APPENDIX I

Diesel Engine Lubricating Oils

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I. Introduction

The significance of the sulfur contribution from lubricating oils to engine exhaust emissions becomes apparent with reducing diesel fuel sulfur to 15 ppm. Diesel fuel with 15 ppm sulfur enables the use of control technologies to meet the new 2007 model year emissions standards for heavy-duty diesel (HDD) vehicles.[1, 2] The sulfur contribution from lubricating oils has been estimated to be up to 7 ppm in the exhaust thus increasing sulfur by about 50%.[3, 4] This increase in sulfur can significantly decrease the effectiveness of exhaust after treatment devices for reducing NOx and particulate matter (PM).

In addition to sulfur, lubricating oils contain other compounds and material that are possible sources of after treatment degradation. These compounds, containing calcium, phosphorus, zinc, magnesium and other metals, are found in the lubricating oil additives.[5, 6] Also, the inorganic components in these compounds, being incombustible, contribute to the ash content of the oil. Ash concentrations in lubricating oils can range from 1 to 1.3% of the finished product.[7]

II. Impact of Sulfur on After Treatment Devices

A. NOx Adsorbers

NOx adsorbers that are being developed for treating diesel exhaust are extremely sensitive to sulfur poisoning due to the similarity in chemical properties of sulfur oxide (SO_2) and nitrogen oxide. Sulfur oxide in the exhaust can react with the adsorptive media to form stable sulfates, thus reducing the adsorbing capabilities of the system.[1, 8] Increasing sulfur concentration in the exhaust from 15 ppm to 22 ppm due to contribution from the lubricating oils can reduce the effectiveness of the NOx adsorber performance by 20 to 30% after 150 hours of operation, based on results from the Diesel Emission Control – Sulfur Effects Program.[8]

B. Catalyzed Diesel Particulate Filters

Sulfur can also inhibit the effectiveness of catalyzed diesel particulate filters (CDPF) through several mechanisms. The best understood mechanism is the catalytic oxidation of exhaust SO_2 to SO_3. SO_3 combines with water to produce sulfuric acid that adds to the PM.[1] Increasing sulfur concentration in the exhaust from 15 ppm to 22 ppm due to contribution from the lubricating oils can result in approximately a 35% increase in PM.[2, 9] Additionally, the sulfur can reduce the regeneration capability of the filter by two different mechanisms depending on the type of catalyzed diesel particulate filter involved.

In a catalytic particulate filter, the catalyst is applied directly to the filter material, whereas in a continuously regenerating diesel particulate filter, the catalyst is upstream of the filter. In the case of a catalytic particulate filter, SO_2 acts to increase the minimum temperature requirement for the filter to properly regenerate itself. This temperature requirement is referred to as the balance point temperature where the rate of combustion of particulate caught in the filter exceeds the rate of particulate deposition. If the temperature of the exhaust gas is lower than the balance point temperature, then PM accumulates in the filter, thus the filter is unable to fully regenerate itself. The continuously regenerating diesel particulate filter relies on a strong oxidant, NO_2, to oxidize the PM caught in the trap. A platinum catalyst upstream of the filter oxidizes NO to

NO_2. Sulfur oxides poison the catalyst by occupying catalyst sites. Thus, the sulfur inhibits the formation of NO_2,[1] lowering the PM oxidation rate and allowing PM accumulation. PM accumulation can lead to reduced engine performance, due to the increased pressure drop of the trap, and ultimately failure of the trap.[2]

III. Impact of Ash on After Treatment Devices

Inorganic compounds from lubricating oil additives are oxidized in the combustion chamber and generate metal oxide ash particles. The particles collect on the diesel particulate filter and are not removed by filter regeneration because they are not combustible. As the ash particles accumulate, they reduce the porosity of the filter. This reduced porosity, or filter blockage, increases the back pressure to the engine which reduces engine efficiency. The increased pressure drop across the filter can also lead to the structural failure of the filter. Periodically the ash must be removed by mechanically cleaning the filter with compressed air or water.

IV. Lubricant Formulation

A. Sulfur

Diesel engine lubricating oils are comprised of approximately 80-85% base oil with the remainder made up of performance additives. The sulfur concentration in the base oil, measured in the finished product (base plus additive), can range from essentially zero (synthetic oils) up to 4,000 ppm. The sulfur in the base oil exists as a contaminant and can be reduced by hydrotreating. Performance additives are the major source of sulfur and ash content in lubricating oils. The additives are used to modify or enhance the properties of the base oil and include detergents, dispersants, oxidation and corrosion inhibitors, antioxidants, viscosity modifiers, antiwear agents, and pour point depressants. Sulfur-containing additives include the anti-wear agents, detergents, corrosion inhibitors, friction modifiers, and anti-oxidants. The sulfur in these additives, in the form of sulfonates, phenol sulfide salts and thiophosphonates, are vital to the performance of the additives.[3, 10] Anti-wear agents are the main source of sulfur in the additives and are primarily zinc dithiopshosphates or ZDDP. While there are non-sulfur containing additives, substitutes for most sulfur containing additives have not been developed.

The sulfur content of current engine lubricating oils can range from 2,500 ppm to as high as 8,000 ppm by weight.[4] Various estimates of the lubricating oil sulfur contribution to the exhaust have been made and vary from nearly zero up to 7 ppm.[4]

The worst case estimate of 7 ppm assumed nominal HDD vehicle fuel and oil consumption rates of 6 miles/gallon and 1 quart per 2,000 miles respectively. Also assumed was a high lubricating oil sulfur content of 8,000 ppm and that all of the lubricating oil sulfur reaches the exhaust stream.[3, 4] This assumption is conservative considering that under normal operation, only a small percentage of the oil consumed by open crankcase ventilation heavy duty diesel engines travels past piston rings and valves and burns in the combustion chamber. The remainder of the consumed oil is lost through evaporation by being emitted through the crankcase ventilation tube and is not combusted. In closed crankcase ventilation systems the evaporated oil is recovered.[4]

The United States Environmental Protection Agency (EPA) estimated a 1 ppm sulfur contribution from the lubricating oil to the exhaust based on the Phase I HD emission standards for PM.[4] They assumed that all of the consumed lubricating oil in the exhaust is emitted as diesel PM and that it makes up 30% of the PM. They set the PM emission rate at the 0.1 g/bhp-hr PM emission rate for all classes of heavy duty diesel vehicles, allowing them to calculate a lubricating oil consumption rate. They combined these assumptions with a nominal specific fuel consumption of 136 g/bhp-hr and lubricating oil fuel sulfur concentration of 5,000 ppm to estimate a lubricating oil sulfur contribution to the exhaust of 1 ppm.

The EPA also analyzed sulfate PM results from the Diesel Emission Control – Sulfur Effects (DECSE) Program to evaluate the contribution of lubricating oil to sulfur in the exhaust. The DECSE used fuel with sulfur levels of 3 ppm and 30 ppm and lubricating oil with a sulfur content of approximately 3,500 ppm. They extrapolated the data to zero fuel sulfur to estimate the sulfur contribution of the lubricating oil and determined that the contribution was not measurable. They concluded from this evaluation that although some amounts of sulfur from lubricating oils are present in the exhaust, it is not likely a significant fraction of the total sulfur, even at fuel sulfur levels of 15 ppm.[4]

B. Ash

Ash content in lubricating oil controls the acidification rate of the oil (maintains total base number, or TBN control). The acidification rate of the oil is due largely to the sulfur content of the fuel and the sulfuric acid that it forms. Without the ability to control acidification of the lubricating oil, engine wear increases significantly. However the proposed lowering of sulfur in diesel fuel will require less of a need for TBN control or less ash content in the lubricating oils. Consequently, manufacturers are investigating with the lubricant industry the potential of lower ash oils for use in engines operated on low sulfur diesel fuel and equipped with particulate traps. However, manufacturers are concerned about potential use of possible low ash oils in fleets using high sulfur diesel if the proposed 15 ppm sulfur requirements are phased in over time.[11] This should not be a concern for California since the proposed 15 ppm sulfur requirement will not be phased in.

V. Research Efforts

There are two major research efforts seeking data on the impact of lubricating oils and lubricant additives on emissions and emission control devises. These efforts are not restricted to sulfur effects but will investigate the different chemical compounds that are found in both the lubricant base stock and additives. The lubricants work group of the Advanced Petroleum-Based Fuels Program Diesel Emission Control - Sulfur Effects (APBF-DECSE) program directs one of these efforts. The other effort has been initiated by a private research consortium formed by the Southwest Research Institute (SwRI). This consortium, called Diesel Aftertreatment Sensitivity to Lubricant/Non-Thermal Catalyst Deactivation (DASL/N-TCD), intends to compliment the research directed by the APBF-DEC lubricants workgroup.

A. APBF Program

The APBF Program is a joint effort of the U.S. Department of Energy's Office of Heavy Vehicle Technologies and Office of Advanced Automotive Technologies. This program is focused on meeting emissions standards and improving compression ignition (CI) efficiency. The lubricants work group of the APBF-DEC program has defined a two-phase plan for testing. The objective of the testing is to determine which, if any, lubricating oil-derived emissions components are detrimental to the performance or the durability of diesel emission control devices.[12] The investigation includes assessing the contribution of lubricating oils to both the soluble and insoluble fraction of the PM, approaches to reduce the contribution of lubricating oils to PM through both reduced oil consumption and determining oils less likely to produce PM, and the impacts of fuel changes on engine lubricating oil requirements.[13]

The first phase of the tests, characterizing the effect of lubricating oils on engine out emissions from a multi-cylinder engine without a catalyst, has been completed.[14,15] Tests were performed on four different oil basestocks and approximately 12 additive packages containing various levels of ash, sulfur, phosphorous, selected metals and other key components.[12] Emissions measurements included PM, total and/or non-methane hydrocarbons, carbon monoxide, oxides of nitrogen, and SO_2. The PM analysis included total PM mass, soluble organic fraction including fuel/lubricant contribution, sulfate fraction, polycyclic aromatic hydrocarbons (PAH) content, and metals. Engine oil consumption was determined for each test-operating mode and checked routinely throughout the test program.[14]

Preliminary results from Part 1 have shown that emissions of sulfur, zinc, phosphorous and calcium are proportional to their concentrations in the oils, as illustrated for sulfur and zinc in Figure 1 and Figure 2 respectively, below. These figures, which give the measured sulfur and zinc emissions as a function of calculated emissions, based on oil consumption and oil sulfur and zinc levels, show linear relationships. However, the unexpectedly high sulfur emissions for some oil formulations, shown in Figure 1, indicate that there may be a formulation dependency for some formulations. For these oils, the emissions were several times higher than expected based on the oil consumption and oil sulfur content. This indicates that simple constraints on content may not be sufficient. Another preliminary conclusion is that emissions of zinc and calcium are lower than expected from measured oil consumption. Figure 2, which shows zinc emissions, illustrates, that zinc emissions were approximately 40% of what would be expected. One possible explanation is that the zinc, derived from the anti-wear additives, is surface active and the missing zinc is possibly lost to a surface.

Figure 1 Preliminary APBF-DEC Phase I Test Results: Sulfur Mass Balance[15]

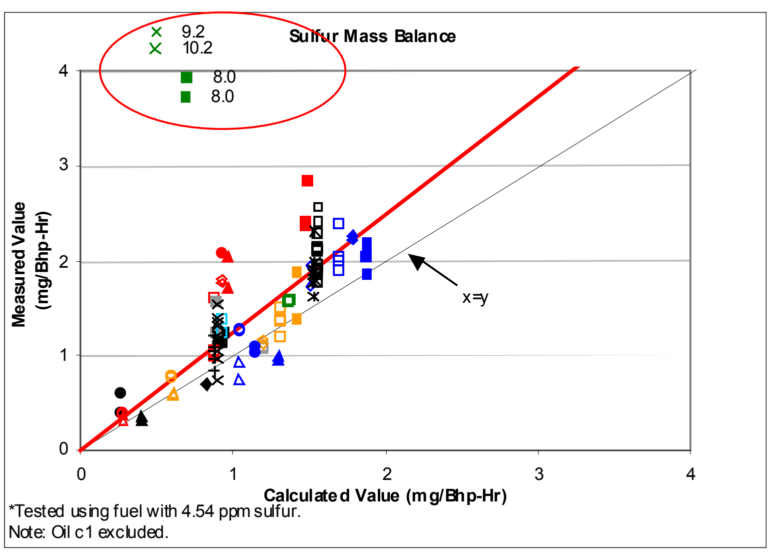
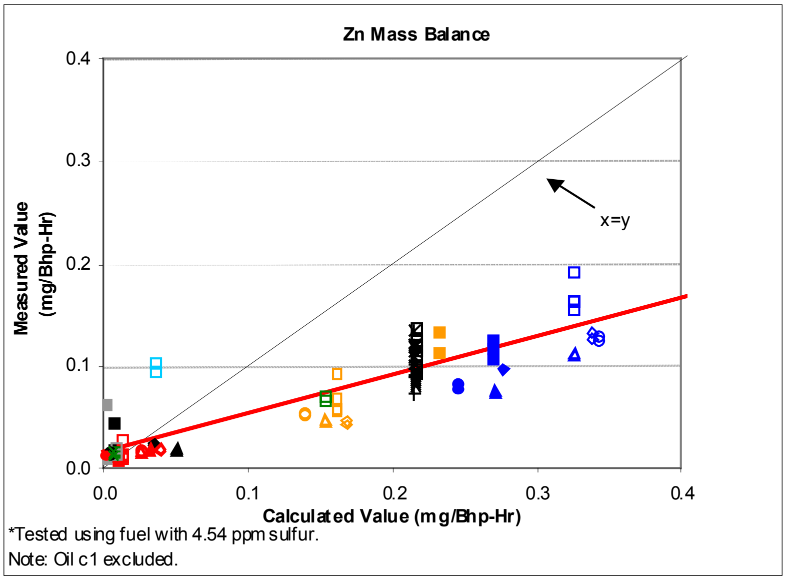


Figure 2 Preliminary APBF-DEC Phase I Test Results: Zinc Mass Balance[15]



The second phase of the program will focus on evaluating the impact of lubricating oil-derived species on the emission control systems. A Cummins 2003 ISB engine with a production EGR system is expected to be used for this Phase II testing. It is expected that the project will focus on impacts on NO_x adsorber catalyst systems.

B. DASL Consortium

The DASL/N-TCD consortium was formed from two previously separate consortiums. The two parts of the new consortium are concerned with similar subjects but with different emphases. They were combined into one program due to an apparent reduction in research funding available in the corporate community. The two segments of the new consortium will retain their individual emphasis but share funding, allowing work to begin in both areas while reducing overall membership costs.

The DASL segment of the consortium, formulated with the intention of complimenting the APBF-DEC lubricants program, intends to initiate their investigation with lubricating oil and additive effects on catalyzed PM filters. The PM filter will normally be upstream of any additional after treatment devices, such as a NOx adsorber or a selective catalytic reduction (SCR) system. The importance of investigating the effect of ash on these downstream aftertreatment devices is reduced since the PM filter will prevent lubricating oil ash from reaching them. However, since sulfur can pass through the PM filter, it will still be an issue with these other devices.[16] A possible track for their study may be to accelerate "aging" of the emissions control system with extra-high doses of the lubricating oil components, then compare results with lubricating oils using normal additive concentrations. The results are expected to give engine and emission control system manufacturers insight into the magnitude of the potential problems and help oil additive/component makers in formulating future additive packages.[17]

VI. ASTM Proposed Engine Oil Category

An ASTM Heavy Duty Engine Oil Classification Panel has been formed to develop a new engine oil classification, called Proposed Category 10, for use with advanced after treatment technology. This effort will be exploring the performance of oil formulations with reduced sulfur, phosphorous and sulfated ash. Oil licensing for this new classification is scheduled for mid 2006.

VII. Future Activities

Staff will continue to gather information on the effect of the sulfur and ash content of lubricating oils on emissions and the performance of the emission control system. Staff will follow the APBF-DEC lubricants work group test program that will provide data on the emissions impact of different lubricating oil formulations on aftertreatment devices. Staff will investigate the development of non-sulfur containing additive packages, the effect of removing sulfur from the lubricating oil on oil performance, and the effect of other compounds in non-sulfur containing replacement additives on aftertreatment devices.

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