New High Performance Synthetic Hydrocarbon Base Stocks

Increased demands in the synthetic lubricant industry have created a need for low cost, high performance alternatives to polyalphaolefins (PAO). A new synthetic base stock was developed, and the feasibility of this technology was demonstrated in a pilot plant scale study. Inexpensive olefin monomers such as ethylene, propylene and butene were copolymerized with single-site catalysts to form liquid copolymers, and the synthesis was carried out in a broad range of temperatures at low pressures with high efficiency. The composition and structure of the liquid products could be tailored to achieve outstanding performance properties. Laboratory and engine test results have proved that this new synthetic fluid performed similarly to the commercial PAO, and could be used as a synthetic base stock in applications requiring premium lubricants.

WEI SONG, I-CHING CHIU, WILLIAM J. HEILMAN, NAM T. NGUYEN and JOHN W. AMSZI
Pennzoil-Quaker State Company
The Woodlands, Texas 77380
and
JAMES C. W. CHIEN
Amherst Polymer Technology
Amherst, Massachusetts 01003

KEY WORDS

Synthetic Lubricants; Hydrocarbons; Materials, Properties and Tribology; Polymeric; Lubricant Degradation/Stability; Oxidation

INTRODUCTION

One of the most important performance requirements for lubricants is their oxidative stability. In the past extensive mechanistic studies have been conducted to understand oxidation reactions of hydrocarbons (Dexter, (1991), Klemchuck, (1985)). It is generally accepted that hydrocarbon materials, such as lubricant base oils, undergo autoxidation when subjected to high temperatures and high shearing stresses. Three reactions, initiation, propagation and termination, have been used to explain this behavior. In the initiation step, as shown in Eq. [1], the alkyl radicals are generated from the hydrocarbon materials by homolytic chain cleavage. In addition, there is always a trace amount of hydroperoxides present in hydrocarbons, which can decompose and generate radicals as well.

Initiation

\[
RH \rightarrow R^\bullet, ROO^\bullet, RO^\bullet, HO^\bullet, \text{ etc.}
\]

[1]

Immediately after the alkyl radicals are generated, they react with molecular oxygen very quickly to form peroxy radicals. This process, shown in Eq. [2], is known as the propagation step and is shown in Eq. [2]. The subsequent reaction between the peroxy radicals and hydrogen atoms of a hydrocarbon chain is much slower, and the reaction rate is very much dependent on the type of hydrogens involved. This step was described in Eq. [3]. Tertiary hydrogens, which react with radicals more than ten times faster than secondary hydrogens; so they are usually considered the weak spots in a molecule since they get are oxidized easily. Once the oxidation process starts, the concentration of hydroperoxides grows to becomes appreciable,

(Continued on next page)
(Continued from previous page)

and their decomposition becomes the main source of radical initiators. These steps were described in Eqs. [4] and [5], respectively.

**Propagation**

\[ R^* + O_2 \xrightarrow{\text{fast}} ROO^- \]  

[2]

\[ \begin{align*} &\text{ROO}^- + \text{RH} \xrightarrow{\text{slow}} \text{ROOH} + \text{R}^* \\ &\text{RH} \quad \text{secondary} \\ &\text{center} > 10 \end{align*} \]  

[3]

\[ \text{ROOH} \rightarrow \text{RO}^* + \cdot \text{OH} \]  

[4]

\[ 2 \text{ROOH} \rightarrow \text{ROO}^* + \text{RO}^* + \text{H}_2\text{O} \]  

[5]

Alternating tertiary hydrogens, such as those present in polypropylene, are especially vulnerable to oxidation according to a mechanism proposed by Chien et al. (Chien, et al. (1967)). Once a hydroperoxide is generated, it undergoes intramolecular hydrogen abstraction via a favored six-member transition state and results in the formation of neighboring hydroperoxides. By this process, the buildup rate of hydroperoxide is an increases exponentially function, and all of the tertiary hydrogens are oxidized quickly. This process was described in Eq. [6].

![Diagram of hydroperoxide formation](image)

In the final or radical terminating step, the peroxo and alkyl radicals can react with each other to form nonradical species as shown in Eqs. [7] to [9], respectively. Sometimes, an undesirable viscosity increase can result from the combination of radicals leading to partial cross-linking of the hydrocarbon material as well as attractive forces between polar oxidation products.

**Termination**

\[ 2 \text{R}^* \rightarrow \text{R} - \text{R} \]  

[7]

\[ \text{ROO}^* + \text{R}^* \rightarrow \text{ROOR} \]  

[8]

\[ 2 \text{ROO}^* \rightarrow \text{ROR, RCOR, RCOH, ROH, etc.} \]  

[9]

![Diagram of termination reaction](image)

**Fig. 1—Ideal structures of PAO oligomers.**

In lubrication applications, hydrocarbon base stocks can be selected from a wide variety of fluids such as mineral oil, PAO, etc. These fluids have diverse performance properties suitable for end use in different markets. Mineral oils, the most widely used base stock due to their low cost, are complex mixtures of paraffinic, naphthenic and aromatic compounds with a broad range of molecular sizes and structures. They typically contain a significant amount of tertiary hydrogens. As a result, mineral oils tend to have relatively poor oxidation stability.

PAO has been the dominant synthetic lubricant base stock since 1970s because of its excellent physical properties including high viscosity index (VI) and superb oxidative, shear and thermal stabilities. It's typically a mixture of oligomers, such as trimer, tetramer, etc., of 1-decene or other long chain alpha olefins. The ideal structures of PAO's are shown in Fig. 1. They have a very limited number of tertiary hydrogens. Yet, commercial PAO molecules normally go through structural isomerization during synthesis, and as a result extra branches and tertiary hydrogens are introduced into these molecules (Shubkin, (1993)). Hence, the oxidative stability of PAO molecules are is adversely affected although it is still considerably superior to that of mineral oils. A key to ensure high oxidation resistance is to minimize the number of tertiary hydrogens per molecule, especially the ones with tertiary carbons in 1, 3- arrangements as shown in Eq. [6].

Traditionally, the PAO manufacturing process consists of two steps. The first step is a high-temperature, high-pressure reaction in which ethylene monomer is integrated oligomerized by an aluminum alkyl catalyst. The product is a mixture of linear alpha olefins (LAO's). Altogether, more than 15 different LAO's are generated having carbon numbers ranging from C4 to C30+ are generated. About 25 wt.% of this mixture is 1-decene. In the second step, 1-decene is oligomerized into dimers, trimers, tertiarmers, etc. in the presence of a cationic type catalyst. This salt catalyst is typically a boron trifluoride/alcohol complex. Then, the oligomers are fractionated to form PAO base stocks of various viscosity grades.

The biggest commercial applications for LAO's are for productions of alcohols and olefin copolymers. Therefore, the supply of 1-decene is limited for synthetic lubricant applications. The value per unit weight of 1-decene is more than twice that of ethylene. Consequently, PAO's cost much
more than base stocks made from mineral oils and are too expensive for many consumer and industrial applications. The worldwide PAO consumption now is estimated to be around 100 million gallons a year and grows at a rate of 10% per year. This is due to both heightened interests in high-performance synthetic lubricants among consumers and more demanding specifications from original equipment manufacturers (Synthetic Lubricants and Functional Fluids, 1999). At this rate, current PAO production capacity won’t be able to meet the market demands. This creates an opportunity for the development of a lower cost high performance alternative to PAO.

It is well known that ethylene and other olefin monomers can be polymerized by heterogeneous Ziegler-Natta catalysts into high molecular weight polymers valued for their outstanding mechanical strength and other physical properties. Since the mid 1980s, metallocene catalysts have revolutionized commercial olefin polymer manufacturing with their exceptional versatility and reactivity (Brintzinger, et al., 1995, Mohring, et. al., 1994, Beredikt et. al., 1998, Togni, et. al., 1998). Because metallocene catalysts normally have active species of identical catalytic characteristics, they are frequently referred to as single-site catalysts (SSC). SSC have significant attributes such as high catalytic efficiency under milder reaction conditions and accurate control over polymer molecular structures. Copolymers synthesized with SSC tend to have uniform comonomer incorporation for both high and low molecular weight fractions and highly random distribution of comonomers along the copolymer chain. For example, a copolymer of ethylene and propylene synthesized with SSC has mostly isolated propylene units separated by multiple ethylene units in the copolymer chain, owing to activity difference between the two monomers. Therefore, the copolymer contains only a small amount of alternating tertiary hydrogens. So in contrast to the oxidation of polypropylene illustrated in Eq. [6], the ethylene-propylene copolymer possesses much better oxidation stability since the propagation of radicals along the copolymer chain is better suppressed.

By utilizing SSC, the authors have developed an innovative technology that directly polymerizes inexpensive and abundant olefin monomers including ethylene, propylene and butene into liquid copolymers (Heilman, et. al., 2000). The polymerization reaction typically occurs at 50°C and 2atm with high monomer conversion. Reaction products have been demonstrated to exhibit comparable physical and chemical properties to PAO’s. In this paper, the synthetic base stocks produced through the new technology is referred to as EOP fluids, which stands for “Ethylene – alpha-Olefin Polymer” fluids.

EXPERIMENTAL PROCEDURE

A pilot plant scale continuous process has been built to synthesize EOP products. It consists of the following major steps.

Step (1) Polymerization

The polymerization reaction took place in a five-gallon continuous-flow stirred-tank reactor (CSTR) operated at around 50°C and 2atm of total pressure. The reactor was charged with 2 gallons of toluene (low water, purchased from Mallinckrodt Baker) to start up the polymerization reaction. A mixture of ethylene, propylene, butene, and hydrogen was introduced into the gas phase of the reactor and dissolved in the liquid phase with the help of two mixing impellers. The hydrogen gas was present to control the molecular weight of the polymerization product and accordingly, the viscosity of the fluids produced. A single-site catalyst in combination with a co-catalyst activator, both in toluene solutions, was continuously injected into the reactor. An example of this catalyst/cocatalyst combination is bis(cyclopentadienyl)zirconium dichloride (Cp2ZrCl2, purchased from Strem Chemical) with poly(methylaluminoxane) (PMAO, 10 wt.% Al content in toluene, purchased from Akzo Nobel Chemicals). A small fraction of the gas phase inside the reactor was purged to remove the buildup of non-reactant gases such as methane, propane, nitrogen, etc. The liquid stream drawn at the bottom of the reactor was the CSTR effluent containing the raw product.

Step (2) Removal of Catalyst Residue

The existence of the catalyst residue in the CSTR effluent, especially residual unreacted PMAO, could cause operating problems in the downstream processing steps as well as harm the performance of the finished products. Upon being exposed to the air, PMAO would form gel-like materials difficult to be removed and easy to plug transfer lines and distillation columns. An acid washing step was applied to remove the residual catalysts from the CSTR effluent. PMAO reacted with aqueous acid solution to form a water-soluble salt while the raw product remained in the oil phase. The liquid mixture was decanted to recover the raw product. The product was then washed with water several times to remove traces of salt and acid.

Step (3) Distillation of Solvent

Toluene, used as the carrier for catalysis, was distilled off along with a small amount of a low boiling (<204°C) product in an atmospheric tower. The lube boiling-range (<460°C) product was also collected at this stage.

Step (4) Thermal Cracking

The high viscosity product was thermally cracked (343°C – 466°C) at standard atmospheric pressure into lubes and lighter fractions in this step. The heavy end was charged to a plug flow reactor filled with inert packing where thermal cracking occurred. The reactor effluent was distilled into a light end, a lube boiling-range product and a residuum. The residuum was recycled to the cracker and went through cracking again to extinction.

Step (5) Hydrogenation

The lube boiling-range product was hydrogenated at 67atm -100atm of hydrogen pressure and 204°C-327°C to

(Continued on next page)
improve the oxidative stability and remove color of the product. The reactor was a trickle-bed reactor packed with a hydrogenation catalyst, and the controlled property was the Bromine number. After having been degassed, the hydrogenation reactor effluent was charged across a series of distillation columns to recover the finished products.

Step (6) Fractionation

The hydrogenated material was finally fractionated to make EOP products having the right viscosity and volatility.

RESULTS AND DISCUSSION

Many reaction variables, such as catalyst flow rate, monomer pressure, hydrogen concentration, total pressure and reaction temperature, can be adjusted to influence control polymerization activity and product properties. For the polymerization reaction, the flow rate of Cp2ZrCl2 catalyst was around 1 x 10^3 mole/hr with Al/Zr ratio in the range of 100–200. The polymerization activity was up to 1 x 10^2 g of polymer/mole of Zr. The viscosity of polymerization product rose with increasing reaction pressure, which is typical for olefin polymerizations by SSM. Basically higher molecular weight copolymers are formed when monomer concentrations in the liquid phase go up due to raised pressure.

Table 1 lists a systematic comparison of physical properties between EOP fluids and commercial PAO’s of equivalent viscosities. The data showed that EOP fluids had slightly higher VI than their PAO counterparts. On the other hand, pour points of EOP fluids were also higher than PAO’s. This was probably caused by polyethylene segments present in the copolymer chain that would crystallize at low temperatures, thus increasing pour point of the fluid. Yet EOP fluids were very responsive to additives such as pour point depressants (PPD). For example, with the addition of only 0.1 wt.% of a PPD, the pour point of a 4 cSt EOP fluid in Table 1 dropped from -27°C to -53°C.

Physical properties of EOP fluids can be easily adjusted by changing the composition and structure of the copolymer due to the extreme versatility of single-site catalysts. For instance, as shown in Table 2, sample No. 1 was a copolymer of ethylene and propylene with ethylene content of 72 mole%. Both samples No. 2 and No. 3 were copolymers of ethylene, propylene and butene. By increasing the butene content from 0 to 6 mole%, the pour point of the fluid was lowered from -3°C to -24°C. This decrease of pour point was because due to the short chain branching, introduced to the copolymer chain by the incorporation of butene, that interfered with the crystallization of polyethylene segments, therefore decreasing the pour point of the fluid. Meanwhile, other properties of the fluids including viscosity and molecular weight changed only slightly except for VI, which decreased with increasing butene content. This was expected since the VI of a fluid is generally proportional to the linearity of hydrocarbon molecule, as confirmed in Fig. 2.

The oxidative stability of liquid hydrocarbons can be evaluated with pressurized differential scanning calorimetry (PDSC). PDSC measures the induction time before a sample is oxidized and rates oxidative stability as a function of increasing induction time. Figure 3 shows PDSC results of a series of EOP fluids with various ethylene contents. For reasons explained earlier in Eqs. [1] through [5], tertiary hydrogens are usually considered the weak sites in a molecule since they are easily oxidized. Thus, the oxidative stability of a material should improve with declining numbers of tertiary hydrogens in its molecule. This was in good agreement with experimental observations for EOP fluids since higher ethylene contents correspond to fewer numbers of tertiary hydrogens in the copolymer molecule. Consequently, the fluid has better oxidative stability.

PDSC measurements (at 195°C under 33 atm of O2 pressure) were also used to compare fully formulated 5W30 engine oils based on an EOP fluid, a commercial PAO and a
Group-III base oil with the same additive package at an identical treat rate. This Group-III base oil was a complex mixture of various compounds with broad molecular weight and structural variations. The PDSC results were 71 minutes, 73 minutes and 59 minutes for EOP, PAO and Group-III oil based samples, respectively. It showed that the EOP fluid had comparable oxidative stability with its PAO counterpart and was much better than the Group-III base oil. (Where is this information?)

Sequence III-E and V-E engine tests were also run to compare formulated 5W30 engine oils based on an EOP fluid and a commercial PAO in aspects such as their oxidative stability and sludge formation. The results were shown in Tables 3 and 4. Both oil samples passed the tests, and the difference in performance was within test measurement error. In addition, a field test was conducted for 100 cSt EOP fluid based gear oil for coal mine applications. The results once again indicated that its performance was equivalent or superior to the PAO based products. (Where is this information?)

CONCLUSION

The new EOP technology has a number of important technical advantages. First, it’s highly efficient and capable of tailoring the copolymers’ composition and structure to target a specific performance property. Second, the products are of uniform structure and do not isomerize during the polymerization reaction, in contrast to the current PAO synthesis methods. Third, the process is equally efficient when applied to produce high or low viscosity grade products. This feature becomes even more significant when compared with the commercial manufacturing method for heavy PAO’s. Fourth, both laboratory and engine test results have demonstrated that the performance of formulated synthetic lubricants based on EOP and PAO products are comparable to each other. Fifth, the EOP process utilizes inexpensive and abundant feed stocks such as ethylene, propylene and butene to directly generate premium base stocks circumventing supply restrictions of 1-decene or other long chain linear alpha olefins. Finally, EOP has the potential to be used as an alternative high performance, low cost synthetic base stock to conventional PAO.

ACKNOWLEDGMENT

The authors would like to thank R&D management at Pennzoil-Quaker State Company for their continuous support of this project.

REFERENCES