TECH BEAT

Dr. Neil Canter / Contributing Editor

SPECIAL REPORT

Use of antioxidants in automotive lubricants

The lubricants industry continues exploring alternatives to ZDDPs. Our experts comment on the newest additive technologies and why the future remains an uncertain road.

KEY CONCEPTS:

- Antioxidants function by interrupting the three-step oxidation process either through reaction with free radicals or decomposing peroxide radicals.
- The reduction in the use of ZDDP means that the automotive lubricant industry must incorporate alternatives which are mainly ashless antioxidants.
- The rising use of biofuels also is increasing the need to improve the antioxidation performance of automotive lubricants, particularly when biodiesel is used.
- Developments in automotive engine technology and automotive lubricant specifications are two factors that will influence the demand for new antioxidant chemistries in the future.

More attention has been placed on the role that antioxidants are playing in extending the life of automotive lubricants and reducing vehicular emissions. In September 2006, TLT delved into the current additive challenges faced in meeting new automotive engine specifications.[1] One of the key issues was how to replace the multifunctional additive class known as zinc dialkyldithiophosphates (ZDDPs).

Besides functioning as an antiwear additive, ZDDPs also are very effective antioxidants. The reduced use of ZDDPs in automotive lubricants is placing more emphasis on the need to utilize other technologies to fill the gap.

Recently we interviewed representatives from the leading suppliers of automotive lubricant additives and antioxidants to obtain insight on how useful the current types of antioxidants are in supplementing the performance of ZDDPs in automotive lubricants.

Antioxidants function in two different fashions. To provide insight on the types of antioxidants available for use in automotive lubricants, it is important to better understand how they function to extend the life of a fluid.

Figure 1 | **Antioxidants are required in the engine oil poured into your vehicle to maintain optimal performance over an extended operating life.** *(Courtesy of Ciba Corp.)*

ANTIOXIDANT TYPES

Once poured into the engine, as shown in Figure 1, an automotive lubricant fluid undergoes oxidation in air due to a number of factors including heat, severe pressure and the presence of metal. This re-

sults in the decomposition of lubricant basestocks and additives that can severely limit the operating life and effectiveness of the fluid.

Oxidation occurs through a three-step process known as initiation, propagation and termination. In the initiation stage, one of the external factors causes a free radical (or unpaired electron) to be generated in one of the organic species (R) that is part of the lubricant. This process involves breaking a bond with a hydrogen atom and is shown in equation (1).

$$RH \rightarrow R\cdot + H\cdot \qquad (1)$$

The free radical is a highly reactive species that can react with oxygen to form a peroxide radical that can generate additional radicals through reaction with more components in the lubricant. This step shown in equation (2) is known as propagation and leads to further decomposition of the lubricant.

$$R\cdot + O_2 \rightarrow ROO\cdot + RH \rightarrow ROOH + R\cdot \qquad (2)$$

Eventually two of the radical species combine and form a stable compound. This is designated as the termination step because it removes free radicals from the system, as shown in equation (3).

$$R\cdot + R'\cdot \rightarrow R\text{-}R' \qquad (3)$$

If unchecked, the oxidation process can eventually lead to the total breakdown of the components in the lubricant. Some free radicals will be consumed during termination, but more will be formed during propagation as long as the external conditions exist to promote this process.

Antioxidants react with free radicals to form stable species and disrupt the degradation process shown above. There are two main types known as primary and secondary antioxidants. The former inhibits oxidation by reacting with chain propagating free radicals to form stable molecules. The reaction showing how free radicals are eliminated by primary antioxidants is shown in equation (4). The "antioxidant" moiety is a stabilized free radical that does not react with any other species.

$$R\cdot + \text{antioxidant} \rightarrow RH + \text{antioxidant}\cdot \qquad (4)$$

Secondary antioxidants are the other type, and they act by specifically decomposing peroxide radicals. In some cases, antioxidants can be regenerated as part of this process.

Examples of primary antioxidants are hindered phenols and secondary arylamines (such as alkylated diphenylamines). Both generate stable free radicals that are nonreactive. Included in the secondary antioxidant category are phosphites and a variety of sulfur compounds such as thioesters.

ZDDP

All of the respondents contacted for this study indicate that ZDDP is a very effective antioxidant. STLE-member Vince Gatto, new business development manager for Albemarle Corp. in Baton Rouge, La., says, "We determined in a recent study using the TEOST MHT (Thermo-oxidation Engine Oil Simulation Test; Moderate High Temperature Procedure – ASTM D7097) that a 50% reduction in ZDDP concentration from 1,000 to 500 ppm phosphorus leads approximately to a doubling of the TEOST MHT-4 total rod deposits (*see Figure 2*).[2]"

Greg Guinther, senior advisor-engine oils R&D for Afton Chemical Corp. in Richmond, Va., says, "ZDDP is an

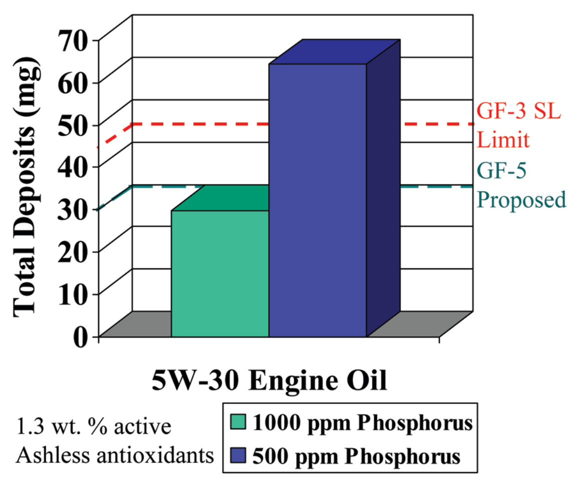

Figure 2 | **The effectiveness of ZDDP as an antioxidant is demonstrated by the nearly doubling of TEOST MHT-4 total rod deposits when the level of ZDDP is reduced by 50%.** *(Courtesy of Albemarle Corp.)*

extremely potent, cost-effective antioxidant and may be deemed as essential in today's automotive lubricants."

Robert S. Johnson, global crankcase technology manager for Infineum Corp. in Linden, N.J., explains, "Unfortunately, the phosphorus in ZDDP has been implicated in adversely affecting the efficiency of catalytic convertors present in modern, environmentally friendly vehicles. This limits the amount of ZDDP that can be used in oil and, therefore, restricts its contribution to the overall oxidation performance."

Mayur Shah, global engine oil additives technology manager for The Lubrizol Corp. in Wickliffe, Ohio, indicates that ZDDP impacts the performance of the three-way catalyst (TWC) used in automotive catalytic converters. He says, "For the new passenger car motor oil (PCMO) specification, GF-5, a new performance requirement for protection of the TWC, has been added. Picking the right ZDDP technology will be critical in meeting this new requirement and maintaining performance."

A phosphorus retention test known as the Sequence IIIGB is being developed for GF-5 to determine the impact of phosphorus on the vehicle's emission system.

STLE-member Dr. David Chasan, head global application and technical center for Ciba Corp. in Tarrytown, N.Y., stressed that the reason for ZDDP's declining use is limits on SAPS (sulfated ash, phosphorus and sulfur). He says, "ZDDP is very effective, but with the current SAPS limits and emission systems requirements, the use of ZDDP will continue to be limited—and these limits are under constant review."

How does ZDDP function as an antioxidant? STLE-member, Dr. Ashok Cholli, founder of Polnox Corp. in Chelmsford, Mass., says, "ZDDP is effective in combating peroxy radicals and hydroperoxides. It does not perform like a primary antioxidant to inhibit the propagation of energetic free alkyl radicals."

The phosphorus content in passenger car motor oils has dropped from 0.12% in GF-1 to 0.08% in GF-4. Current thinking for GF-5 is that the phosphorus content will range from 0.06% to 0.08%. With the drop in ZDDP usage, the lubricant industry has needed to turn to other alternatives to ensure that the antioxidant properties are maintained.

Alex Boffa, staff chemist for Chevron Oronite Co. in Richmond, Calif., says, "ZDDP is a very effective antioxidant and its reduction has driven the need for alternatives. The biggest increase in use is attributed to alkylated diphenylamines, but metal-containing antioxidants and hindered phenolics are also being used at higher treat rates. More stringent performance tests such as the industry's move from the Sequence IIIE to the Sequence IIIG are also driving the increasing use of supplemental antioxidants."

Deposits from a failing and passing piston that went through the Sequence IIIG test are shown in Figure 3.

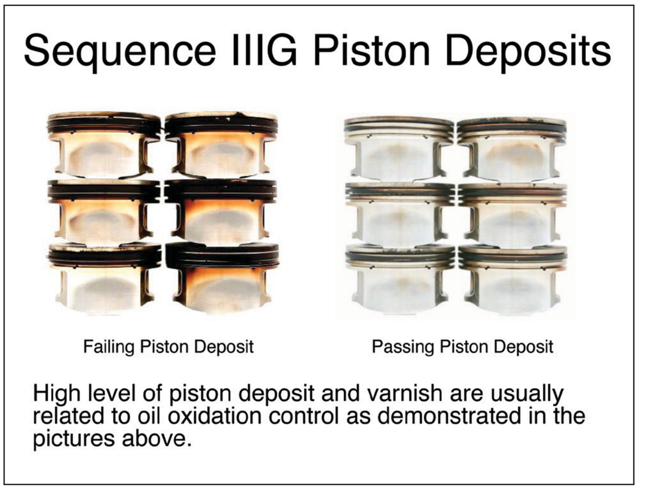

Figure 3 | **The Sequence IIIG test measures deposits left on pistons under high temperature conditions. A failing piston deposit is seen on the left while a passing deposit is shown on the right.** *(Courtesy of Infineum Corp.)*

Shah comments, "Formulating is a balancing act. When you reduce the ZDDP, you need to compensate for the impact of that reduction. Accordingly, regulators need to be cautious when making changes; they need to take into account all the impacts and ramifications of restricting the use of a multifunctional component such as ZDDP."

Gatto indicates that the reduction in ZDDP content forced formulators to rebalance engine oils in favor of more ashless antioxidants such as alkylated diphenylamines and hindered phenolics. He says, "A GF-4 PCMO contains from 30% to 50% more ashless antioxidant compared to a GF-1 PCMO."

Work carried out by Gatto shows that the loss of TEOST MHT-4 deposit control can be corrected through the addition of an equal percentage of ashless antioxidant. He says, "A reduction in ZDDP of 0.6% by weight would require approximately 0.6% by weight of ashless antioxidant."

Johnson maintains that the reduction in the phosphorus level accompanying each successive engine oil specification has not resulted in a corresponding reduction in the oxidation performance of the oils. He says, "Indeed, GF-4 lubricants provide several-fold greater oxidation control than their GF-1 counterparts. The reason is quite simple: Each successive engine oil category has not only imposed a tighter restriction on the amount of phosphorus in the oil than the previous category but also has required a higher level of oxidation performance."

A similar trend has been seen with heavy-duty diesel (HDD) oils, as covered by the new API CJ-4 specification. Guinther says, "CJ-4 oils require increased antioxidant performance due to the reduction of ZDDP."

Johnson believes CJ-4 not only addresses oxidation concerns but encompasses most other parameters used to evaluate heavy-duty diesel engine performance. He says, "API CJ-4 products are the most advanced heavy-duty diesel engine oils within the API specification system. Combined with Ultra Low Sulfur Diesel (ULSD) fuel, they represent increased engine protection in essentially every performance metric, including oxidation performance. SAPS restrictions only limit the types and amounts of additives that can be used to formulate new products but without compromising their engine performance."

Gatto sees the issues of dealing with ZDDP reduction to be more challenging in HDD oils than PCMOs. SAPS reduction also has forced the formulator to lower the levels of sulfurized additives that act as secondary antioxidants and corrosion inhibitors. He adds, "Solving the antioxidant problem with HDD oils is more difficult because of greater sensitivity to varnish formation and corrosion. This means that certain types of alkylated diphenylamines and hindered phenolics have limited effectiveness.

"Simply adding more ashless antioxidants may not work in HDD oils," he adds. "The solution involves a complete rebalancing of the formulation plus a rebalancing of the existing antioxidant ratios. Modifications possibly need to be made to other additives in the formulation such as detergents and dispersants."

Gatto feels that the antioxidant ratios that need to be adjusted include not just the ratio of alkylated diphenylamines to hindered phenolics but also the ratio of ZDDP to both ashless antioxidants.

OTHER FACTORS

Changes in the design of automotive engines, longer lubricant drain intervals, the use of exhaust gas recirculation (EGR) in heavy-duty diesel engines and an upgrade to better quality base oils have all contributed to challenging formulators to maintain the antioxidant properties of automotive lubricants.

Shah says, "Engine design changes resulting in increased thermal stress, exhaust gas recirculation and fuel dilution are some of the factors that have increased the demand for oxidative stability and the demand for antioxidants."

Johnson shares a similar view emphasizing that passenger cars are running hotter because of the move to smaller, more powerful engines. He explains, "The aerodynamic considerations in vehicle designs have lead to smaller engine compartments, more crowding under the hood and, thus, reduced air flow around the engine block. Another important factor is the consumer preference for longer drain intervals. All of these have combined to increase the level of thermal and oxidative stresses on engine oils."

Use of smaller engines is also being accelerated by the need for vehicles with greater fuel economy. The rapid increase in fuel pricing is providing added motivation for this trend.

Johnson also sees EGR as potentially adding to the burden on oxidation control in HDD engines. He says, "The use of EGR to reduce NO_X emissions has resulted in increased levels of partially burned fuel in the oil sump, which adds to oxidation stresses on the oil. In recent times, the use of externally cooled EGR in certain engines has lead to corrosive acidic species from the exhaust gases being recycled back to the engine. This puts added burden on engine oils to suppress the generation of acids produced via the oxidation processes."

Boffa comments, "The reduction of ZDDP's sulfur contribution is the biggest factor in reducing antioxidant properties in HDD oils. I agree that EGR also is another driver boosting the greater need for other antioxidant chemistries."

Gatto stressed that a proposed reduction in the Total Rod Deposit limit for the TEOST MHT will make it more difficult to maintain the antioxidant characteristics of the automotive lubricant. He says, "The proposed reduction in the TEOST MHT Total Rod Deposit limit from 45 milligrams (mg) in GF-3 to 30 mg in GF-5 puts greater demands on additives to control deposits. As a result, even greater amounts of ashless antioxidants will be needed. It appears future reductions in phosphorus levels may make the TEOST MHT the test that determines ashless antioxidant treat levels."

One factor that has improved the oxidative stability of automotive lubricants is the greater use of Group II and Group III mineral oil basestocks. Guinther says, "Base oil quality is evolutionary and has greatly improved since GF-1. With this improvement has come increased oxidation stability,"

Gatto believes there is a detrimental aspect to the greater use of Group II and Group III base oils because of added concerns about deposit formation in certain engine tests. He says, "Group II and Group III base oils are more oxidatively stable but tend to form deposits more readily due to their poor solvent properties. Thus, the overall effect over time has been more oxidatively stable lubricants that are more prone to deposit formation."

Besides base oil, Johnson points out that the use of one other additive chemistry has made a positive contribution to antioxidation properties. He says, "Certain detergent technologies such as salicylates, typically used in certain top tier lubricants, have also contributed to the antioxidant performance of automotive lubricants."

A second additive type, corrosion inhibitors, has also proven to be beneficial from the standpoint of antioxidation. Chasan says, "Industry continues to use standard antioxidant technology at higher treat levels to cope with oxidation problems and are reluctant to adopt new antioxidants that often are higher priced. However, a trend to use multimetal corrosion inhibitors to prevent corrosion which can adversely affect oxidation is emerging. This has the added positive effect of increasing the antioxidation properties of automotive lubricants."

BIOFUELS

The rising cost of petroleum-based fuel is spurring growth in the demand of fuels such as ethanol and biodiesel from natural sources. Double-digit growth is anticipated on an annual basis worldwide at least through 2011.

The lubricant industry has been evaluating the impact of biofuel and blends of biofuel and petroleum fuel on the automotive lubricant. Boffa sees a greater need for antioxidants if biodiesel is used as compared to ethanol. He says, "We found that ethanol does not impact the oxidation of the automotive lubricant. In contrast, the high unsaturated content of biodiesel leads to more severe oxidation, particularly if the source of the biodiesel is soybean oil."

Shah agrees. "We have not seen an adverse effect of ethanol/gasoline blends on passenger car lubricant oxidative stability," he says. "For diesel applications—based on certain operating conditions—biodiesel accumulates in the sump, which affects several performance parameters, including oxidative stability."

Gatto is concerned that peroxide buildup may be occurring in fuels when ethanol is used. He adds, "One might expect fewer issues with ethanol in gasoline due to the greater oxidative stability of ethanol compared to biodiesel. However, there have been reports of peroxide buildup in oxygenated fuels, so this application also needs to be monitored closely. Antioxidants are very effective at suppressing peroxide buildup."

One of the problems with biodiesel is the high degree of polyunsaturated fatty chains (such as linoleic) in feedstocks such as soybean (primarily used in North America) and high erucic rapeseed oil (used mainly in the EU). These polyunsaturated fatty chains are readily oxidized, leading to an increase in engine deposits.

Guinther concurs, "Biodiesel (B20-20% biodiesel/80% petroleum diesel blend) fuel increases the oxidation of HDD CJ-4 oils in addition to increasing engine deposits."

Johnson agrees that the level of unsaturation in biofuels plays an important role in rendering an automotive lubricant more vulnerable to oxidation. He says, "As biofuel components mix with oil in the engine, the unsaturation points in their backbone become easy targets for oxidation and so increase the oxidation load on the lubricant. Generally speaking, the greater the degree of unsaturation in the fatty acid, the more prone it is to oxidation. However, in real life there are a number of factors that must be considered, making it nearly impossible to generalize.

Gatto believes that the current oxidation test for biodiesels, the Rancimet procedure (EN 14112), is insufficient to truly measure oxidation of these renewable fuels. He says, "The current specifications are set at limits that do not require the use of antioxidants. I believe this is potentially dangerous for the diesel engine. Not enough is known about the effects of different biodiesel sources on lubricant properties and diesel engine requirements."

Test data taken from a modified version of the Pressure Differential Scanning Calorimeter (PDSC) procedure and the Bulk Oxidation GFC (Groupement Francais de Coordination) test indicates that biodiesel prepared from soybean and rapeseed methyl esters display inferior performance.[3] The former showed an increase in the biodiesel content of a fuel blend leads to increased oxidation over a shorter time frame. Fuel blended with 6% biodiesel met the test limit of the latter while 20% blends failed prematurely.

Cholli believes that in the case of biofuels, current antioxidant technology may not be able to handle the problems associated with high levels of polyunsaturated fatty acid chains. He is proposing an alternative macromolecular antioxidant technology that testing has shown to be very effective compared to commercial antioxidants.

Cholli says, "We evaluated a macromolecular antioxidant vs. a commercial antioxidant at concentrations ranging from 0.5% to 2.0% in a biolubricant using the PDSC technique in ASTM D6186. The macromolecular antioxidant displayed 400% superior performance, as shown in the chart in Figure 4."

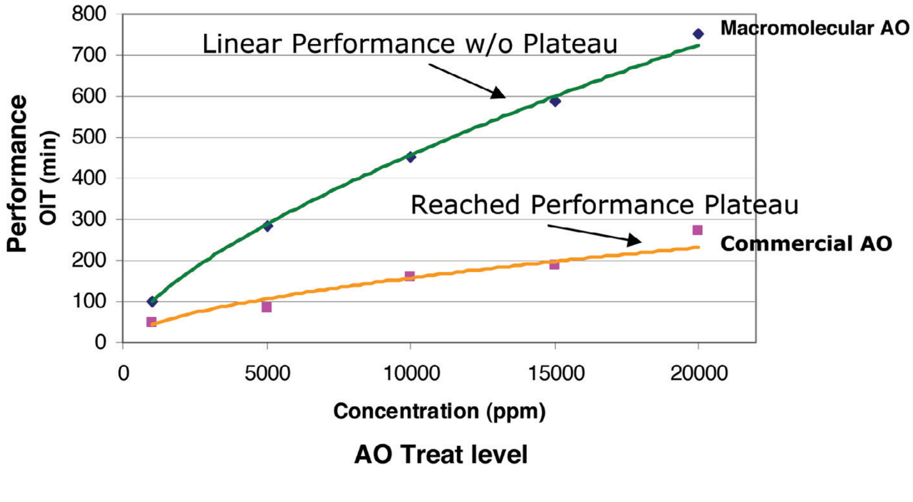

Figure 4 | **The superior performance of a macromolecular antioxidant in the Pressure Differential Scanning Calorimeter (PDSC) test is shown as a function of the oxygen induction time (OIT) and antioxidant concentration.** *(Courtesy of Polnox Corp.)*

Figure 5 | **The Rotary Bomb Oxidation Test is used to measure the effectiveness of antioxidants in lubricants under severe lab conditions.** *(Courtesy of The Lubrizol Corp.)*

Lubricant oxidation testing is carried out under rigorous lab conditions. A figure showing the lab setup for the Rotary Bomb Oxidation Technique is provided in Figure 5.

ASHLESS ANTIOXIDANT TECHNOLOGIES

Several ashless antioxidants are options as an alternative to ZDDPs. Guinther says, "Phenolics, aminics and sulfurous ashless antioxidants have been used in conjunction with ZDDPs in automotive lubricants and will likely continue to be used in GF-5 as improved oxidation control is emphasized. They may not be deemed as cost-effective as ZDDPs."

Johnson adds, "Two well-known ashless antioxidants used in automotive lubricants are aminics and phenolics. Each of these chemistries has its own strengths and weaknesses. In addition, many additive suppliers have their own proprietary antioxidant technologies. When formulation practices vary widely, most modern lubricants contain a combination of several different antioxidants to deliver a balanced performance across the range of oxidation regimes encountered in the engine."

Boffa indicates that synergisms can be found with the alternative antioxidants available to the formulator. He says, "Synergisms can be found, but it is not as simple as adding antioxidants in certain percentages to an automotive lubricant formulation. The oils must be properly formulated to get the most of the antioxidants used."

Gatto predicts that ashless phenolics will play a larger role due to changes in the automotive lubricant specifications. He adds, "There are greater limits on the levels of amine antioxidants that can be used compared to hindered phenolics due to varnish and deposit formation by amines at low temperatures. Thus, as SAP levels continue to drop, it is likely hindered phenolics will play a greater role as antioxidants."

Chasan believes that new ashless TBN (Total Base Number) additives also will provide a benefit. He says, "Besides traditional aminic and phenolic antioxidants, new ashless TBN additives and multimetal corrosion inhibitors can provide value to a reduced SAPS formulation."

All representatives contacted for this article feel that the current ashless antioxidant technologies are more than adequate to be used to replace ZDDPs in the short term as the industry moves to GF-5.

MOLYBDENUM COMPOUNDS

Organomolybdenum compounds have been looked at as alternatives for ZDDPs because they provide multifunctional performance.[4] A recent paper evaluated four molybdenum compounds in a conventional Group I engine oil and in a low phosphorus Group II engine oil.[5] The study shows that organomolybdenum compounds display strong antioxidant behavior in the Group I oil and weaker performance in the Group II oil.

One of the authors, Gatto comments for this article, "While organomolybdenum compounds function as antioxidants, they may not be the most cost-effective option."

Chasan sees limitations with using organomolybdenum compounds. He says, "Molybdenum compounds are not sufficient to carry the entire antioxidant needs of their engine oils on their own and, therefore, need to be supplemented with other antioxidants. Because molybdenum is a metal, there are limits as to how much can be used, similar to limits on ZDDP. Some molybdenum compounds also are quite dark in color, and this also limits the amount which can be used."

A FUZZY FUTURE

No one interviewed has a clear picture about what the antioxidant needs of the industry will look like in 25 years. Shah says, "The need/demand for antioxidants will be driven by equipment technology and specifications. At this time, all one could do is speculate. We are constantly working on developing novel, more efficient additive technologies and will deploy them to meet future performance needs."

Guinther indicates there will be a need for new antioxidant technologies, but the needs will be based on a large number of factors. He says, "Antioxidant needs will hinge on engine technologies, base oil and fuel qualities, service intervals, engine performance levels on cleanliness/wear, fuel economy requirements and environmental concerns."

Gatto sees new, more wear-resistant engine design based on advanced coatings which will enable formulators to move away from ZDDP and potentially all SAPS. The fuel used will contain a high renewable sources content and much less petroleum oil. He says, "The main function of the lubricant may switch to cooling with the additive chemistries different and their treat rates lower than today." But it is a long way off to predict.

Boffa feels that there is likely to be new antioxidant technology. He adds, "Antioxidant technology in 25 years is likely to be different. If the concentration of ZDDP does go down to zero in the future, there is sufficient antioxidant technology currently available to compensate for its absence."

Whatever happens, Johnson provides an optimistic view of how the lubricant industry will handle this challenge. He says, "Given the very turbulent nature of the energy industry, it is hazardous to predict the changes that will take place in fuels, combustion technology and engine hardware in the next 25 years. It is, therefore, difficult to predict the performance requirements that engine oils will be called upon to deliver over that period. We believe that no matter what the challenges, the lubricant industry will be up to the task. A close working relationship with engine manufacturers and a passion for innovation will see us through these exciting and challenging times." TLT

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