Methods for achieving favorable air release properties, methods for blending a lubricant composition and lubricant compositions are disclosed. In one embodiment, the method comprises the steps of obtaining at least one base stock and at least one thickener, blending the base stock(s) and the thickener wherein the treat rates of the base stock and thickener are chosen to achieve a favorable air release property using a relationship between the thickener, lubricant viscosity, and viscosity of at least one base stock.
FIGURE 1
FIGURE 2
FIGURE 3
FIGURE 4
FIGURE 5
FIGURE 6
NOVEL APPLICATION OF THICKENERS TO ACHIEVE FAVORABLE AIR RELEASE IN LUBRICANTS

This application claims benefit of U.S. Ser. No. 60/833,870 filed Jul. 28, 2006.

BACKGROUND

The art or formulating lubricating oil compositions has become more complex as a result of increased government and user environmental standards and increased user performance requirements. Air release is very important in lubricants particularly industrial lubricants. Lubricants which release entrained air faster will exhibit performance benefits versus fluids which release air more slowly.

Recently, equipment manufacturers are requiring improved air release properties at many different viscosity grades. All lubricating oil systems contain some air. It can be found in four phases: free air, dissolved air, entrained air and foam. Free air is trapped in a system, such as an air pocket in a hydraulic line. Dissolved air is in solution with the oil and is not visible to the naked eye. Foam is a collection of closely packed bubbles surrounded by thin films of oil that collect on the surface of the oil.

Air entrainment is a small amount of air in the form of extremely small bubbles (generally less than 1 mm in diameter) dispersed throughout the bulk of the oil. Agitation of lubricating oil with air in equipment, such as bearings, couplings, gears, pumps, and oil return lines, may produce a dispersion of finely divided air bubbles in the oil. If the residence time in the reservoir is too short to allow the air bubbles to rise to the oil surface, a mixture of air and oil will circulate through the lubricating oil system. This may result in an inability to maintain oil pressure (particularly with centrifugal pumps), incomplete oil films in bearings and gears, and poor hydraulic system performance or failure. Air entrainment is treated differently than foam, and is most often a completely separate problem. A partial list of potential effects of air entrainment include: pump cavitation, spongy, erratic operation of hydraulics, loss of precision control, vibrations, oil oxidation, component wear due to reduced lubricant viscosity, equipment shut down when low oil pressure switches trip, “micro-dieselizing” due to ignition of the bubble sheath at the high temperatures generated by compressed air bubbles, safety problems in turbines if overspeed devices do not react quickly enough, and loss of head in centrifugal pumps.

Antifoams, including but not limited to silicone additives, produce smaller bubbles in the bulk of the oil as an unintended consequence of their use. In stagnant systems, the combination of smaller bubbles and greater sheath density can cause serious air entrainment problems.

Casual exposure to silicone can have a significant effect on the lubricant. There are reports of air entrainment resulting from oil passing through hoses that had been formed on a silicone-coated mandrel. Other known causes of entrainment problems include contaminants, overalldizing and reservoir design.

One commonly used method to measure air release properties of petroleum oils is ASTM D 3427. This test method measures air content via density at given time intervals following aeration at temperatures specified by viscosity grade. Air release performance is reported either in air content at various time intervals or the time required for the air entrained in the oil to reduce in volume to either 0.1% or 0.2% is recorded as the air release time.

SUMMARY

Most solutions to the air entrainment problem have been to redesign the reservoir or choose additives not likely to cause aeration issues. There is a need to create new understanding of both the base stocks and additives to achieve favorable air release properties and reduce aeration issues. Accordingly, this invention satisfies that need.

A method of achieving favorable air release properties is disclosed. The method comprises the steps of obtaining a lubricating oil comprising at least one base stock and at least one thickener, blending the base stock(s) and the thickener wherein the treat rates of the base stock(s) and thickener are chosen to achieve a favorable air release property using a relationship between the thickener, lubricant viscosity, and viscosity of at least one base stock, and lubricating a machine with the lubricant.

In a second embodiment, a novel lubricant formulation is disclosed. In one embodiment the novel lubricant formulation comprises at least one base stock and at least one thickener, wherein the treat rates for the thickener and base stock(s) are chosen to achieve a favorable air release property by using a relationship between the thickener, lubricant viscosity and viscosity of at least one base stock.

In a third embodiment a method for blending a novel formulation is also disclosed. The method comprises obtaining at least one base stock and at least one thickener, blending the base stock(s) and the thickener wherein the treat rates of the base stock(s) and thickener are chosen to achieve a favorable air release property using a relationship between the thickener, lubricant viscosity, and viscosity of the base stock(s).

FIG. 1 is a graphical representation of ASTM D3427 air content versus time for paper machine oil with a viscosity grade of ISO 220;

FIG. 2 is a graph of 600 neutral Group I base stocks plotted against percent air entrainment at 1 minute using ASTM D3427;

FIG. 3 is a graph of predicted versus actual air release values;

FIG. 4 is a contour plot of air content at 1 minute of 600 neutral Group I base stocks based on PIB treat rates;

FIG. 5 is a graph of 600 neutral Group II base stocks plotted against percent air entrainment at 1 minute using ASTM D3427;

FIG. 6 illustrates the same blend study as shown in FIG. 5, with another modeled value, viscosity index, being plotted against the air release performance;

FIG. 7 is a graph of predicted versus actual air release values. The predicted values versus actual values profile 16 align well, showing no bias towards either end of the design spectrum.

DETAILED DESCRIPTION

We have discovered a novel combination of base stocks and additives that provide unexpected favorable improvements in air release properties. In general, the higher a fluid viscosity, the slower the air release. We have discovered, an unexpected air release benefit of using high viscosity polymers such as Polymethacrylate (“PMA”) or Polysobutene (“PIB”) to achieve base oil viscosity with favorable air release versus prior art base oil blending. In one embodiment, this discovery enables formulating high performance industrial fluids that meet required Original Equipment Manufacturer (“OEM”) specifications while achieving optimum fluid life and extended equipment life.
In one embodiment, the lubricants are blended wherein treat rates or amounts of the thickener and additives are chosen to achieve a favorable air release property by using a qualitative relationship between the thickener, lubricant viscosity and viscosity of at least one base stock. The statistical analysis can be performed with many different commercially available software programs that are commonly used in the industry. One suitable software program is StatEase Design Expert 6.01. The steps for using this software are explained in more detail in the examples.

In another embodiment, the relationship is quantitatively determined through the use of statistical analysis of air release data for a defined system of base stock(s), thickener, and lubricant viscosity. The resultant relationship or model is then applied to optimize the air release performance.

The air release performance of base stocks follows the pattern of light viscosities are better than heavy viscosities which are better than ultra heavy viscosity components. In other words, light viscosities exhibit the best performance whereas the ultra heavy viscosity components exhibit the worst air release properties.

In a preferred embodiment, the use of thickener can be utilized to achieve a target viscosity. The use of thickeners permits the heavier and poorer air release performance base stock components to be reduced or eliminated while maintaining necessary viscosity grades.

Suitable light neutral base stocks include but are not limited to 100-150 neutral Group I, II, III, IV, V and light viscosity Gas to Liquid ("GTL"). Suitable heavy neutral thickener include but are not limited to 500-600 neutral Group I, II, III, IV, V and heavy viscosity GTL such as GTL 15. In addition, ultra heavy viscosity components are typically classified as >2500 SUS including Group I (Bright Stock and Cylinder Stock), IV, and V. Table 1 is included below for general reference, as the industry standard methods of viscosity reporting vary by API Group. Group I and II are generally referred to in SUS, Groups III & IV are reported in cSt (mm²/s) at 100°C, and finished lubricant viscosities are reported in cSt at 40°C.

<table>
<thead>
<tr>
<th>Viscosity Classifications</th>
<th>SUS mm²/s 40°C</th>
<th>mm²/s 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Viscosity</td>
<td>80-150</td>
<td>18-38</td>
</tr>
<tr>
<td>Heavy Viscosity</td>
<td>500-600</td>
<td>100-130</td>
</tr>
<tr>
<td>Ultra Heavy</td>
<td>2500+</td>
<td>460+</td>
</tr>
</tbody>
</table>

For purposes of this invention, thickeners shall include both traditional thickeners and viscosity index improvers ("VII"). Traditional thickeners include but are not limited to PIB and high viscosity PAO. A new type of Metallocene catalyzed PAO provides a light molecular weight distribution at higher viscosities and could be used both as a thickener and base stock in this invention. Thickeners that are Viscosity Index improvers include but are not limited to PMA, olefin co-polymer ("OCP"), styrene butadiene copolymers, styrene isoprene polymers, and SV Star polymers. The SV star polymers consist of a core (divinyl benzene) with arms of isoprene that radiate out from the core. Commercial molecules include SV200 (4 SSI), SV250 (13 SSI), SV260 (25 SSI), SV270, SV300 (59 SSI). In progressing from SV200 to SV300, the length of the isoprene arms increases. As the arm length increases, the molecular weight of the molecule increases, the thickening efficiency increase, and the shear stability decreases. The impact on shear stability is reflected by the parameter "SSI". The higher the SSI value, the greater the viscosity loss in the industry shearing test ASTM D6578.

Table 2 demonstrates the impact Polymethacrylate has on hydraulic oil air release. As shown in table 2, the PMA containing formulations exhibit dramatically reduced air release times. The use of PMA as a viscosity modifier enables the blending of lower amount of pour point depressant and permits the use of higher percentage of lighter neutral Group I base stocks to achieve the desired viscosity grades. In the comparative examples given in Table 1 the use of PMA enables higher amounts of 150 neutral Group I base stocks and thus decreases the amount of 600 neutral Group I base stocks. This provides for better air release properties at the desired viscosities.

<table>
<thead>
<tr>
<th>Viscosity grade</th>
<th>68</th>
<th>68</th>
<th>100</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1 150 neutral</td>
<td>36.00%</td>
<td>71.00%</td>
<td>11.85%</td>
<td>48.08%</td>
</tr>
<tr>
<td>Group 1 600 neutral</td>
<td>62.85%</td>
<td>21.65%</td>
<td>87.00%</td>
<td>42.57%</td>
</tr>
<tr>
<td>Industrial Performance</td>
<td>0.85%</td>
<td>0.85%</td>
<td>0.85%</td>
<td>0.85%</td>
</tr>
<tr>
<td>Additives</td>
<td>PIB</td>
<td>0.30%</td>
<td>0.10%</td>
<td>0.10%</td>
</tr>
<tr>
<td></td>
<td>PMA VM</td>
<td>0.00%</td>
<td>6.40%</td>
<td>0.00%</td>
</tr>
<tr>
<td>ASTM D3427 - 50°C</td>
<td>100.00%</td>
<td>100.00%</td>
<td>100.00%</td>
<td>100.00%</td>
</tr>
<tr>
<td>Time to 0.2% air (min)</td>
<td>8.3</td>
<td>4.7</td>
<td>14.3</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Table 3 demonstrates the impact of PIB on paper machine oil air release. As shown in Table 3, the higher PIB concentrations exhibit reduced air release times. The use of PIB as a thickener permits the blending of higher percentage of lighter 600 neutral Group I base stocks to achieve the desired viscosity grades. In the comparative examples given in Table 3 the use of PIB enables higher amounts of 600 neutral Group I base stocks and thus decreases the amount of bright stock. This provides for better air release properties at the desired viscosities.

<table>
<thead>
<tr>
<th>Viscosity Grade</th>
<th>ISO 220</th>
<th>ISO 220</th>
<th>XRL</th>
<th>XRL</th>
<th>XRL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PMO</td>
<td>PMO</td>
<td>2023-</td>
<td>2023-</td>
<td>2023-</td>
</tr>
<tr>
<td>5.8% PIB</td>
<td>0% PIB</td>
<td>0% PIB</td>
<td>6% PIB</td>
<td>4% PIB</td>
<td>0% PIB</td>
</tr>
<tr>
<td>6 CS/3 GRI III</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>600 N</td>
<td>66.48%</td>
<td>49%</td>
<td>61.35%</td>
<td>58.35%</td>
<td>47.35%</td>
</tr>
<tr>
<td>Bright Stock</td>
<td>25.2%</td>
<td>48.28%</td>
<td>30%</td>
<td>35%</td>
<td>50%</td>
</tr>
<tr>
<td>Performance Additives</td>
<td>2.72%</td>
<td>2.72%</td>
<td>2.65%</td>
<td>2.65%</td>
<td>2.65%</td>
</tr>
<tr>
<td>PIB</td>
<td>5.80%</td>
<td>0%</td>
<td>6%</td>
<td>4%</td>
<td>0%</td>
</tr>
<tr>
<td>100.00%</td>
<td>100.00%</td>
<td>100.00%</td>
<td>100.00%</td>
<td>100.00%</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 3-continued

<table>
<thead>
<tr>
<th>Viscosity Grade</th>
<th>ISO 220</th>
<th>ISO 220</th>
<th>XRL</th>
<th>XRL</th>
<th>XRL</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMO</td>
<td>5.8% PIB</td>
<td>0% PIB</td>
<td>6% PIB</td>
<td>4% PIB</td>
<td>0% PIB</td>
</tr>
</tbody>
</table>

**ASTM D3427 - 50 C.**

<table>
<thead>
<tr>
<th>Time to</th>
<th>41.9</th>
<th>46.0</th>
<th>45.8</th>
<th>46.3</th>
<th>51.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1% air</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time to</td>
<td>37.1</td>
<td>40.0</td>
<td>35.5</td>
<td>39.3</td>
<td>45.0</td>
</tr>
<tr>
<td>0.2% air</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[0028] FIG. 1 is a graphical representation of ASTM D3427 air content versus time for paper machine oil with a viscosity grade of ISO 220. As shown in FIG. 1, the formulation with 5.8% PIB as shown by reference numeral 3 provides superior air entrainment results when compared to the formulation with no PIB as shown by reference numeral 5 throughout the ASTM D3427 test.

[0029] In one embodiment thickener fluids are used to achieve the desired air release properties and final viscosity grades. The improvement of air release is a quadratic relationship as described by the following:

\[
\text{Air}_{\text{min}} = c_1 - c_2 \text{A} + c_3 \text{V} + c_4 \text{B} + c_5 \text{A}^2 + c_6 \text{V}^2 + c_7 \text{B}^2 + c_8 \text{A} \text{B}
\]

**Eq. 1**

Wherein:

- \( \text{Air}_{\text{min}} \) is the air content at 1 minute following aeration by ASTM D3427
- \( c \) terms are constants that will vary based upon type of thickener, type of heavy neutral and co-blending stock, and finished blend viscosity range.

- **A** = Heavy neutral treat rate
- **B** = Thickener treat rate

[0030] In this situation, the viscosity of the finished fluid is fixed and the other variables implied by the values of A and B include co-blending stock amounts and thickener molecular weights.

[0032] To create a set of constants for this equation, a set of blends must be designed to cover the design spectrum for a desired viscosity grade and system of base stock(s) and thickener. The A and B values and the resultant air release data can be statistically analyzed to determine the specifics of the model and the constants appropriate for that system.

[0033] The quadratic relationship indicates there is a defined range where an air release benefit will occur due to replacing the heavier blending components with a thickener. However, the thickeners are not completely neutral towards air release performance and a performance deficit will occur if taken too far for a given set of variables. See the example 1 below for more detail on this relationship.

[0034] In a second embodiment the thickener is a viscosity index improver. In this embodiment, improvement of air release is a linear relationship as described by the following relationship:

\[
T_{0.1%} = c + c_1 \text{A} + c_2 \text{V} + c_3 \text{B} + c_4 \text{A} \text{B}
\]

**Eq. 2**

Wherein:

- \( T_{0.1%} \) is the time required to reach 0.1% air following aeration by ASTM D3427
- **C** = Constants that will vary based upon type of VI improver, type of heavy neutral and co-blending stock, and finished blend viscosity range.

- **A** = Viscosity index
- **B** = Kinematic viscosity at 40° C. of Lubricant
- **C** = Amount of heavy neutral present in blend

- **D** = Amount of viscosity improvers present in blend

[0035] The variables that are not in the model but are implied by the other terms are viscosity index improver, molecular weight, and amount of co-blending stock. The linear relationship indicates that an air release benefit will continue to accrue as more viscosity index improvers are used to reduce the ratio of heavier to lighter stocks in the blend. See example 2 for detail.

**Base Stocks:**

[0036] Groups I, II, III, IV and V are broad categories of base oil stocks developed and defined by the American Petroleum Institute (API Publication 1509; www.API.org) to create guidelines for lubricant base oils. Group I base stocks generally have a viscosity index of between about 80 to 120 and contain greater than about 0.03% sulfur and/or less than about 90% saturates. Group II base stocks generally have a viscosity index of between about 80 to 120, and contain less than or equal to about 0.03% sulfur and greater than or equal to about 90% saturates. Group III stock generally has a viscosity index greater than about 120 and contains less than or equal to about 0.03% sulfur and greater than about 90% saturates. Group IV includes polyalphaolefins (PAO). Group V base stocks include base stocks not included in Groups I-IV. Table 4 summarizes properties of each of these five groups.

<table>
<thead>
<tr>
<th>Base Stock Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturates</td>
</tr>
<tr>
<td>Group I</td>
</tr>
<tr>
<td>Group II</td>
</tr>
<tr>
<td>Group III</td>
</tr>
<tr>
<td>Group IV</td>
</tr>
<tr>
<td>Group V</td>
</tr>
</tbody>
</table>

[0037] In a preferred embodiment, the base stocks include at least one base stock of synthetic oils and most preferably include at least one base stock of API Group IV Poly Alpha Olefins. Synthetic oil for purposes of this application shall include all oils that are not naturally occurring mineral oils. Naturally occurring mineral oils are often referred to as API Group I oils.

[0038] Gas to liquid (GTL) base stocks can also be preferentially used with the components of this invention as a portion or all of the base stocks used to formulate the finished lubricant. We have discovered, favorable improve-
ment when the components of this invention are added to lubricating systems comprising primarily Group II, Group III and/or GTL base stocks compared to lesser quantities of alternate fluids.

[0039] GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds, and/or elements as feedstocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butanes. GTL base stocks and base oils are GTL materials of lubricating viscosity that are generally derived from hydrocarbons, for example waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feedstocks. GTL base stock(s) include oils boiling in the lube oil boiling range separated/fractionated from GTL materials such as by, for example, distillation or thermal diffusion, and subsequently subjected to well-known catalytic or solvent dewaxing processes to produce lube oils of reduced/lower pour point; wax isomerates, comprising, for example, hydroisomerized or isodewaxed synthesized hydrocarbons; hydro-isomerized or isodewaxed Fischer-Tropsch ("F-T") material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydroisomerized or isodewaxed F-T hydrocarbons or hydroisomerized or isodewaxed F-T waxes, hydroisomerized or isodewaxed synthesized waxes, or mixtures thereof.

[0040] GTL base stock(s) derived from GTL materials, especially hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax derived base stock(s) are characterized typically as having kinematic viscosities at 100° C. of from about 2 mm²/s to about 50 mm²/s, preferably from about 3 mm²/s to about 50 mm²/s, more preferably from about 3.5 mm²/s to about 30 mm²/s, as exemplified by a GTL base stock derived by the isodewaxing of F-T wax, which has a kinematic viscosity of about 4 mm²/s at 100° C. and a viscosity index of about 130 or greater. The term GTL base oil/base stock and/or wax isomerate base oil/base stock as used herein and in the claims is to be understood as encompassing individual fractions of GTL base stock/base oil or wax isomerate base stock/base oil as recovered in the production process, mixtures of two or more GTL base stocks/base oil fractions and/or wax isomerate base stocks/base oil fractions, as well as mixtures of one or two or more low viscosity GTL base stock(s/base oil fraction(s) and/or wax isomerate base stock(s/base oil fraction(s) with one, two or more high viscosity GTL base stock(s/base oil fraction(s) and/or wax isomerate base stock(s/base oil fraction(s) to produce a bi-modal blend wherein the blend exhibits a viscosity within the aforesaid recited range. Reference herein to Kinematic Viscosity refers to a measurement made by ASTM method D445.

[0041] GTL base stocks and base oils derived from GTL materials, especially hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax-derived base stock(s), such as wax hydroisomerates/isodewaxates, which can be used as base stock components of this invention are further characterized typically as having pour points of about 5°C or lower, preferably about 10°C or lower, more preferably about 15°C or lower, still more preferably about 20°C or lower, and under some conditions may have advantageous pour points of about -25°C or lower, with useful pour points of about -30°C to about -40°C or lower. If necessary, a separate dewaxing step may be practiced to achieve the desired pour point. References herein to pour point refer to measurement made by ASTM D97 and similar automated versions.

[0042] The GTL base stock(s) derived from GTL materials, especially hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax-derived base stock(s) which are base stock components which can be used in this invention are also characterized typically as having viscosity indices of 80 or greater, preferably 100 or greater, and more preferably 120 or greater. Additionally, in certain particular instances, viscosity index of these base stocks may be preferably 130 or greater, more preferably 135 or greater, and even more preferably 140 or greater. For example, GTL base stock(s) that derive from GTL materials preferably F-T materials especially F-T wax generally have a viscosity index of 130 or greater. References herein to viscosity index refer to ASTM method D2270.

[0043] In addition, the GTL base stock(s) are typically highly paraffinic of greater than 90 percent saturates and may contain mixtures of monocyclic paraffins and multicyclic paraffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stocks and base oils typically have very low sulfur and nitrogen content, generally containing less than about 10 ppm, and more typically less than about 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock and base oil obtained by the hydroisomerization/isodewaxing of F-T material, especially F-T wax is essentially nil.

[0044] In a preferred embodiment, the GTL base stock(s) comprises paraffinic materials that consist predominantly of non-cyclic isoparaffins and only minor amounts of cycloparaffins. These GTL base stock(s) typically comprise paraffinic materials that consist of greater than 60 wt % non-cyclic isoparaffins, preferably greater than 80 wt % non-cyclic isoparaffins, more preferably greater than 85 wt % non-cyclic isoparaffins, and most preferably greater than 90 wt % non-cyclic isoparaffins.

[0045] Useful compositions of GTL base stock(s), hydroisomerized or isodewaxed F-T material derived base stock(s), and wax-derived hydroisomerized/isodewaxed base stock(s), such as wax isomerates/isodewaxates, are recited in U.S. Pat. Nos. 6,080,301; 6,090,989, and 6,165,949 for example.

Additives:

[0046] The additives include various commercially available industrial oil components and packages, which may include antiwear, antioxidant, defoamant, demulsifier, detergent, dispersant, metal passivation, and rust inhibition additive chemistries to deliver desired performance.

[0047] The preferred ashless antioxidants are hindered phenols and arylamines. Typical examples are butylated/ocytlated/styrenated/nonylated/dodecylated diphenylamines, 4,4’-methylen bis (2,6-di tert-butylphenol), 2,6-di tert-buty1 p-cresol, octylated phenyl alpha naphthylamine, alkyl ester of 3,5-di tert-butyl 4 hydroxy-
phenyl propionic acid, and many others. Sulfur-containing antioxidants, such as sulfur linked hindered phenols and thiol esters can also be used.

Suitable dispersants include borated and non-borated succinimides, succinic acid-esters and amides, alkylphenol-polyamine coupled Mannich adducts, other related components and any combination thereof. In some embodiments, it can often be advantageous to use mixtures of such above described dispersants and other related dispersants. Examples include additives that are borated, those that are primarily of higher molecular weight, those that consist of primarily mono-succinimide, bis-succinimide, or mixtures of above, those made with different amines, those that are end-capped, dispersants wherein the back-bone is derived from polymerization of branched olefins such as polyisobutylene or from polymers such as other polyolefins other than polyisobutylene, such as ethylene, propylene, butene, similar dispersants and any combination thereof. The averaged molecular weight of the hydrocarbon backbone of most dispersants, including polyisobutylene, is in the range from 1000 to 6000, preferably from 1500 to 3000 and most preferably around 2200.

Suitable detersants include but are not limited to calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates, metal carbonates, related components including borated detersants, and any combination thereof. The detersants can be neutral, mildly overbased, or highly overbased. The amount of detersants usually contributes a total base number (TBN) in a range from 1 to 9 for the formulated lubricant composition. Metal detersants have been chosen from alkali or alkaline earth calcium or magnesium phenates, sulfonates, salicylates, carbonates and similar compounds.

Inhibitors and antiwear additives may be used as needed. Seal swell control components and defoamants may be used with the mixtures of this invention. Suitable defoamants include polydimethyl siloxane and polymeric acid esters.

Various antiwear and/or friction modifiers may also be utilized. Examples include but are not limited to alkylated dithiocarbamates, alkyl phosphate esters, ary phosphate esters, thiophosphates, amine phosphates, and dithiophosphates, alkylated phosphonate esters, aliphatic succinimides, molybdenum compounds, acid amides, and any combination thereof.

**EXAMPLES**

Two embodiment examples were blended and tested for air release using ASTM D3427. These examples were tested at 50°C. for viscosity grades less than ISO viscosity grade 100 and 75°C. for viscosity grades greater than ISO viscosity grade 100.

The statistical analysis used in these examples can be completed with many commercially available software programs. In these examples the modeling was completed using Stat-Ease Design Expert 6.01. Below are some example steps for using Stat-Ease Design expert.

First a central composite design was selected with the number of numerical factors and the number of response factors which in both examples was 1—air release property. For the paper machine oil example the number of numerical factors was two and the hydraulic oil example had 4. Second, the data was inputted into the software in the appropriate columns. Third, the design status and evaluation are viewed to determine the recommended model. If optimizing for a new set of data, it is preferable to add or subtract numerical factors to obtain the best model F-value and R squared. Fourth, a model analysis was completed to determine if any transforms are recommended, view the analysis of the fit summary, complete ANOVA (analysis of variance), and view model diagnostics (Normal plot of residuals, residuals vs. predicted, residuals versus factor, outliers, cook’s distance, leverage, predicted versus actuals, and box-plot for power transforms). Finally, upon finding the most suitable statistical model for the given experiment, the equation and constants are taken from ANOVA “Final equation in terms of actual factors”.

**Example 1**

**Table 5**

<table>
<thead>
<tr>
<th>ISO VG 220 Circulating Oil Formulations in wt %</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>15ON</td>
<td>7.0</td>
<td>7.0</td>
<td>30.0</td>
<td>10.0</td>
<td>35.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600N</td>
<td>48.9</td>
<td>64.0</td>
<td>77.0</td>
<td>75.8</td>
<td>73.0</td>
<td>80.8</td>
<td>52.8</td>
<td>74.0</td>
<td>77.8</td>
<td>47.8</td>
</tr>
<tr>
<td>Bright Stock</td>
<td>48.9</td>
<td>28.8</td>
<td>10.8</td>
<td>19.8</td>
<td>18.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PIB - MW 1300</td>
<td>5.0</td>
<td>10.0</td>
<td>15.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PIB - MW 2200</td>
<td>5.0</td>
<td>10.0</td>
<td>15.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PIB - MW 2500</td>
<td>5.0</td>
<td>10.0</td>
<td>15.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additives</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
</tr>
</tbody>
</table>

**D3427 data** was collected on all blends and input into a statistical analysis software package. A quadratic fit model is the preferred model shown by data analysis. The model F-value is 5.47, suggesting a 10% chance this value would occur due to noise. This model yields the algorithm shown as Eq. 3.

**Eq. 3**
Wherein
A=600 neutral Group II treat rate
B=PIB treat rate
St. Dev. = 0.19
\( R^2 = 0.9011 \)

**[0057]** PIB molecular weight and bright stock treat were not factors included in the model, as they are directly tied to 600 neutral treat rate and PIB treat levels to achieve an ISO 220 viscosity grade.

**[0058]** FIG. 2 is a graph of 600 neutral Group I base stocks plotted against percent air entrainment at 1 minute using ASTM D3427. In FIG. 2, the defined optimum performance area as show by reference numeral 12 cover the range of about 60 to 75 percent 600 neutral Group II content.

**[0059]** FIG. 3 is a graph of predicted versus actual air release values. The predicted values versus actual values profile 13 align well, showing no bias towards either end of the design spectrum.

**[0060]** FIG. 4 is a contour plot of air content at 1 minute of 600 neutral Group I base stocks based on PIB treat rates. The air release contours 14 of FIG. 4 aligns well with FIG. 3, showing improved air release for about 55 wt % to 70 wt % 600 neutral base stock and less than 7 percent PIB.

Example 2

**[0061]** In example 2, an ISO VG 68 lubricant was blended comprised of varying concentrations of 150 neutral, 600 neutral, Polymethylacrylate VI improvers of varying molecular weights (expressed in terms of their viscosity (cSt at 100°C.) in the table below, and a commercially available hydraulic additive oil package.

<table>
<thead>
<tr>
<th>ISO VG 68 Hydraulic Oil Formulations in Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>150N</td>
</tr>
<tr>
<td>600N</td>
</tr>
<tr>
<td>PMA-1600</td>
</tr>
<tr>
<td>PMA-800</td>
</tr>
<tr>
<td>PMA-315</td>
</tr>
<tr>
<td>PMA-170</td>
</tr>
<tr>
<td>Additive</td>
</tr>
</tbody>
</table>

Air release data was collected and input into a statistical analysis software package. A linear fit model is suggested by data analysis. Model F-value=15.46, showing the model is significant, with <0.01% chance that a Model F-value this large could occur due to noise. This linear fit model algorithm is represented by Eq. 4.

\[ T_{in} = 0.084609 + 0.93216E + 0.0370*V + 0.067041 * cSt(40) + 0.031392 * 600N - 0.032042 * PMA \]

\( T_{in} \) is the air content at 1 minute following aeration by ASTM D3427 at 40°C. 66-68.5 cSt@40°C. are added into the model, the cSt@40°C. factor can be considered constant and removed from the analysis. Polymer molecular weight was run in the model but has very low impact, suggesting the implications of that term are already accounted for in the percent of 600 neutral Group II and viscosity index modifiers results that are in the model already.

**[0064]** Diagnostics of the model show there are no problems with data analysis. FIG. 5 is a graph of 600 neutral Group II base stocks plotted against percent air entrainment at 1 minute using ASTM D3427. In FIG. 5, the defined optimum performance area as show by reference numeral 15 cover the range of about 60 to 75 percent 600 neutral Group II content.

**[0065]** FIG. 6 illustrates the same blend study as shown in FIG. 5, with another modeled value, viscosity index, being plotted against the air release performance. Directional improvement in air release properties can be seen with increasing viscosity index. In this example decreasing 600 neutral base stock content tracks with increase in viscosity index.

**[0066]** FIG. 7 is a graph of predicted versus actual air release values. The predicted values versus actual values profile 16 align well, showing no bias towards either end of the design spectrum. Although the examples used all industrial lubricants the relationships can be applied to all lubricants including engine oils.

What is claimed is:
1. A lubricating oil, comprising:
   a) at least one base stock;
   b) at least one thickener;
   c) wherein treat rates of the thickener and base stock are chosen to achieve a favorable air release property by using a relationship between the thickener, lubricant viscosity and viscosity of at least one base stock.
2. The composition of claim 1 wherein the relationship further comprises lubricant viscosity index.
3. The composition of claim 1 wherein the relationship is represented by algorithm:

\[ \text{Air}_{in} = c_1 + c_2 * B + c_3 * c_4 * B^2 + c_5 * B^3 + c_6 * B^4 + c_7 * B^5 + c_8 * B^6 + c_9 * B^7 + c_{10} * B^8 + c_{11} * B^9 \]

Wherein:
- Air\( _{in} \) is the air content at 1 minute following aeration by ASTM D3427.
- c terms are constants that will vary based on type of thickener, type of heavy neutral and co-blending stock, and finished blend viscosity range.
- A=Heavy neutral treating rate
- B=Thickener treating rate
4. The composition of claim 1 wherein the relationship is represented by algorithm:

\[ T_{0.150} = \text{constant} + a \times \text{viscosity index} + b \times (\text{constant}) + c \times (\text{constant}) + d \times (\text{constant}) \]

Wherein:
- \( T_{0.150} \) is the time required to reach 0.1% air following aeration by ASTM D3427
- Constants that will vary based upon type of VI improver, type of heavy neutral and co-blending stock, and finished blend viscosity range.
- A = Viscosity index
- B = Kinematic viscosity at 40° C. of lubricant
- C = Amount of heavy neutral present in blend
- D = Amount of viscosity improvers present in blend

5. The composition of claim 1 further comprising a Group I 600 neutral base stock and a Group I 150 neutral base stock wherein at least 45 percent of the lubricant is the Group I 600 neutral base stock and less than 40 percent of the lubricant is the Group I 150 neutral base stock with a PIB additive to achieve a final viscosity of ISO viscosity grade of 220.

6. The composition of claim 1 further comprising a Group I 600 neutral base stock wherein less than 65 percent of the lubricant is a Group I 600 neutral base stock and greater than 35 percent of the lubricant is a Group I 150 neutral base stock with a PMA additive to achieve a final viscosity of ISO viscosity grade of 68.

7. The composition of claim 1 wherein the relationship further comprises lubricant viscosity index, molecular weight of base stocks, and amount of additional base stocks, and any combination thereof.

8. A method of improving air release in a lubricant comprising:
   a) obtaining at least one base stock
   b) obtaining at least one thickener
   c) blending the base stock and the thickener to create the lubricant wherein treat rates of the base stock and thickener are chosen to achieve a favorable air release property using a relationship between the thickener, lubricant viscosity, and viscosity of at least one base stock;
   d) lubricating with the lubricant.

9. The method of claim 8 wherein the relationship further comprises lubricant viscosity index.

10. The method of claim 8 wherein the relationship is represented by algorithm:

\[ A_{\text{air}, 150} = \text{constant} + a \times \text{viscosity index} + b \times (\text{constant}) + c \times (\text{constant}) + d \times (\text{constant}) \]

Wherein:
- \( A_{\text{air}, 150} \) is the air content at 1 minute following aeration by ASTM D3427
- Constants that will vary based upon type of thickener, type of heavy neutral and co-blending stock, and finished blend viscosity range.
- A = Heavy Neutral Treat rate
- B = Thickener Treat rate

11. The method of claim 8 wherein the relationship is represented by algorithm:

\[ T_{0.150} = \text{constant} + a \times \text{viscosity index} + b \times (\text{constant}) + c \times (\text{constant}) + d \times (\text{constant}) \]

Wherein:
- \( T_{0.150} \) is the time required to reach 0.1% air following aeration by ASTM D3427
- Constants that will vary based upon type of VI improver, type of heavy neutral and co-blending stock, and finished blend viscosity range.
- A = Viscosity index
- B = Kinematic viscosity at 40° C. of Lubricant
- C = Amount of heavy neutral present in blend
- D = Amount of viscosity improvers present in blend

12. The method of claim 8 wherein the lubricant further comprises a Group I 600 neutral base stock and a Group I 150 neutral base stock wherein at least 45 percent of the lubricant is the Group I 600 neutral base stock and less than 40 percent of the lubricant is the Group I 150 neutral base stock with a PIB additive to achieve a final viscosity of ISO viscosity grade of 220.

13. The method of claim 8 wherein the lubricant further comprises a Group I 600 neutral base stock and a Group I 150 neutral base stock wherein less than 65 percent of the lubricant is a Group I 600 neutral base stock and greater than 35 percent of the lubricant is a Group I 150 neutral base stock with a PMA additive to achieve a final viscosity of ISO viscosity grade of 68.

14. The method of claim 8 wherein the relationship further comprises lubricant viscosity index, molecular weight of base stocks, and amount of additional base stocks, and any combination thereof.

15. The method of claim 8 wherein the relationship is quantified through the use of statistical analysis of air release for a defined system of the base stock, the thickener, and the lubricant viscosity.

16. A method of formulating a lubricant comprising:
   a) obtaining at least one base stock
   b) obtaining at least one thickener
   c) blending the base stock and the thickener wherein treat rates of the base stock and thickener are chosen to achieve a favorable air release property using a relationship between the thickener, lubricant viscosity, and viscosity of at least one base stock.

17. The method of claim 16 wherein the relationship further comprises lubricant viscosity index.

18. The method of claim 16 wherein the relationship is represented by algorithm:

\[ A_{\text{air}, 150} = \text{constant} + a \times \text{viscosity index} + b \times (\text{constant}) + c \times (\text{constant}) + d \times (\text{constant}) \]

Wherein:
- \( A_{\text{air}, 150} \) is the air content at 1 minute following aeration by ASTM D3427
- Terms are constants that will vary based upon type of thickener, type of heavy neutral and co-blending stock, and finished blend viscosity range.
- A = Heavy Neutral Treat rate
- B = Thickener Treat rate

19. The method of claim 16 wherein the relationship is represented by algorithm:

\[ T_{0.150} = \text{constant} + a \times \text{viscosity index} + b \times (\text{constant}) + c \times (\text{constant}) + d \times (\text{constant}) \]

Wherein:
- \( T_{0.150} \) is the time required to reach 0.1% air following aeration by ASTM D3427
- Constants that will vary based upon type of VI improver, type of heavy neutral and co-blending stock, and finished blend viscosity range.
- A = Viscosity index
- B = Kinematic viscosity at 40° C. of Lubricant
- C = Amount of heavy neutral present in blend
- D = Amount of viscosity improvers present in blend
lubricant is the Group I 600 neutral base stock and less than 40 percent of the lubricant is the Group I 150 neutral base stock with a PIB additive to achieve a final viscosity of ISO viscosity grade of 220.

21. The method of claim 16 wherein the lubricant further comprises a Group I 600 neutral base stock and a Group I 150 neutral base stock wherein less than 65 percent of the lubricant is a Group I 600 neutral base stock and greater than 35 percent of the lubricant is a Group I 150 neutral base stock with a PMA additive to achieve a final viscosity of ISO viscosity grade of 68.

22. The method of claim 16 wherein the relationship further comprises lubricant viscosity index, molecular weight of base stocks, and amount of additional base stocks, and any combination thereof.

23. The method of claim 16 further wherein the relationship is quantified through the use of statistical analysis of air release for a defined system of the base stock, the thickener, and the lubricant viscosity.

24. The use of at least one high viscosity polymer to improve the air release properties of a lubricant composition.

25. The use according to claim 24, wherein the high viscosity polymer is a polymethacrylate or a polyisobutene.

26. The use according to any one of claims 24 or 25, wherein the amount of high viscosity polymer suitable to achieve the improvement has been predetermined using the relationship represented by algorithm;

\[ \text{Air}_{t_{1, \text{min}}} = c - \log(t) + c_1 \log(B) + c_2 \log(B^2) + c_3 \log(B^3) \]

Wherein:
- \( \text{Air}_{t_{1, \text{min}}} \) is the air content at 1 minute following aeration by ASTM D3427
- \( c_1, c_2, c_3 \) terms are constants that will vary based upon type of thickener, type of heavy neutral and co-blending stock, and finished blend viscosity range.
- \( A \) = Heavy neutral treat rate
- \( B \) = Thickener treat rate

27. The use according to any one of claims 24 or 25, wherein the amount of high viscosity polymer suitable to achieve the improvement has been predetermined using the relationship represented by algorithm;

\[ T_{0.1, \text{vis}} = c - \log(t) + c_1 \log(B) + c_2 \log(B^2) + c_3 \log(B^3) \]

Wherein:
- \( T_{0.1, \text{vis}} \) is the time required to reach 0.1% air following aeration by ASTM D3427
- \( C \) = Constants that will vary based upon type of VI improver, type of heavy neutral and co-blending stock, and finished blend viscosity range.
- \( A \) = Viscosity index
- \( B \) = Kinematic viscosity at 40° C. of lubricant
- \( C \) = Amount of heavy neutral present in blend
- \( D \) = Amount of viscosity improvers present in blend

* * * * *