Lubricant basestocks from vegetable oils

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Abstract

Compared to the lubricants made of petroleum, vegetable-based lubricants are much more biodegradable but inferior in many other technical characteristics. The basestock typically contributes to more than 80% of lubricant and must meet performance criteria in such aspects as cleanliness, viscometric properties, volatility, oxidative and hydrolytic stability, deposit forming tendencies, solvency, miscibility or compatibility with system elastomers and other. For vegetable-based lubricants, oxidative stability and low temperature problems are considered the most critical. Thin film oxidation test was used to compare oxidative stabilities. Vegetable oils appear an order of magnitude less stable than mineral oils or synthetic biodegradable basestocks, such as isooalkyl adipates or poly alphaolefins. Low temperature performance of vegetable oils, namely pour points and cold storage, was also problematic. These problems can only partially be relieved by lubricant additives, thus vegetable oils have to be modified chemically to eliminate sites susceptible to oxidation and to disrupt formation of crystals at low temperatures. Published by Elsevier Science B.V.

Keywords: Vegetable oil; Soybean; High oleic sunflower; Lubricants; Viscosity; Oxidation; Pour points

1. Introduction

Increasing attention to the environmental issues drives the lubricant industry to increase the ecological friendliness of its products. For the last decade, the industry has been trying to formulate biodegradable lubricants with technical characteristics superior to those based on mineral oil (petroleum). Volumes of lubricants, especially engine oils and hydraulic fluids, are relatively large and most of them are based on mineral oils. Lubricants based on vegetable oils still comprise a narrow segment; however, they are finding their way into such applications as chainsaw bar lubricants, drilling muds and oils, straight metalworking fluids, food industry lubricants, open gear oils, biodegradable grease, hydraulic fluids, marine oils and outboard engine lubricants, oils for water and underground pumps, rail flange lubricants, shock absorber lubricants, tractor oils, agricultural

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equipment lubricants, elevator oils, mould release oils, two stroke engine lubricants and other. Hydraulic fluids, which are consumed at ≈ 5 million metric tons per year rate in the US (Padavich and Honary, 1995), have the highest need for biodegradable lubricants. Although vegetable oils have reputation of a low-cost candidate for the biodegradable replacement of mineral oils due to their high inherent biodegradability (Battersby et al., 1992; Randles and Wright, 1992), unsatisfactory performance curbs their more widespread utilization as lubricants.

The performance limitations of vegetable based lubricants stem from inherent properties of the vegetable oil basestocks rather than composition of additive package. Basestocks usually comprise more than 80% lubricant and nearly entirely pre-define properties such as high biodegradability, low volatility, ideal cleanliness, high solvency for lubricant additives, miscibility with other types of system fluids, negligible effects on seals and elastomers and other less significant properties (e.g. density or heat conductivity). Basestocks are also a major factor in determining oxidative stability, deposit forming tendencies, low temperature solidification, hydrolytic stability and viscometric properties. On the other hand, parameters like lubricity, antiwear protection, load carrying capacity, corrosion (rust) prevention, acidity, ash content, color, foaming, de-emulsification (so called demulsibility), water rejection and a number of others are mostly dependent on the additives or impurities/contaminants. Therefore, when a given fluid is considered for its suitability as a lubricant, first of all the basestock -dependent parameters are evaluated. In addition to biodegradability, the following characteristics must be given attention: cleanliness (particle count), compatibility with mineral oil lubricants and homogeneity during long term storage, water content and acidity, viscosity, viscosity index, pour point, cloud point, cold storage, volatility, oxidative stability (for vegetable oils also iodine value), elastomer compatibility and possibly other properties, depending on intended application. Water rejection, demulsibility, corrosion protection, ash content and foaming could also be tested if contamination of the additive-free oil is suspected.

In some of the listed properties, volatility or viscosity index being cited the most often, vegetable oils clearly outperform mineral oils. Many of the other properties are similar between the fluids or may be manipulated with additives. However, low resistance to oxidative degradation and poor low temperature properties are major issues for vegetable oils. The lubricant industry's inability to overcome these limitations ignited a rapid rise in demand of highly biodegradable synthetic basestocks as low molecular weight poly α-olefins (PAO 2 or PAO 4, essentially 20:1 and 10:1 mixtures of hydrogenated dimers:trimers of alpha-decene), di alkyl adipates (iso decyl, iso tridecyl) or polyol esters (mostly neopentyl glycol or trimethylol propane with fatty acids). The synthetic basestocks also have some imperfections, such as higher volatility of PAOs, seal swelling of adipates, questionable biodegradability of some polyols, and, frequently the major issue, costs of nearly three times higher than that of vegetable oils. Nevertheless, for many original equipment manufacturers the improvement in lubricants performance outweighs the expenses and imperfections.

In this study the two major factors, oxidative stability and low temperature properties, are investigated experimentally. Oxidative stability of the oils can be evaluated using a number of techniques. Micro oxidation is a family of thin film oxidation tests widespread in lubricant industry (Perez et al., 1987) and appears to be more suitable in testing antioxidant-free basestocks than other oxidation tests, such as Oil Stability Index, Pressurized Differential Scanning Calorimetry or Rotary Bomb Oxidation Test. These tests were performed in this work on a series of vegetable oils and synthetic
basestocks to compare their suitability for biodegradable lubricants.

2. Materials and methods

2.1. Testing materials

Alkali refined soybean oil (refined, bleached, deodorized) was a commercial product of Bunge Edible Oil (Kankakee, IL). Its fatty acid content, as reported by the supplier, was 16% palmitic/stearic, 23% oleic, 53% linoleic and 8% linolenic, tocopherol level ≥ 500 ppm. High oleic sunflower oil (90% oleic oil), supplied by International Flora Technologies (Gilbert, AZ), had fatty acid content of 5% palmitic/stearic, 90% oleic and 5% linoleic/linolenic, tocopherol level ≥ 1000 ppm. Both oils were stored below -5°C under nitrogen atmosphere. Poly alkyl methacrylate copolymer-based pour point depressant EF-133V (PPD), designed for vegetable oils (RohMax, 1995), had MW ≥ 8000 and was supplied by RohMax (Philadelphia, PA) in ~50% (w/w) of canola oil carrier. As a PAO, p-alpha olefin PAO 4 (notation 4 indicates approximate kinematic viscosity in mm²/s at 100°C and differentiates it from PAO 2, PAO 6, PAO 10, etc.), which essentially represents a 80:20 mixture of hydrogenated dimers and trimers of 1-decene, was from Amoco (Lisle, IL). Ninety-nine percent pure di isodecyl adipate (Adipate) was provided by Hatco (Fords, NJ). Additive free super refined ‘white’ mineral oil with very low sulfur contents (Mineral oil) had boiling range of 360–530°C and met MIL-L-7828 specifications (Klaus et al., 1980).

2.2. Testing of kinematic viscosities

Kinematic viscosities of the fluids were measured according D 445 (ASTM, 1991b). Cannon-Fenske capillary viscometers and the constant temperature bath were from Cannon Instruments, State College, PA. Temperature of 40 ± 0.2°C was maintained throughout the experiments. The viscometers were calibrated for 10–50 cSt viscosity range using calibration fluids provided by the manufacturer.

2.3. Oxidative stability testing

The employed version of micro oxidation test utilized 40 µl of analyte placed on a nearly flat low-carbon-steel pan in the form of a thin film and subjected to specified durations of oxidation under controlled temperature and inlet air flow. As heating media, a hot plate (Mirak™ with built-in thermocouple controller by Thermolyne, Dubuque, IA) was used which was able to maintain temperatures of up to 200°C with ±1°C accuracy without considerable temperature gradients across the heating surface. A rectangular aluminum slab (25 × 125 × 125 mm) was placed on the top of the hot plate to assure the heat transfer to the sample coupons. The slab had a hole drilled on a side to insert a thermocouple (Teflon coated Ni-Al and Ni-Cd supplied with the hot plate) for the temperature control. Four sample coupons loaded with analytes were placed on the slab and covered with the bottomless impingers. Either flat sample coupons were used (verifying that the surface tension forces prevent the fluid from spillage), or the edge of the coupon was slightly raised to reduce the risk of spills. Analytes were applied in a form of homogeneous film on the coupons before placing the coupons on the heated block. The coupons with the samples were weighed, placed on the slab and covered with the glass impingers. Size of the glass impinger and controlled air flow assured the absence of oxygen concentration gradients in the gas phase as well as effective elimination of volatile oxidation products by condensation on the impinger walls, while keeping the sample heat losses minimal.

The procedure of micro oxidation, analogous to that of heated block micro oxidation (Asadauskas, 1997), involved polishing the coupons and heating block, weighing the empty coupons, applying 40 mm³ (~36 mg) of sample in a form of homogeneous film, placing the coupons on the thermally equilibrated aluminum slab, covering with the bottomless impinger and supplying 0.1 MPa dry air flow at 20 cm³/min. After a given duration the sample pan was removed and placed on a clean cold metal surface for shock-cooling. Then the pan was weighed and oxidized sample
washed off with tetrahydrofuran (THF). The weighing before washing with THF permitted determination of volatile loss (or gain due to oxidation), whereas the weighing after the washing determined possible formation of solids or corrosion of the surface metal. Gel permeation chromatography (GPC) was employed to investigate oxypolymerization kinetics.

GPC analyses were carried out on the instrument of Thermo Separations with a P 4000 pump and AS 3000 autosampler/injector. THF flowrate of 3 ml/min used partial recirculation through Peak Cutter™ by Waters-Millipore. Four columns of PLgel 5 µm, 10E5A 300 × 7.5 mm and an adequate guard-column by Polymer Laboratories (UK) were maintained in the air bath at 40 ± 1°C. Each injection consumed ~0.3 ml of the ~1% sample solution in THF. Refractive index detector data from Waters M411 Differential Refractometer versus retention time was collected at 0.6 s intervals and then transferred to a spreadsheet for further analysis.

Three key elements were identified as most influential when comparing the traditional micro oxidation to its modified version used in this study: (1) possibility of more pronounced temperature gradients on the heated block surface as compared to liquid metal bath; (2) effect of the surface roughness of both sample pan and heating block on heat transfer to the sample as compared to heat transfer from liquid metal bath to sample pan via impinger glass wall and (3) influence of the sample film distribution on oxidation rates of unsaturated materials as compared to those of usually unsaturation-free lubricating fluids. All three factors were investigated experimentally and it was found that factors 1 and 2 do not contribute to the actual temperature in the sample substantially, whereas the sample film thickness and its homogeneity need to be controlled more accurately in vegetable oils than in petroleum liquids. Unsaturated materials are more susceptible to oxidation; therefore, oxygen concentration gradients are more pronounced within the film. Assuming minor fluctuations of the film thickness (due to surface profile inconsistencies or oxidative evaporation) do not have an appreciable effect (Tseregounis et al., 1987), the amount of sample was held constant at 40 mm³ ± 5%.

2.4. Low temperature testing

Pour points were measured strictly according D 97 (ASTM, 1991a), which determines pour points by placing a test jar containing 50 ml of the sample into a metal cylinder submerged into cooling media. Sample temperature was measured in 3°C increments at the top of the sample until it stopped pouring, whereas the temperature of cooling media was kept constant below the sample temperature. When the sample temperature reached the specified range (e.g., three of the ranges are +9 to -6, -6 to -24 and -24 to -42°C), the temperature of cooling media was also reduced to the specified value (-18, -33 and -51°C, respectively). The pour point is defined as temperature where sample still pours. Statistically, the test has shown satisfactory accuracy; as described in a precision statement (ASTM, 1991a,b), the difference between two test results from independent laboratories exceeding 6°C in only one case of 20 with repeatability of 2.87°C at 95% confidence.

The same equipment as in ASTM D 97 was used in the cold storage test as well. The samples were kept at -30°C and visually inspected every 24 h for 7 days. Failing criteria consisted of crystallization, solidification and formation of solid particulate but did not include haziness or loss of transparency.

3. Results and discussion

Soybean oil (SBO) and high oleic (90%) sunflower oil (HOSO) were chosen for evaluation as examples of vegetable oils. PAO and adipate represented widely used synthetic biodegradable lubricating basestocks. The mineral oil was a typical 'non-biodegradable' basestock mostly used for formulations of automotive lubricants. Except for natural antioxidants, the above fluids did not have any additives.

Initially, kinematic viscosities at 40°C and pour points of the fluids were determined, results shown in Table 1. It appears that low temperature properties of vegetable oils are much more inferior to those of synthetic basestocks or even min-
Table 1  
Viscosities and pour points of major lubricating basestocks

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Viscosity, cSt at 40°C</th>
<th>Pour points, °C</th>
<th>Storage at −25°C, days</th>
</tr>
</thead>
</table>
|                        |                        |                 | No additives | With 1% PPD
| Soybean oil            | 31.5                   | −9              | 0          | 0          |
| 90% Oleic Sunflower oil| 40.3                   | −12             | 0          | 0          |
| Di i−C₁₃ adipate       | 27.2                   | −54             | 7+         | 7+         |
| PAO 4ᵇ                 | 17.4                   | −63             | 7+         | 7+         |
| Mineral oil            | 71.2                   | −21             | 0          | 7+         |

ᵃ Poly alkyl methacrylate copolymer of ~8000 amu, canola oil carrier 1:1.
ᵇ Poly-alpha olefin (kinematic viscosity 4 mm²/s).

eral oil. Cold storage properties of vegetable oils evidently do not appreciably respond to the pour point depressants (PPD), as opposed to mineral oils. This is consistent with earlier observations (Asadauskas and Erhan, 1999). Oxidative stabilities of the oils are compared in Table 2.

The data also compares oxypolymerization and volatility tendencies of the fluids. Temperature of 150°C and durations of 30–60 min chosen for testing were high enough to cause a quantifiable polymerization in unsaturation-free basestocks yet not too severe to result in oxidative gelation of vegetable oils. Therefore, the side processes, such as oxidative cleavage and formation of solids, were not too substantial. It appears from the data that vegetable oils oxypolymerize considerably faster than unsaturation-free fluids.

This is further highlighted in a kinetic chart for oxypolymerization, as shown in Fig. 1.

Although HOSO containing only 5% of linoleic acid shows higher resistance to oxypolymerization than SBO, its oxidative stability is far less than those of PAO or adipate. Oxypolymerization proceeds much faster and slows down only when side processes, especially formation of solids, become more pronounced. It has been established that methylene interrupted polyunsaturation is the key factor causing low oxidative stability of vegetable oils (Gardner, 1989; Gunstone, 1994). This is also evident comparing micro oxidation data for different vegetable oils (Fig. 2).

Chemical modification is necessary to improve these performance limitations with the focus on eliminating bis-allylic hydrogen functionalities in methylene interrupted polyunsaturation and optimal extent of structural alteration for improved low temperature performance. Sufficient experimental evidence is not yet available, however, it can be suggested that such modification pathways as alkylation, alkoxylation, interesterification and oligomerization might appreciably improve overall lubricant properties of vegetable oils.

Table 2  
Oxidative degradation tendencies

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Micro oxidation, 30 min at 150°C, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxypolymers</td>
</tr>
<tr>
<td>Soybean oil</td>
<td>48</td>
</tr>
<tr>
<td>90% Oleic sunflower oil</td>
<td>13</td>
</tr>
<tr>
<td>Di i−C₁₃ adipate</td>
<td>3</td>
</tr>
<tr>
<td>PAO 4ᵇ</td>
<td>6</td>
</tr>
<tr>
<td>Mineral oil</td>
<td>5</td>
</tr>
</tbody>
</table>

ᵃ Polyalphaolefin with viscosity of ~4 cSt at 100°C (hydrogenated dimers:trimers of 2-decene).
Fig. 2. Oxypolymerization tendencies of soybean, canola and high oleic sunflower oil and 100% triolein. Thin film micro oxidation test on low carbon steel surface.

4. Conclusions

- Oxidative stability of vegetable oils is much lower.
- Low temperature performance of vegetable oils is poor.
- Chemical modification of triglycerides is necessary to:
  - completely eliminate polyunsaturation (for better oxidative stability);
  - find an optimal extent of chemical alteration (improved low temperature behavior).

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References

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