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THE RISE AND FALL OF LEAD IN PETROL

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While organic lead compounds have been a crucial addition to petrol for over half a century, they have more recently come to be seen as undesirable. Why and how are they being replaced?

For over fifty years organic lead compounds have found worldwide applications as additives to boost the quality of petrol. Their use has made a major contribution to the improved efficiency of the spark ignition engine and the efficient use of fuels. Now there is a commitment in all the major petrol markets in the world to the reduction and eventual abandonment of the use of lead additives in petrol.

There are, however, wide variations in the rate of progress in different countries. Japan, some twelve years after unleaded petrol was first introduced, has just become the first country to complete the changeover with the disappearance of all leaded petrol. The USA, which first offered unleaded motor fuel in mid-1974, had by early 1987 reached a market split of around 75% unleaded and 25% leaded. On the other hand Europe is only just starting on the introduction of unleaded petrol. Why this reversal of policy with regard to lead? Why the delay in the European approach? What are the implications of forgoing the addition of lead to petrol?

Function of lead additives

Before addressing these questions it is useful to look at the role of lead. Early in the development of the petrol engine attention focused on the compression ratio, that is the extent to which the fuel and air mixture is compressed before ignition. In practice it is measured by the ratio of the maximum to the minimum volume of the cylinder as defined by the piston at its extreme positions. It was found that the higher the compression ratio of the engine, the greater the power obtained and the better the fuel

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economy. It was also found that the benefit of a higher compression ratio was limited by the phenomenon of engine knock, which proved to be a function of fuel quality and engine design.

Under balanced conditions the flame front initiated in the cylinder by the spark advances steadily until all the mixture is ignited and the cycle proceeds smoothly. If the compression ratio and fuel quality are not balanced, fuel mixture remote from the spark plug can ignite or detonate spontaneously before the arrival of the flame front, giving rise to the knock or pinking sometimes heard in engines. Audible pinking is rarely damaging to engines but causes loss of power and inefficiency because the 'end-gas' detonation is frequently premature, that is it occurs while the piston is still on the compression part of the cycle. It should be noted, however, that another type of knock, which occurs at high engine speeds and is inaudible, can cause serious engine damage.

During and immediately after the 1914–18 Great War much research was carried out to improve the quality of fuels in order to resist engine knock. Petrol is a low-boiling-point mixture of many hundreds of different hydrocarbon compounds, with the composition varying significantly with the source of the original crude oil and with the refining processes used in its manufacture. Researchers found that the primary determinant of the propensity of the fuel to knock was its chemical composition: of the three basic hydrocarbon types, the straight-chain paraffins are the worst (i.e., the most likely to cause knock), the naphthenes are much better and the aromatics the best. It was also found that additives could also be used to improve the quality of petrol. Benzol, a commercial mixture of benzene, toluene and xylene, and also alcohols were found to allow the adoption of higher-compression engines giving improved power output.

Encouraged by the possibility that other compounds might also be able to improve resistance to knock, a major research project was commenced by General Motors Research Division in the USA. In 1921 after screening many thousands of candidates, Midgely and Boyd discovered the remarkable anti-knock properties of lead alkyl compounds. Quite small quantities of liquid tetraethyl lead (TEL) or tetramethyl lead (TML) produced spectacular improvements in fuel quality. Early problems caused by lead oxide deposits in the combustion chamber were solved by including small amounts of organic halides as scavengers in the additive package. These lead additives proved to be astonishingly efficient at promoting smooth burning of the fuel without detonation so as to liberate the maximum possible energy. Their anti-knock properties which allow the use of higher compression ratio engines are unique.

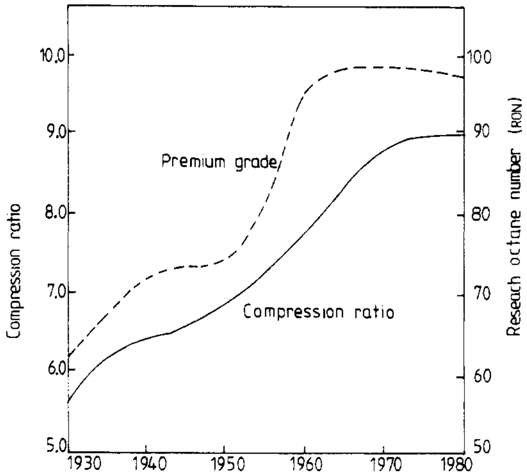

Figure 1. Trends in engine compression ratio and petrol octane quality.

No other compound remotely approaches the enhancement conferred by lead on motor fuel.

Octane quality of petrol

The susceptibility of a petrol to knock is measured against an arbitrary scale of 'octane numbers' which ranges from 0 to 100. Two pure paraffinic hydrocarbons have been selected as reference fuels. In most respects they have very similar properties but one, normal heptane (C_7H_{16}), produces knock in an engine under virtually any circumstances, while the other, iso-octane (C_8H_{18}), has a very high knock resistance. The former is ascribed an octane rating of 0 and the other 100. By blending the two compounds across the full range of volumetric ratios and testing in a standard single-cylinder engine which has a facility for varying the compression ratio while it is running, it is possible to set up a 'comparator' scale. To determine the octane number of a petrol, it is used to fuel the standard engine and the compression ratio is increased until the point where knock occurs; the octane number is accordingly that of the corresponding mixture of n-heptane and iso-octane which produces the same result. For example, 95 octane petrol will begin to knock in the standard engine at the same point as a mixture of 5% n-heptane and 95% iso-octane.

The octane scale is thus artificial rather than absolute but has now been universally adopted for some 50 years. Besides being used to express the octane rating of a fuel it also enables the basic octane requirement of any engine to be determined by establishing the octane number at which knocking is first detected. A test simulating acceleration from relatively low speeds allows the research octane number (RON) to be derived; higher-speed performance is related to motor octane number (MON).

Octane is thus a quality concept which embraces both the fuel and the engine. Evolution of the octane scale has provided a tool for measuring both fuel quality and engine performance. On the fuel side, recognition of the widely differing octane values of different hydrocarbon types has stimulated the development of refining technology directed at improving both the yield (i.e. the proportion of petrol derived per barrel of crude oil) and the quality of petrol. The combination of lead additives and improved refining has raised octane quality from around 60 RON in 1930 to the 90–97 RON range typical today. This in turn has enabled engine designers to increase compression ratios dramatically, virtually doubling them to 10:1 or better, and thus to vastly improve both performance and fuel economy (figure 1).

Lead as lubricant

In addition to improving the octane quality of petrol, lead additives also confer another remarkable benefit on engine operation. The lead compounds protect the valve seat from high-temperature wear by forming a soft film. The presence of lead has made it possible to use relatively soft cast-iron valve seats cut directly in the cylinder block with hardened valves actuated with powerful springs and cams — a combination which can be designed to give trouble-free performance for the life of the engine. Without lead in the petrol it is necessary to use specially hardened valve seats, such as the hard inserts already incorporated for aluminium alloy cylinder blocks, or to adopt induction hardening of the cast iron at the valve seats.

In the absence of lead, a soft valve seat suffers erosion and pitting, apparently due to a micro impact fusion mechanism. Under the repeated hammering sustained during opening and closing of the valve at high temperature, tiny particles of material are torn from the seating forming a fine debris which is exhausted with the products of combustion. The erosion leads to valve recession which, being irregular, allows gas leakage and eventually results in loss of power and efficiency (figure 2).

The removal of lead from petrol presents no technical problems to car manufacturers so far as valve design is concerned. Indeed most European cars in current production are now being fitted with hardened valve seats which will operate satisfactorily on unleaded fuels. However, the persistent use of unleaded fuel in a car manufactured with unhardened valve seats will result in valve recession problems. Since the protective lead compound film formed by leaded grades of petrol has some degree of persistence and because the erosion takes some time to develop, it appears that a single inadvertent fill of unleaded petrol is unlikely to induce significant damage. However, engines with valve metallurgy designed for petrols containing lead additives should continue to use leaded grade fuels.

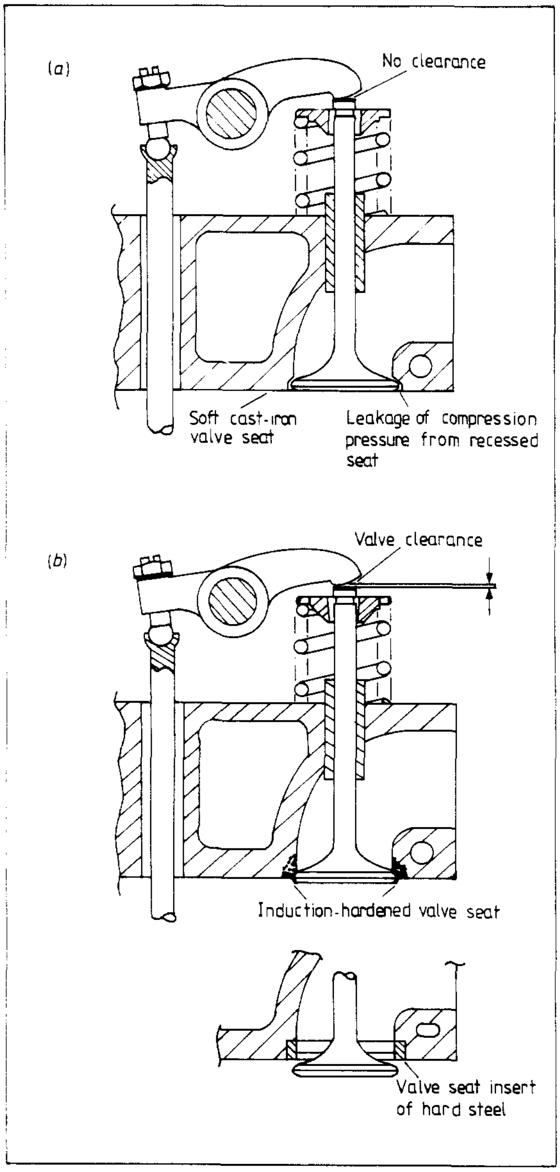

Figure 2.(*a*) Valve recession with unleaded petrol; (*b*) remedial designs. (*From Cmnd 8852* Lead in the Environment, *courtesy HMSO.*)

Environmental concerns

Although a relatively common metal in the earth's crust, most of the lead present in air, soil and water in mankind's environment is anthropogenic — the direct or indirect results of man's activities. It has long been recognised that lead and its compounds are poisonous above certain concentrations. However, it was not until the late 1960s that concern began to be expressed in several countries that lead and lead compounds in the atmosphere derived from petrol might be reaching levels that put human health in jeopardy. With the tremendous increase in the world consumption of leaded petrol in three previous decades the total lead burden had increased greatly. Although there was, and remains, much dispute between medical experts on the health dangers, several countries embarked on what was to be a long sequence of stepwise reductions in the permissible levels of lead in petrol. Table 1 shows the lead reduction programme followed in the UK.

Perhaps surprisingly, however, the main factor during the move towards eventual abandonment of the use of lead additives has been the concern about other forms of air pollution arising from car exhaust emissions. Serious air pollution was first encountered in the Los Angeles basin during the late 1950s and it was realised that fumes from car exhausts were a major contributor to the urban smogs. Similar problems were recognised in other large conurbations including Tokyo, where on occasion the smog from vehicle exhausts reached levels where it caused widespread eye irritation. Exhaust emission regulations were introduced first in California in the 1960s but in the 1970s general controls were applied in both the USA and Japan.

In most cases these controls required special catalytic converters to be fitted to the exhaust systems of cars. These comprise a stainless-steel casing similar to that of an exhaust silencer fitted with an open matrix on which are deposited tiny amounts of platinum alloy catalyst. Sometimes termed a 'three-way' catalytic converter, these units are capable of reducing the emissions of the three main noxious constituents of auto exhausts – carbon monoxide, nitrogen oxides and hydrocarbons – by over 90%. These catalyst units require close control over the oxygen content of the exhaust gas in order to function, which reduces engine fuel efficiency and further increases the initial cost of fitting the system. However, the major implication of the decision to fit catalytic converters is that the presence of lead in petrol poisons the catalyst and prevents it from operating. In fact, prolonged misfuelling with leaded fuel renders the catalyst permanently inoperative.

Thus it was the decision to set emission control limits which could only be met by adoption of the catalyst solution in the USA and Japan that necessitated the introduction of unleaded petrol. In both those countries all new vehicles sold after the mid-1970s were fitted with catalytic converters, were equipped with valve systems capable of operating in the absence of lead and needed unleaded fuel. Other countries have followed that same route more recently; in 1985 Australia introduced regulations requiring converters to be fitted to all new cars and simultaneously introduced unleaded petrol, and Sweden and Norway are now following similar programmes.

The elimination of lead from petrol results in loss of octane rating. In the USA the specification for the unleaded grade first offered in 1974 was fixed at a minimum of 91 RON which was substantially below the quality of leaded petrol then available. To accommodate this reduced octane the automobile industry produced 1975-model-year vehicles with compression ratios averaging 8.0 instead of the 9.5 of the previous model-year. Japan also followed a similar pattern the following year.

European developments: the UK goes unleaded

In Europe during the 1970s national governments and the EEC were deeply involved with the 'energy crisis' problems associated with the two sharp rises in the price of oil which occurred in 1973 and 1979/80. Much effort was directed towards the substitution of oil by other forms of energy. The oil industry was concerned with overcapacity and with major refinery investment needed to readjust to the changes in the pattern of demand, as well as meeting the need to reduce the lead content of petrol without any reduction in octane quality. The motor industry was engaged in development of new ranges of vehicles with dramatically improved fuel consumption. Because of these preoccupations, and perhaps lacking the compulsion to solve urban smog problems, Europe did not in the 1970s approach the question of air pollution from vehicles with anything like the urgency of the two largest petrol markets in the world. Two events were to change European priorities: firstly a series of politico-social developments in the UK and secondly the issue of forest damage in Germany.

In the UK in 1980 the Lawther Committee published its report *Lead and Health*. Set up by the government and chaired by P J Lawther, Professor

Table 1. Progressive reduction in maximum permissible lead in petrol in UK.

Dates	Maximum lead content ($g\ l^{-1}$)
1967–1972	0.84
1973	0.64
1975	0.55
1976	0.50
1978	0.45
1981	0.40
1986	0.15
1989†	0.013–0.15

† Directive 85/210/EEC requires unleaded grade with 0.013 $g\ l^{-1}$ lead to be available from October 1989 but low-lead grade (0.15 $g\ l^{-1}$) will continue to be available at least until 2000.

of Environmental and Preventive Medicine at St Bartholomew's Hospital, London, the Committee carried out an exhaustive review of the evidence linking lead and health. Nearly 3000 papers were studied by a team of epidemiologists, pathologists and psychologists who found food to be the main pathway for lead into the body and saw no evidence that airborne lead, and specifically lead from petrol, contributed significantly to raised concentrations of lead in the body. However, the Committee did recommend that all reasonable steps should be taken to further reduce lead in the environment. Responding, the government announced in 1981 a decision to reduce the maximum allowable lead from 0.4 gl^{-1} to 0.15 gl^{-1} at the end of 1985. This step was implemented without any reduction of the octane specification and necessitated refinery investment of some £300m, as well as about 2.5% more crude oil to manufacture the same volume of petrol.

The Lawther conclusions and the government's decision to reduce but not abandon lead additions to petrol did not please everybody in the UK. A vigorous campaign was mounted in 1982 and the issue became politicised with all three opposition parties calling for the introduction of unleaded petrol. A Royal Commission which reported in April 1983 concluded that it could 'find no compelling arguments for the retention of leaded petrol except as an interim measure to enable the majority of existing cars to be phased out'. It concluded that it would be prudent to phase out lead additives altogether as soon as practicable. The government accepted the conclusions within the hour of the Commission's report being published, agreeing to commence the introduction of unleaded petrol no later than 1990. Lead in petrol was not an issue at the general election hustings the following month.

Germany's *Waldes Angst*

During the early 1980s there was increasing dismay in Germany and some other European countries about the dramatic increase in tree die-back, which in some areas resulted in major damage to large tracts of forest. Although the problem is ascribed to so called acid rain, the cause and the mechanism of the forest damage remain to be clarified. Sulphur dioxide and nitrogen oxide emission from coal- and lignite-burning power stations are certainly involved but it seems likely that auto emissions are also implicated. In 1983 the German government decided that vehicle emission controls should be considerably tightened up, and pressed initially within the EEC for the US approach involving catalytic converters to be adopted in Europe. For this, unleaded petrol would be required and Germany decided that it would commence phasing out lead additives.

The EEC did not accept the German emissions proposals in their entirety, but instead chose to allow the European car industry more time to develop other techniques for auto emission reduction. The European Council recognised that the catalytic converter route involved an increase in fuel consumption which was in contradiction to the objectives of the Community to strive for improved and rational utilisation of energy. It was considered that emerging engine designs promising good fuel economy and reduced emissions such as the lean-burn concept (very high air/fuel ratios) would be ruled out by imposition of the catalyst route which demands near-stoichiometric air/fuel ratios to function.

However, the EEC did recognise that satisfactory emission standards in large engines, above 2 l capacity, could only be met with catalysts – which necessitated unleaded petrol. That factor, plus the decisions already taken by two Community countries to phase out lead, resulted in the EEC Commission developing, separately from the emission regulation, the necessary legislation covering the phasing out of leaded petrol.

Before leaving the subject of auto emissions it is worth noting that little progress has been made toward EEC agreement on an emissions Directive, though a draft tabled in 1985 has the agreement in principle of all States other than Denmark and Greece. This covers new reduced-limit values for carbon monoxide, nitrogen oxides and hydrocarbon exhaust emissions which would be applicable to new models from 1 October 1989 and all new vehicles from 1 October 1991. Meanwhile a number of non-EEC European countries anxious to reduce car emission levels quickly, such as Austria, Switzerland, Sweden, Norway and Finland, who would have followed an EEC emissions decision, have opted to adopt the US approach mandating catalytic converters on all new vehicles within the near future. All these countries are thus also committed to unleaded petrol and are all aligned with the EEC unleaded petrol Directive discussed below.

EEC Directive on unleaded petrol

Because of the international nature of both the motor and oil industries and the need to maintain reasonable compatibility between engines and fuels across Europe to allow unimpeded vehicle movements, European agreement was needed on two points. Firstly all countries had to agree a common timetable for the latest date when unleaded had to be made available. Secondly agreement was needed on the properties of unleaded to be introduced, particularly with regard to the octane quality to be specified.

Once these two parameters were fixed, refinery

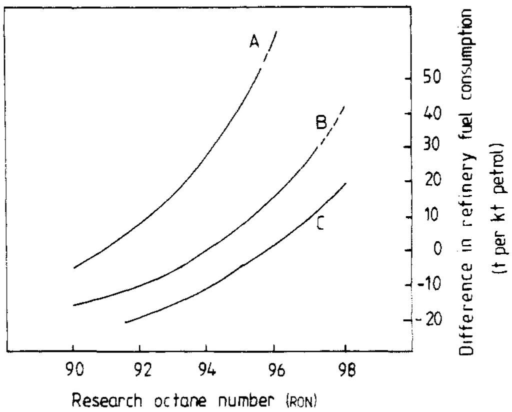

Figure 3. Effect of lead content on refinery fuel consumption: plots of incremental crude against RON at constant petrol consumption (base case: 1 kt petrol, 96 RON, 0.40 g l^{-1} lead content). Curve A, unleaded petrol: B, 0.15 g l^{-1} lead content; C, 0.40 g l^{-1} lead content.

planning and investment for the production of unleaded fuel and the design of engines to run on unleaded could proceed. The Directive (85/210/EEC) which was agreed in March 1985 and is now fully ratified, is a relatively simple document which requires Member States 'to ensure the availability and balanced distribution within their territories of unleaded petrol from 1 October 1989' and which specifies the minimum octane level, the maximum lead concentration and maximum benzene content.

The debate between the oil and car industries that took place in the year preceding agreement of the Directive on the octane level to be specified was strongly argued. Most of the arguments revolved around the overall energy costs attaching to different possible unleaded grade octane qualities and the investment that each of the two industries involved would have to make at the various octane scenarios considered.

Deciding the octane of unleaded fuel

Petrol-engined vehicles consume close to 11% of all energy used in Europe and even modest changes in the patterns of petrol used thus have a major effect in energy terms. Fuel consumption may be reduced by engine design changes such as described earlier, by increasing the engine compression ratio, which in turn requires a higher-octane petrol. Conversely changes in petrol quality may require a change in engine design.

Measures directed towards protection of the environment, such as emission control, which involves changes in engine design or the addition of special equipment, or reduction of lead content of petrol, may result in higher fuel consumption in the engine and also in the use of more crude oil in the manufacture of the petrol. There is therefore a complex inter-relationship between total energy consumption, economics, petrol quality, engine design and emission control.

The progressive reduction of lead in petrol results in a loss of octane number which can be made good by more intensive refining. However, this more severe refining consumes more energy. Figure 3 illustrates the relationship between refinery fuel consumption and lead content; reducing lead from 0.15 g l^{-1} to zero results in either a loss of 3 RON or an energy debit, in terms of refinery fuel, of between 2 and 5% of the petrol produced depending on the level of RON aimed at. Refinery energy consumption increases with increasing RON number.

Independently, it is possible to assess how vehicle petrol consumption varies with compression ratio and consequently octane requirement. Although there is in practice a significant variation in the consumption response of different engines to a change of RON, a reduction of one RON number increases fuel use by around 1%. Vehicle energy consumption decreases with increasing RON number for a fixed mileage.

By combining the total energy needed for both the refinery and the vehicle fleet at each RON number in terms of crude oil, it is possible to derive the optimum octane number. This optimum is at the point where the energy requirement is minimum.

Figure 4. Optimum crude oil use (*a*) and investment costs (*b*) for unleaded petrol.

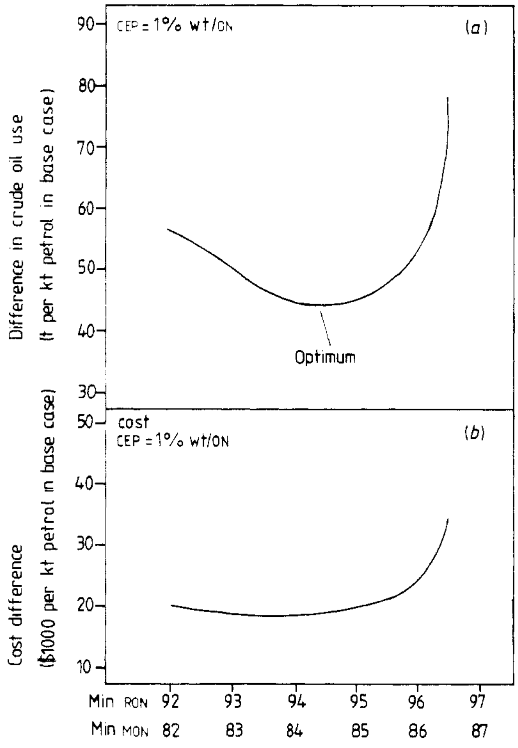

Figure 4 was developed during the 1984 studies and shows an octane optimum of 94.5 RON for the overall energy position.

Following a similar optimisation process for the composite investment costs of the oil and motor industries a much flatter curve was derived (see figure 4(*b*)) with broadly similar costs between 93 and 95 RON.

Following these studies the EEC decided that the octane of the unleaded petrol which had to be made available should be fixed at 95 RON minimum and was to be termed 'premium' unleaded grade. This is the grade which must be provided from October 1989 but countries are free to allow another, lower-octane grade to be marketed as well if they wish.

Production of unleaded petrol

Octane quality can be enhanced by refining operations which increase the proportion of aromatic compounds. Catalytic cracking, reforming and isomerisation are amongst those refinery processes which selectively produce high proportions of hydrocarbons having naturally high octane numbers. These processes have been used increasingly to replace octane quality lost as the lead content has been progressively reduced, and also to convert unwanted fuel oil produced during primary distillation into transport fuels. Each step down to the current UK lead level of 0.15 g l^{-1} has been achieved without reduction of the specified octane level of petrol by more severe refining using such processes. The final step to unleaded grade will be accompanied by some loss of octane and, consequently, some reduction in compression ratio in engines.

As mentioned earlier, certain additives, such as alcohols and other oxygenate compounds, can contribute to improved octane. Availability of these oxygenates is still low but, to the extent that they are available, they can at least partially replace lead. Uncontrolled addition of oxygenates could lead to problems in vehicle operation and another EEC Directive has been put in place to set appropriate limits on oxygenate concentrations in petrol throughout Europe.

The Directive includes a requirement that benzene must not exceed 5%. This is because benzene content may increase along with other aromatics and the EEC Commission has recognised that changes in petrol composition to compensate for loss of lead additives must not entail the emission of other pollutants. A maximum permitted lead level is also fixed by the Directive in order to protect the catalyst in those vehicles fitted with converters

The shift to unleaded petrol has necessitated major investment by both the refining and the motor industries. In the UK the final reduction from 0.15 g l^{-1} to unleaded will cost the refining industry around £200m in capital terms and the retooling of vehicles for modified valve and compression ratios will amount to a similar figure. Additionally, energy consumption in refining and in vehicles will increase by around 3%, worth some £50m per year at an $18 barrel. In Europe the total investment in both industries for eliminating lead from petrol from a base of 0.4 g l^{-1} (a level which still applies in France, Italy and Spain) has been put at between $\$2 \times 10^9$ and $\$3 \times 10^9$.

Beginning the European transition

Unleaded petrol has been on sale in Europe since 1985. Though initially much was low-octane material of around 91 RON, the premium 95 RON is becoming increasingly available. Germany, Austria and Switzerland were the first countries to sell unleaded petrol and also offered price-reduction incentives to motorists purchasing cars fitted with catalytic converters. Sweden and Norway have been close behind with similar policies.

Because of the need to provide refuelling facilities for motorists driving cars fitted with catalytic converters, 'tourist' networks of filling stations offering unleaded petrol have become established in all European countries. In addition, because the Directive urges Member States to encourage 'the widest possible use of unleaded petrol in all existing vehicles capable of running on such fuel' many countries have introduced lower duty rates on unleaded grades than on leaded in order to stimulate demand.

In 1986 unleaded petrol accounted for around 2% of all European petrol sales. The percentage will continue to grow and uptake may be expected to accelerate once the mandatory date of 1st October 1989 is reached. However, leaded petrol will continue to be available side by side with unleaded until into the early years of the next century by when lead additives in petrol will have achieved a span of three score years and ten.

Further reading

Assessment of the Energy Balances and Economic Consequences of the Reduction and Elimination of Lead in Gasoline 1983 Report no 11/83R of CONCAWE (Oil Companies' European Organisation for Environmental and Health Protection)

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Lead and Health 1980 DHSS (Lawther) Working Party report (London: HMSO)

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Lead in the Environment 1983 Ninth Report of Royal Commission on Environmental Pollution (Cmnd 8852)