Directive on Registration, Evaluation, Authorisation and restriction of Chemicals) registrations this substance is fatal if swallowed, is fatal in contact with skin, is fatal if inhaled, may damage fertility or the unborn child, is very toxic to aquatic life, is very toxic to aquatic life with long lasting effects and may cause damage to organs through prolonged or repeated exposure.

The description fatal refers to acute toxicity 1 or 2, being the most acute toxic categories under CLP (European Classification, Labelling, and Packaging regulation).

At least one company has indicated that the substance classification is affected by impurities or additives.

This substance is covered by several Harmonised Classifications and Labelling's (CLH) entries approved by the European Union. Differentiating between the different CLH's entries requires manual verification.

The use of TEL is severely restricted in Europe.

4.1.2 Toxicity of TML

According to the classification provided by companies to ECHA in CLP notifications this substance is fatal if swallowed, is fatal in contact with skin, is fatal if inhaled, may damage fertility or the unborn child, is very toxic to aquatic life with long lasting effects, may cause damage to organs through prolonged or repeated exposure and is a flammable liquid and vapour.

This substance is covered by several Harmonised Classifications and Labelling's (CLH) entries approved by the European Union. Differentiating between the different CLH's entries requires manual verification.

4.2 MMT (Methylcyclopentadienyl Manganese Tricarbonyl, $C_9H_7MnO_3$)

The reddish-brown deposits on cylinder walls, valves, spark plugs, and catalysts, containing manganese, has been shared as visual illustrations of the concern with the MMT fuel additive which has been around since the 1950’s as a replacement of TEL. Only a small amount of MMT is needed to increase the octane number by about 10 points from low octane levels, e.g., with blending stock. With higher baseline fuels, the extra increase in octane number is limited to about 3 points. MMT is highly toxic and unstable in light.

4.2.1 Toxicity of MMT

According to the classification provided by companies to ECHA in CLP notifications this substance is fatal if swallowed, is fatal in contact with skin and is fatal if inhaled.
The description fatal refers to acute toxicity 1 or 2, being the most acute toxic categories under CLP.

4.3 Ferrocene ($Fe(C_5H_5)_2$)

Ferrocene has been around since the 1940's from the start of organometallic chemistry. It is used in many different chemical applications, also as anti-knock agents and effective to reduce smoke in diesel engines and heating installations. It can increase octane number by about 5 points. The iron oxides may form deposits at different locations, and the concerns are linked to the studies on MMT because of these deposits.

4.3.1 Toxicity of Ferrocene

Ferrocene is highly toxic. According to the classification provided by companies to ECHA in REACH registrations this substance may damage fertility or the unborn child, is very toxic to aquatic life with long lasting effects, is a flammable solid, is harmful if swallowed, is harmful if inhaled and may cause damage to organs through prolonged or repeated exposure.

4.4 Iron pentacarbonyl ($Fe(CO)_5$)

Iron pentacarbonyl is mentioned as antiknock agent. It was developed in Germany in the 1930's by I.G. Farben, but it was phased out in favour of TEL and other anti-knock agents. It falls in the category of metal compounds like MMT and ferrocene. The deposits of iron oxides in the engine and aftertreatment, and the search of scavenger chemicals to reduce deposits has been ongoing.

4.4.1 Toxicity of iron pentacarbonyl

According to the classification provided by companies to ECHA in REACH registrations this substance is fatal if swallowed, is fatal in contact with skin, is fatal if inhaled, causes damage to organs through prolonged or repeated exposure and is a highly flammable liquid and vapour. The description fatal refers to acute toxicity 1 or 2, being the most acute toxic categories.

4.5 NMA (N-Methylaniline)

NMA is a variant of xylidine, with fewer methyl groups. It is an antiknock agent that increases the octane number by 8 to 10 points with a substantial fraction added. The fuel legislation does not mention NMA, but its production and sales is restricted because of the high toxicity. There are reported fatalities by contact with skin.

4.5.1 Toxicity of NMA

According to the harmonised classification and labelling (CLP00) approved by the European Union, this substance is toxic if swallowed, is toxic in contact with skin, is toxic if inhaled, is very toxic to aquatic life, is very toxic to aquatic life with long lasting effects and may cause damage to organs through prolonged or repeated exposure.

4.6 Xylidine (xylene amines, dimethylaniline)

In World War II, xylene amines were introduced as antiknock agents for fighter planes. It is a group of molecules related to NMA. Currently, it does not seem to be in use as fuel additives and is replaced by NMA.

4.6.1 Toxicity of xylidine

According to the classification provided by companies to ECHA in CLP notifications this substance is toxic to aquatic life with long lasting effects, is toxic in contact with skin, is toxic if inhaled, is toxic if swallowed and may cause damage to organs through prolonged or repeated exposure.

4.7 BTEX (Aromatics)

The aromatic hydrocarbons: benzene, toluene, ethyl-benzene, and xylene (collectively known as BTEX), are good antiknock agents, but restricted in EU petrol to levels of 1% for benzene, and 35% for the total of aromatics. The substances are harmful in themselves, therefore spills during fuelling and evaporation is already an environmental risk. During partial combustion they may be released but also form other aromatic and poly-aromatic compounds. Among these substances benzene is the most toxic, and separately restricted to 1% in the European fuel quality standard. Toluene has similar toxicity as benzene, like carcinogenic, but less severe. The effects are well known, because both benzene and toluene were used as solvents, albeit restricted nowadays.

4.7.1 Toxicity of benzene

According to the harmonised classification and labelling (CLP00) approved by the European Union, this substance may be fatal if swallowed and enters airways, may cause genetic defects, may cause cancer, causes damage to organs through prolonged or repeated exposure, is a highly flammable liquid and vapour, causes serious eye irritation and causes skin irritation. The description fatal refers to acute toxicity 1 or 2, being the most acute toxic categories under CLP.

4.7.2 Toxicity of toluene

According to the harmonised classification and labelling (CLP00) approved by the European Union, this substance may be fatal if swallowed and enters airways, is a highly flammable liquid and vapour, is suspected of damaging the unborn child, may cause damage to organs through prolonged or repeated exposure, causes skin irritation and may cause drowsiness or dizziness.

Additionally, the classification provided by companies to ECHA in REACH registrations identifies that this substance may cause genetic defects, may cause cancer, is suspected of damaging fertility or the unborn child and is harmful to aquatic life with long lasting effects.

4.7.3 Toxicity of xylene

According to the harmonised classification and labelling (CLP00) approved by the European Union, this substance is a flammable liquid and vapour, is harmful in contact with skin, is harmful if inhaled and causes skin irritation.

4.7.4 Toxicity of ethyl-benzene

According to the harmonised classification and labelling (ATP06) approved by the European Union, this substance may be fatal if swallowed and enters airways, is a highly flammable liquid and vapour, is harmful if inhaled and may cause damage to organs through prolonged or repeated exposure.

Additionally, the classification provided by companies to ECHA in REACH registrations identifies that this substance may cause genetic defects, may cause cancer, is harmful to aquatic life with long lasting effects and is harmful if swallowed.

4.8 MTBE (methyl tert-butyl ether)

MTBE has been the main replacement of TEL in developed regions, with the complete ban of lead in petrol from 1993 in the USA and 2000 in Europe. MTBE and ETBE can be synthesised using biogenetic methanol and ethanol. The toxicity of MTBE, and contamination of ground water, led in 2007 in the USA to a ban on its use. In Europe, MTBE is not banned and used in petrol. Its use can be part of renewable fuels, with 22% (MTBE) and 37% (ETBE) fractions renewable energy, if ethanol and methanol of renewable sources are used. With the restriction of BTEX, i.e., lower benzene and aromatics limits, the need of MTBE has increased from 2006, but declined with E5 and E10. In 2015 in the Netherlands a range of 0% to 4% MTBE was found in combination of 5% ethanol, with one outlier of 11% MTBE in premium petrol, without ethanol, often used for older vehicles. A few years later the fraction of MTBE increased slightly to 2%-3%.

4.8.1 Toxicity of MTBE

According to the harmonised classification and labelling (CLP00) approved by the European Union, this substance is a highly flammable liquid and vapour and causes skin irritation.

In the USA MTBE was banned as fuel additive on the ground of potential human carcinogen at high doses and other observed health effects.

4.9 Iso-octane (trimethylpentane)

The investigations into knock and antiknock agents and compounds focusses strongly on fuel composition, and the standard for antiknock became iso-octane (C_8H_{18}) an isomer of octane consisting of three joined methyl groups, and thus commonly known as trimethylpentane. The bottom end of the scale, i.e., the highest knock, is the n-heptane (C_7H_{16}), a long chain, or alkene hydrocarbon. Petrol engines are designed to have no knock and 95 octane number, which restricts temperatures and pressures in the cylinder during combustion.

Given the definition of antiknock on the basis of octane, the use of octane as antiknock agent is only logical. The amount of octane needed to limit knock is substantial, i.e., in the order of 10% of the fuel. Since this compound must be formed by synthesis of smaller hydrocarbons, the use of octane as antiknock is limited in practice. As an antiknock agent the high volume needed makes it too expensive as additive for market fuel.

4.9.1 Toxicity of iso-octane

According to the harmonised classification and labelling (ATP01) approved by the European Union, this substance may be fatal if swallowed and enters airways, is very toxic to aquatic life, is very toxic to aquatic life with long lasting effects, is a highly flammable liquid and vapour, causes skin irritation and may cause drowsiness or dizziness. The description fatal refers to acute toxicity 1 or 2, being the most acute toxic categories under CLP.

4.10 Ethanol

Ethanol has become the preferred antiknock agent in petrol for policymakers and legislators. The use of ethanol (E5, E10) is one of the dominant routes chosen by fuel supplier to comply with obligations under the European Renewable Energy Directive (RED). In current emission legislation petrol vehicles must be tested with E10, earlier, from 2009 onwards, E5 was required. It is therefore standard fuel for vehicles of 15 years and younger. In terms of fuel additives it requires some chemical and technological adaptations. It increases the vapour pressure, some automotive materials suitable for hydrocarbons, were not suited for ethanol, and there are increased risks of separation, water, and deterioration of the fuel.
However, with Euro-5 (2009) ethanol admixture became standard in Europe, following the USA. The USA even banned MTBE on the basis that ethanol was an appropriate alternative without the health risks.

5 Deterioration through deposits

There are over hundred research papers and reports regarding metallic fuel additives. Good overviews are given in the review papers by S. Kent Hoekman and Amber Broch and by Gil Oudijk. Not all of these studies are easily traceable or accessible. Some are internal research reports by car manufacturers, others are court and legislative filings by the fuel additives suppliers in formal processes. Each group is about half of the total output, with a small fraction of studies by independent researchers. The emission testing is not always conclusive, or in some cases of elevated emissions with metallic fuel additives are still below the emission limits. The most telling, albeit indirect, evidence in many of the research papers are the side-by-side photographs of deposits on engine and catalyst parts, containing the metals used in additives. For engineers dealing with durability of engines and emission control systems such deposits are considered the pre-stage of defects and malfunctions.

Cylinder walls, spark plugs, sensors, valves, and the catalytic surfaces are all places where metallic substrates may form and they can affect the emission performance of the vehicle in different ways. This is part of deterioration, and the rate of depositing may depend on flow, temperature, and specific configurations. Hence, singling out effects of one species is difficult in the general deterioration of the vehicle's performance over time.

From the metal-based antiknock agents, TEL and MMT, are best known to cause deposit, because of the visual characteristics and from chemical analyses of lead and manganese specifically, that is unlikely from other sources.

5.1 Cylinder wall

Near the wall the combustion is already hampered, and deposits of metals may bind more unburned fuel, which is consequently emitted as hydrocarbons. This has been observed in a number of cases with the use of MMT. The increase of hydrocarbon emissions is therefore most clearly correlated with the use of MMT.

Another feature of deposits on the cylinder wall is the reduced heat transfer to the coolant, and higher temperatures during combustion. Higher temperatures lead to higher NO_x formation, which may not be anticipated fully by the emission control technology.

5.2 Sensors

Sensors are essential for the correct operation of many active systems of the engine and the emission control technology. The durability of the sensors is strongly linked to deposits. The sensors often contain catalytic surfaces to be selective for certain components in the exhaust gas, and the catalytic efficiency of such surfaces can be affected by deposits.

Deposits on sensors are well known and reduce the lifetime of the sensor significantly.

Sensors with older engine technologies, e.g., retrofit and monitoring systems, tend to have a limited lifetime of a few years. The sensors durability is dependent on the exhaust gas composition it is exposed to. The metallic and metal oxides deposits are an unknown factor.

5.3 Valve and catalyst flow

At the inlet of catalysts, especially with high cell density (> 400-600 cpsi, e.g., Euro-4) manganese-containing deposits are observed. These observations are from vehicles with warrantee issues concerning the catalyst efficiencies. The deposits partially blocks the flow. The formation of deposits depends strongly on the geometry of the exhaust line. More bends and sharper corners in the exhaust line will increase deposits. Modern closed coupled catalysts, introduced to have higher temperatures in the catalysts, require compact designs, and thus more flow-related deposit issues.

Distorting the flow, either by poorly closing or opening valves, or by restricting the exhaust gas passage through catalysts, is at the heart of the basic functioning of the engine and the aftertreatment technology. Therefore, the effects of poor valve operation can be manifold and cascading to a failure to function. Modern engines are often restricted in their lifetime because of this reason, rather than mechanical wear and tear.

5.4 Catalytic surface

The catalytic surfaces are known to lose their effectiveness over time through poisoning and (mineral) ash deposits. Base durability is set at 160,000 for this reason. With a catalyst lower efficiency, the pollutant emissions increase, in the case of petrol of NO_x, HC, and CO. Rather than the environmental impact of TEL, this effect of lead on the catalyst was the main reason for the ban on the use of TEL. Precise mechanism for reduced catalytic efficiency vary. With new catalytic materials and combination with the particle filter, new aspects in catalytic efficiency and aging have emerged.

6 Discussion and conclusions

The evidence of deposits in the engine, on spark plugs, sensors, and in aftertreatment systems, like catalysts, related to metals in petrol, from metallic fuel additives, is plentiful. This does not always give rise to emission increases above the emission limits. Altogether, the use of metallic fuel additives does raise concerns. Studies of a later date are not conclusive, by the confidence requirements set by the European legislator in a protocol for evaluation up to 160,000 kilometres use, and the range of automotive technologies that should be included.

The composition of exhaust gas may also be more toxic with metallic fuel additives, but the effect of manganese are from epidemiological studies related to manganese emissions to ambient air from industrial plants and neurological diseases of miners working in high concentrations of manganese in the air. The true health effects of manganese in fuel, like the effects of lead in petrol before, maybe difficult to attain, especially as they are mixed with all other negative health effects from traffic.

Many of the antiknock metallic fuel additives are highly toxic by themselves. However, lead, mercury, and manganese are specifically known for their neurotoxicity, partly related to the long residence time in the body. They should be handled carefully, and in some cases the use is restricted in Europe by REACH legislation. Since not all fuel is burned and fuel is released in the air, this basic toxicity is another reason for concern.

The clear opposition of the car manufacturing industry, supported by studies, to metallic fuel additives, and the voluntary ban by refineries in different countries, are the strongest indications that the use of metallic fuel additives is undesirable. This combined with the many alternatives, with additional benefits, like climate benefits from additives from the biogenetic resources, allows one to limit the risk of vehicle deterioration and emission increases, by banning metallic fuel additives. Since, fuel composition is not known to the end user, these vehicles owners and user have to rely on industry standards and the agreements between fuel and engine manufacturers. Such agreement does not exist for the use of metallic fuel additives.

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