
Lead TetraEthyl and MTBE

Petrol Additives

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Heavy Metal is Bad for You

Which band are you talking about?

Not any band, but the fact that although metallic lead itself is not toxic, its compounds often are.

Why?

Lumps of lead are insoluble, but many lead compounds dissolve in water and act as neurotoxins in the body. Lead acetate used to be called 'sugar of lead' because of its sweet taste; it was added to wines as a sweetener! Insoluble lead compounds have been used in paints, including lead chromate for "yellow lines". And, of course, it has been used in petrol.

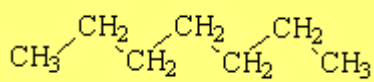
Why was lead put in petrol anyway?

To improve the octane rating.

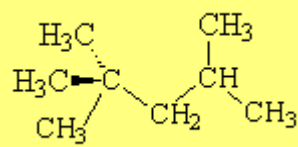
What does 'octane rating' mean?

Petrol is a mixture of compounds of carbon and hydrogen called hydrocarbons; most of the hydrocarbons in petrol are alkanes. In modern car engines, the petrol vapour-air mixture is highly compressed before it is sparked, in order to get the maximum energy from the burning fuel. However, some hydrocarbons tend to ignite under pressure before they are sparked, so that the engine runs roughly; this is known as "knocking". Branched-chain alkanes tend to resist this pre-ignition better than alkanes with unbranched chains. Alkanes and fuel mixtures are given Octane ratings depending on their knocking tendency. 2,2,4-trimethylpentane (which contains 8 carbons and so is an isomer of octane) has an Octane rating of 100; heptane has a rating of 0. The Octane number of a petrol is the % of 2,2,4-trimethylpentane in a mixture with heptane that has the same knocking characteristics as the petrol under test.





Heptane

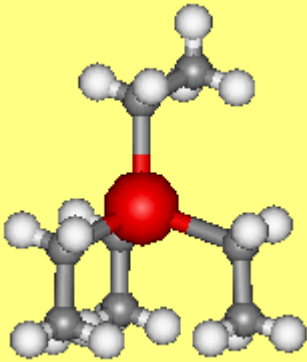


2,2,4-trimethylpentane

The gasoline fraction from refining crude oil has an octane rating below 60, which is why you can't put it straight into a car (which needs 87 octane for 2-star and 93 octane for 4-star).

How does lead improve the octane rating?

In 1922, an American called Thomas Midgely (who also invented CFCs) found that if tetraethyl lead, $\text{Pb}(\text{CH}_2\text{CH}_3)_4$, was put into petrol, particles of lead and lead oxide PbO are formed on combustion. This helps the petrol to burn more slowly and smoothly, preventing knocking and giving higher Octane ratings. 1,2-dibromoethane is also added to the petrol to remove the lead from the cylinder as PbBr_2 , which is a vapour and removed from the engine. (This is how lead is released into the environment from leaded fuels). Using higher-Octane leaded petrol meant that more powerful high-compression engines could be built.



Lead tetraethyl (left) is a lead atom bonded to a tetrahedral arrangement of ethyl groups. Thus, the molecule can be thought of as a metal atom surrounded by a hydrocarbon cage. The C-Pb bond is quite weak, and in the hot environment of an internal combustion engine it fragments producing lead and C_2H_5 radicals which can help terminate the combustion process by radical reactions.

So what's the problem?

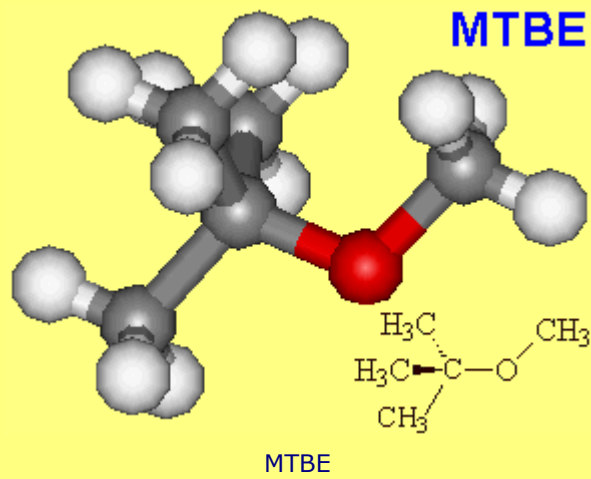
There are two problems. First, the lead that's released from car exhausts is dispersed into the environment, and has been linked to a number of health problems. In particular, studies indicated that children living near motorways seemed to have lower IQs than those living in areas with less lead pollution, suggesting that the lead was somehow linked to a lowering of brain function and intelligence in children.

The second problem is that car exhausts contain environmentally unfriendly gases, such as CO and nitrogen oxides. A catalytic converter can help to remove these gases, but it cannot be used on leaded petrol since the lead 'poisons' the catalyst.



Are there any alternatives to lead tetraethyl ?

Yes, there's another additive called MTBE, which stands for methyl tertiary-butyl ether, and it is designed to reduce carbon monoxide and ozone emissions as well as to boost Octane ratings.

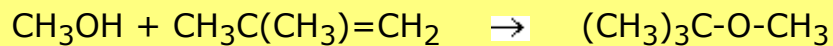


How does it reduce CO levels?

The toxic gas carbon monoxide is formed by incomplete combustion of petrol. The oxygen atom in MTBE helps provide extra oxygen for complete combustion, and helps give it an Octane rating of 116.

How is MTBE made?

By an acid-catalysed addition reaction between methanol and methylpropene. In 1994, MTBE was the 18th most important chemical produced in the USA.



So why is MTBE a problem in the USA?

Leaking petrol storage tanks and spillage have caused MTBE to get into groundwaters in the USA. Although it is not very toxic, it is not very biodegradable either, and has a strong taste and smell, noticeable at the 15 parts per million level. There is now a strong movement to ban it from petrol, in California in particular.

What will they use instead?

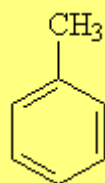
Probably another oxygen-containing compound such as ethanol. This is not so toxic, though it will probably increase the cost of the gasoline.

Is MTBE used in the UK?

No, instead of MTBE we have toxic compounds like benzene and toluene, with Octane ratings of around 106, added to our petrol.



Benzene



Toluene

If there is no lead in it, surely unleaded petrol is safe?

There is quite a lot of benzene in unleaded petrol; it makes up 1.4% of normal unleaded (out of 28 % aromatics) and 2.6% in 4 star unleaded (out of 45% aromatics). Not all the hydrocarbons get burned up in the engine so that some gets passed into the air. Benzene is believed to cause cancers, leukaemia and anaemia. Catalytic converters can help reduce hydrocarbon emissions, but not until they are warmed up.

Further Reading

MTBE

- Environmental Protection Agency report on MTBE
- Drinking Water Inspectorate report on MTBE
- <http://www.agriculturelaw.com/headlines/sept00/sept11i.htm>
- <http://www.foia.org>

Lead Poisoning

- <http://www.minerals.csiro.au/safety/lead.htm>
- <http://www.dartmouth.edu/~toxmetal/TXSHpb.shtml>
- <http://www.emedicine.com/EMERG/topic293.htm>
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- R. Lansdown and W. Yule, *Lead Toxicity. History and Environmental Impact*, John Hopkins University Press, 1986.
- C. Warren, *Brush with Death. A Social History of Lead Poisoning*, John Hopkins University Press, 2000.
- G. Markowitz and D. Rosner, *Deceit and Denial, The Deadly Politics of Industrial Pollution*, University of California Press, 2002.

Tetraethyllead

- Dietmar Seyferth, *The Rise and Fall of Tetraethyllead. 1. Discovery and Slow Development in European Universities, 1853-1920*, *Organometallics*, 2003, 22, 346.
- Dietmar Seyferth, *The Rise and Fall of Tetraethyllead. 2*, *Organometallics*, 2003, 22, 5154
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- B. Kovarik, *Charles F. Kettering and the 1921 Discovery of Tetraethyl Lead In the Context of Technological Alternatives*, at <http://www.radford.edu/~wkovarik/papers/kettering.html>
- <http://www.uwsp.edu/geo/courses/geog100/Lead-Science.htm>

Lead Poisoning in Antiquity

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- S.C. Gilfillan, *Rome's Ruin by Lead Poison*, Wenzel Press, 1990.
- <http://www.nipissingu.ca/departement/history/muhlberger/orb/lead.htm>