Effects of Oil Additives on Autocatalysts

Since the introduction of autocatalysts in the 1970s, the effects of sulfated ash, phosphorus and sulfur (SAPS) in engine oils on catalyst performance and durability have been continuously monitored. However, the deterioration in emissions attributable to the oil can be difficult to quantify. Sulfated ash in oils derives from the salts of alkali and alkaline earth metal detergent additives. These help to keep engine surfaces free of combustion deposits. There is also a contribution from the ZDDP (zinc dialkyldithiophosphate) antiwear, antioxidant agents in the oil (1).

The chief concern over ash levels in oil is that in diesel-engined vehicles non-combustible ash deposits become trapped in the channels of diesel particulate filters. These cause an increase in the back pressure over the filter, which can potentially affect engine performance. The sulfur in engine oils originates from the additive components and the oil base stock. As the amount of sulfur in fuel is being reduced to very low levels there is concern that sulfur in the oil will become more important and it remains a consideration for NOx-traps fitted to lean-burn engines. Oil sulfur has also been shown to contribute to particulate matter (PM) in heavy-duty diesel engines fitted with oxidation catalysts, resulting in failure to meet defined emission limits in some instances.

Many studies have been published examining the effects on gasoline catalyst activity of phosphorus level (from ZDDP) and detergent components, such as calcium, in the engine oils, but there is less published work for diesel catalysts. If compounds such as zinc pyrophosphates (from ZDDP) are deposited on a catalyst they can form a diffusion barrier preventing exhaust gas molecules reaching active sites. The studies were often performed with bench engines and extended ageing was simulated. This was done by passing oil through the engine in a short time period (for example, 100 hours) equivalent to the amount which would have been consumed in 80,000 km of road driving (ageing) by a vehicle. The fuel was doped with lubricating oil and the mixture combusted in the engine. In some cases the engine inlet valve seals were removed to increase oil consumption. The studies generally showed that phosphorus reduced catalyst activity and that increased phosphorus levels enhanced deactivation. However, increasing the ratio of alkaline earth metal to phosphorus decreased the quantity of phosphorus deposited on the catalyst.

Concerns have been expressed that such studies do not simulate real world deactivation because of the accelerated oil consumption, operation at fixed engine speed/load conditions and non-representative means of oil consumption. However, there are further aspects that influence vehicle fleet studies, such as thermal deactivation, shifts in oxygen response characteristics and other engine calibration factors over time, as well as differences in the levels of phosphorus deposition on the catalyst. A few of the vehicle trial results have been published and all conclude that although the vehicles have invariably met the emission limits for which they were designed, the non-destructive removal of phosphorus noticeably improves catalyst performance, especially light-off.

With severer emission limits under discussion, together with extended durability requirements, the impact of SAPS on catalysts and filters is increasing the need to develop low SAPS oils that do not compromise engine wear or oil consumption. The oil additives industry is actively pursuing this, and may ultimately require the availability of ashless, phosphorus- and/or sulfur-free components and the use of higher quality, low-sulfur base stocks, all of which adds complexity and cost to the formulations.

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Reference

1 A. J. J. Wilkins, *Platinum Metals Rev.*, 2003, **47**, (3), 140

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