

Effect of Unleaded Fuel on Octane Requirements of Automobile Engines

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Unleaded fuels are increasingly supplanting lead-treated fuels throughout the world. Initiatives in the USA, in Europe and in many industrialised countries are leading to social and legislative constraints against the use of lead compounds as additives. Alternative gasoline formulations are being developed to restore the octane rating, which for more than fifty years has been boosted by lead. Initially, increased proportions of aromatics were included in the gasoline fraction, but these also have undesirable environmental consequences and substitute oxygenates (alcohols, ketones and ethers) are proving to be excellent octane boosters.

Apart from their octane rating benefits, the use of lead compounds has other consequences. Like certain other metals, lead provides some lubricant properties, eg with inlet and exhaust valve operation. Continuous provision of a miniscule layer of lead on metallic surfaces inside the combustion chamber proved inadvertently to be highly effective as a lubricant for adjacent surfaces sliding against each other at the very high frequency required. Using lead-free fuels may in the long-term alter the life of inlet and exhaust valves and valve stems and other engine components but no great concern on this matter has yet been heard. However a notable feature of the use of lead-free fuel is the progressive increase of octane requirement. Initially, ie, with a new engine, or with "clean"

reconditioned surfaces, octane number is determined by the fuel formulation. Then with lead-free fuel a small but steady increase in octane requirement is noted. This has been attributed to the changed nature of combustion chamber deposits compared with the deposits from leaded fuels.

Combustion chamber deposits may affect octane requirements in three ways:

- 1) by occupying physical volume
- 2) by surface activity catalysing (or inhibiting) combustion reactions
- 3) by heat transfer effects due to changed thermal conductivity.

In our work at Aston we were most concerned with the physical properties of deposits studying the nature of the solid layers with scanning electron microscope to establish comparisons of porosity. Measurement of thermal conductivity was also undertaken since deposit surface temperature is almost certainly a key factor in knock-related reactions which determine octane requirements.

The nature of combustion chamber deposits

High boiling point hydrocarbons condense on the cooled walls and are partly burned off leaving a carbonaceous layer. With leaded fuels a layer of condensed lead compounds will cover and mingle with the carbonaceous layer. Lead oxide initially deposited will form lead salts - halides and sulphates. At low

temperatures, halides are favoured. As the engine warms up only the highest boiling hydrocarbons condense, leading to less carbonaceous material but the lead salts continue to build up, progressively increasing the deposit thickness. The deposit reduces heat transfer to the cooling water leading to increased deposit surface temperature. At this higher temperature lead sulphate formation is favoured.

Deposit removal

Volatilisation effects, which lead to some removal of deposit material, depends on engine operating conditions, higher chamber temperatures leading to greater deposit removal. Changes in chemical composition of deposits were similar to changes resulting from higher wall temperatures suggesting that the insulating effect of the deposit causes significant surface temperature increase as the deposit builds up.

Since engines are commonly run intermittently deposits will be formed in layers so that the deposit presents a stratified structure. Changes in chemical nature of the deposit would be expected as the total deposit layer increases in thickness.

As the deposit layer increases, internal temperature gradients will be set up and are likely to lead to flaking. Any mechanical or thermal shock will accelerate flake detachment. Flecking, or the detachment of small flakes, is also recognised on very thin deposit layers.

Deposit Adhesion

Adhesion of the deposit layers is partly chemical in nature. At higher temperatures the

carbonaceous material will be oxidised forming a link between deposit and wall metal and then between successive deposit layers.

Deposits from Leaded Fuel

The introduction of lead into fuel is reported to lead to a four-fold increase in deposit weight. Dumont⁽¹⁾ showed that 25% of the resulting ORI (octane requirement increase) was due to volume effect and remainder to the insulating effect.

The carbonaceous portion of the deposit also depends on the type of crank-case oil and the amount of oil reaching the combustion chamber surfaces. Synthetic (polymer) lube-oils gave lower ORI values than conventional lube oils. However C¹⁴ tracer experiments have indicated that the fuel is responsible for 70% of the deposit.

Comparison of thermal conductivity

In our work we assessed thermal conductivities in a method designed to simulate *in situ* conditions. Every attempt was made to avoid disturbance of deposit with partial destruction of the porous structure. Heat Flow from a copper bar of larger radius than the piston was monitored as shown in fig 1. It was impracticable to ensure a completely flat contact surface owing to the irregular nature of the deposit surface.

The lower end of the copper bar was drilled to house four 0.75 kW cartridge heaters. Variable voltage input enabled several steady state readings to be obtained for calculation of effective thermal conductivity.

Assessment of permeability and porosity

These properties are important in relation to ORI since a porous deposit may trap residual combustible mixture enabling this to initiate subsequent precombustion reactions. It is also likely to trap exhaust gases discharging heat to the fresh incoming charge. Both phenomena are likely to contribute to ORI.

Permeability and porosity were measured using standard Lea & Nurse apparatus (fig 2).

Experimental Results

Lead-free fuel deposit was obtained on a car using US fuel over 1300 km of average operating conditions for a private passenger car. The leaded fuel deposit was from a similar engine in UK over 1480 km.

Thermal conductivity of the leaded-fuel deposit was $0.75 \text{ Wm}^{-1}\text{K}^{-1}$ while the lead-free fuel deposit showed a value of $0.5 \text{ Wm}^{-1}\text{K}^{-1}$. This lower thermal conductivity will naturally lead to higher surface temperature and increased tendency to induce knock. Furthermore the result of introduction of lead free fuel will be a progressive increase in octane requirement as the deposit builds up on piston head and combustion chamber walls, etc.

Volumetric effect of the deposit was also assessed. It is obvious that even a small change in deposit thickness alters compression ratio significantly. With a possible increase of compression ratio of around 0.25 units, lead-free deposits may well lead to an increased requirement of two octane numbers. Many researchers have reported deposits of much greater thickness.

Permeability and porosity effects are more difficult to quantify. The diffusion of reacting combustion chamber gases into the porous structure of the deposit will affect the influence of the nature of the solid surface on knock-inducing reactions and the relative areas of such surfaces available for contact with the gases. The lead-free deposit was shown microscopically to consist of a two-layer stratum, the outer layer more porous than the inner. Owing to this structure and the size of sample available it was not possible to make a meaningful comparison of deposit permeability.

The chemical nature of the deposits were compared by scanning electron microscope but it is impossible to make quantitative comparisons from the contrasting analyses. Mineral constituents (barium, aluminium and zinc, etc) prominent in the lead-free deposit, presumably arise from processing catalyst residues.

The two-layer structure of the lead-free deposit is clearly visible but otherwise scanning electron microscope photographs merely confirm the contrasting porosity and grain structure of the deposits.

Conclusions

Quantitative conclusions are difficult because of diverse factors affecting engine combustion conditions. Driving behaviour, patterns of use, driving cycle, comparisons of acceleration, high-speed running and idling modes show wide variation across metropolitan, urban, and cross-country areas. These variations and engine size and load variations make precise prediction almost impossible.

However our work has confirmed that deposits from lead-free fuel do throw some light on the octane requirement increase resulting from the elimination of lead.

Further changes may now be expected as new unleaded fuel formulations replace the first generation of lead free fuels. The replacement of aromatics by oxygenates as octane improvers could well have a significant effect on deposit quality, quantity, and volume.

Reference

- (1) Milkita J.J. and Sturgis, B.B. The Chemistry of Combustion Chamber Deposits. S.A.E. Journal 1957 65.

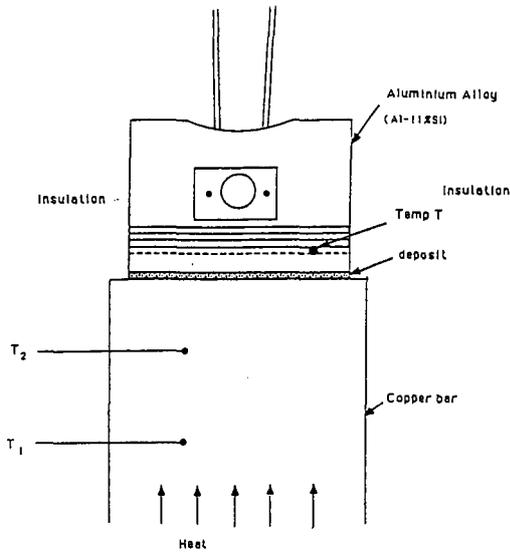


Figure 1. Measurement of Thermal Conductivity

Figure 2. Diagrammatic Presentation of Permeability Apparatus

