



## Lead and Lead Substitutes - The Facts

The lead in petrol is known as Tetra Ethyl Lead (TEL) or Tetra Methyl Lead (TML) and was originally developed in the 1920's by a joint venture between General Motors and Standard Oil (now known as Exxon - Esso in Europe).

The original reasons for adding lead in petrol was not to prevent Valve Seat Recession (VSR) but to raise the octane of the petrol. This octane gain allowed engine designers to increase compression ratios and hence power without any dangers of engine damage. These more modern high compression engines were now able to run at higher revolutions without experiencing knocking or pinking.

Before the development and introduction of lead to fuel, engines were successfully run without lead, albeit at low compression ratios which gave low power and low fuel economy. As engines of the period were not highly stressed valve seat recession did not appear to be a major problem.

The world-wide use of lead and the discovery that lead compounds formed during the combustion of lead alkyls prevented valve seat recession (VSR) by forming thin layers of lead oxides and sulphates on critical valve/seat interfaces was a bonus. This led to the world-wide practice of machining valve seats directly into the cast iron head.

Problems occur with these engines once lead is removed from the petrol and the protection is lost, which is when recession starts. The combustion of the petrol in the cylinders generates extreme heat on the exhaust valve seats as the burnt gases pass through. Each time the valve is hammered open and shut, it momentarily welds itself to the valve seat at the hottest points. This localised welding of the exhaust valves to their seats tends to be followed by 'tearing out' of small fragments of metal from the seat, ie. the valve sticks to its seat and as it is lifted off by the valve gear, it 'rips' away from its micro-welded condition. Small particles of valve seat material are thus embedded in the valve face and are likely to be further oxidised forming 'warts' of hard iron oxide.

The continuous repeated impact of these hard materials on the soft valve seat causes further damage and, if the valve seat rotates, a degree of 'grinding in' will also occur. From this moment on, valve seat wear is both rapid and inexorable leading to engine failure as the valve and seats burn away.

Other than the actual material from which the valve seat is made, the next most important factor in determining whether VSR will take place, is the driving condition. All the technical data produced indicates that engine speed and load are significant factors. VSR has been found to be an exponential function of speed but the relationship with engine load is believed to also be a factor.

The actual occurrence of VSR is related to seat temperature which increases with speed and load eg. acceleration, climbing hills, motorway driving and towing).

The demise of lead from petrol which is set for 1st January 2000, (but will probably become more and more difficult to find from mid 1999), will cause premature failure to those engines which have 'soft' valve seats when used under modern road conditions. Competition use, continental touring and high speed driving will exacerbate the problem.

### Development and Testing

It is widely accepted that lead is the best material for VSR protection and octane response when used at the UK maximum permitted treatment of 150 mg/ltr. Typically however, the current BS 4040 4 star leaded fuel has a concentration in the range of 80-120 mg/ltr or a minimum lead content of 50 mg/ltr. So what are the options for owners of pre 1990 and classic cars and how are these verified?

### Additive Chemistry

The move to unleaded petrol around the world stimulated the development of additives to prevent VSR. The research has led to the availability of several technologies all of which are based on metallic salts:

Sodium

Potassium

Phosphorus

Manganese

Metal Pellets



## Sodium

This type of product was one of the initial materials tested in the US when Pb levels in leaded gasoline were reduced to 26mg per litre. Because of these moves a programme was run jointly by the US Environmental Protection Agency (EPA) and the US Department of Agriculture (USDA) on two basic chemistries, Sodium being one.

Testing in various engines showed that at the recommended treatment some degree of protection against VSR was provided. However, at four times the recommended treatment VSR was eliminated. A negative finding during the testing was that oil black deposits were found in the inlet tracks.

Sodium is also known to form low melting point eutectics in very hot regions. This is known to result in erosion problems, particularly with turbochargers. As a consequence of these findings, Sodium has been withdrawn from the list of chemistries being considered for use in Lead Replacement Petrol (LRP).

## Phosphorous

This material was also included in the original EPA/USDA study. The treatment was tested at about double the recommended treatment and reduced VSR although a wear rate value of 0.022ins/100 hours still signifies future problems.

Additionally, this additive caused deposits to form in the inlet valve area of the engine to the extent that one valve was unable to close fully and was starting to burn at the test completion - 200 hours.

In these tests the fuel treatments (Sodium/Phosphorous) were found to contaminate the crankcase oil. Such contamination has a deleterious effect on the oil normally causing it to thicken. Phosphorous is also known to be a severe poison for catalytic converters which could cause additional problems if mis-applied when filling a car with petrol.

## Potassium

With the demise of Sodium, Potassium has become its natural replacement since test work has shown that Potassium will provide similar levels of VSR protection to Sodium. There is a large body of evidence which demonstrates that potassium in the presence of lead alkyls or associated halogen chemistry scavengers leads to inlet valve burning. While leaded fuel is still available any mis-fuelling and the use of after treatments containing this type of product will remain a concern.

Potassium as a fuel additive has been previously used, not as a VSR treatment but as a fuel performance enhancer. Many motorists may possibly recall the major problems which many cars, and the models of one major car producer in particular, encountered when their cars were run on a well known brand of petrol.

## Metal Pellets

There have been claims over many years that using metal pellets either in the fuel tank or fuel lines reduces VSR. One such device which uses tin pellets was tested and reported in a Classic Car magazine in 1989/90 period.

The published results indicated that VSR protection was not achieved which is hardly surprising since the solubility of metallic tin or lead in petrol is very low, in the order of one part in 10 million (VSCC !((!). This is in contrast to the 30-50ppm of lead concentration generally considered as the minimum for protection.

## Manganese

Manganese in the form of Methylcyclopentadienyl Tricarbonyl (MMT) has been used in virtually all Canadian unleaded petrol without any problems for well over 20 years. Its original use was for the self same reasons that lead was first used - namely to increase octane.

Like the lead it can replace, MMT also protects soft valve seats from recession so it can be said that MMT is the closest alternative to lead.

With MMT being available since the early 1970's it has been subjected to the most vigorous testing of any fuel additive in history with extensive test data to support its important feature:

Helps reduce intake valve deposits in conjunction with fuel detergents.

Does not contribute to valve stick either alone or in combination with detergents.

Completely safe in turbo-charged engines.

No adverse engine deposits formed.

Compatible with all construction materials including plastics and elastomers.

Insoluble in water preventing any interaction problems.

MMT has gained US EPA Waiver for use in unleaded gasoline along with Pipeline distribution approval due to its non-surfactant properties.



## Toxicity of VSR Materials

Any product which is added to fuel to be burnt in engines and expelled through the exhaust will have an effect on emissions. Of all the treatment chemicals examined, only MMT has been subject to in-depth studies. These have shown that no problems are posed in respect of emissions, hence the approval of US EPA.

For catalytically equipped vehicles statistically significant reductions in carbon monoxide (CO) and oxides of nitrogen (NOx) have been observed.

Manganese is a naturally occurring element found in soil, water, food and all living organisms. In the combustion process the Manganese forms Manganese Oxide ( $Mn_3O_4$ ) and only about 0.1% Manganese is emitted from the exhaust. Very high concentrations of Manganese ( $30,000 \text{ mg/m}^3$ ) can have side effects (Parkinson like symptoms) but a recent study conducted by Research Triangle Institute in Toronto, Canada, showed that no citizens of that city are even exposed to the safe recognised scientific level which is set at  $0.025 \mu\text{g/m}^3$ .

Little or no toxicology data is available for other metallic systems but it is considered that phosphorous compounds can lead to highly toxic emissions similar in nature to organo-phosphates which are highly toxic ie. Gulf war syndrome and the use of sheep dip on farms.

## So how do we prevent Valve Seat Recession in most pre-1990 and Classic Cars?

It depends on how long you wish your car engine to last. You can retard the ignition and lose power and then drive your car at very low speeds; never accelerate quickly, slow down when climbing a hill and always decelerate immediately the engine starts to 'pink'.

Your engine may last several years more, but it is a potential risk. Speed and higher engine temperatures will severely damage the valve seats when running on unleaded petrol.

## Can I have the soft seats replaced with hardened valve seats?

It is possible to replace valve seats in aluminium cylinder heads by machining out the old soft seats and replacing them with hardened seats. However, with cast iron heads it is sometimes impossible or excessively expensive to do so. The cost for valve seat replacement in aluminium or cast iron cylinder heads can be several hundred pounds for a 4 cylinder engine and 2, 3 or 4 times that amount for V6's, V8's or V12 engines.

Even then you will still have to retard the ignition to prevent pinking because 4 star leaded petrol is 97 octane whereas premium unleaded is only 95 octane. Consequently you will lose power unless you use an Octane Booster. If you retard the ignition by only 2 degrees you could lose in the region of 5% power at the wheels - more degrees lose even more power. Remember as engines build up deposits with use, there is a requirement for increased octane.

## Will the oil companies offer a lead substitute petrol on their forecourts?

Prior to and after January 2000 some petrol companies may provide a lead substitute fuel at selected filling stations. (One has already stated they won't and older cars should be driven off the road). It is likely to be expensive due to the low demand and the protection given to valve seats may be lower than required for high engine load conditions. The lead substitute content of the fuel is expected to be low to prevent accidental cross contamination of fuels at filling stations as some types of lead substitute fuels will severely damage the modern catalytic converter equipped cars or to avoid any problems from sticking inlet valves.

## Are lead substitute fuel additives the answer?

In many countries where leaded petrol is banned, bottled lead substitutes are on sale at filling stations. A number of alternative lead substitute fuel treatments have been developed for this application but at the present time these have potential drawbacks.

## Millers VSP Plus, Lead Substitute and Octane Booster - Endorsed by the FB HVC

Millers VSP Plus is different, being based on proven manganese additive technology with US Environmental Protection Agency (EPA) waiver for unleaded gasoline.

Millers VSP Plus treatment utilises MMT additive chemistry which mimics the properties provided by lead. It gives a protective lubricant film on valve faces and seats while also increasing octane by 2-3 numbers, something which other treatments have difficulty in achieving in a single treatment.