Work Plan and Methodology

I) Work Plan

Experimental work of this research will be done as per below work plan.

1. Selection of base oil for research work : Two week
2. Testing of physicochemical tests of base oil : 1 month
3. Selection of antioxidant additives : Two week
4. Testing of antioxidant additives for RBOT test : 2 month
5. Testing of antioxidant additives for PDSC test : 2 month
6. Testing of antioxidant additives for IP-48 test : 2 month
7. Testing of antioxidant additives for CEC L 85-T-99 test : 2 month
8. Selection of antiwear additives : Two week
9. Testing of antiwear additives for Four Ball Wear test : 2 month
10. Testing of antiwear additives for HFRR test : 2 month
11. Testing of antiwear additives with UMT : 2 month
12. Selection of antiwear additives : Two week
13. Testing of antiwear additives for Four Ball Wear test : 2 month

II) Methodology

This research work is divided in three parts. Methodology for three parts is as below.

A) Selection and Testing of Base oil

In order to study the structure and performance relation of antioxidants and antiwear additives, first hindered phenolic and aminic antioxidant additives with known chemical structure will be selected from available commercial sources. These additives with known physicochemical properties will be blended with API Group-II base oil.

Selected Base oil will be tested for following parameters.

1. Kinematic Viscosity at 40°and 100°C using ASTM test method D445 [41]
2. Sulphur content by Ultraviolet Fluorescence using ASTM test method D5453 [42]
3. Calculation of Carbon Distribution and Structural Group Analysis by the n-d-M Method using ASTM D 3238 [43]
1. **ASTM D445-12: Kinematic Viscosity**

   *Kinematic viscosity*—a measure of the resistive flow on a fluid under gravity, the pressure head being proportional to the density, of the fluid: for gravity flow under a given hydrostatic head, the pressure head of a liquid is proportional to its density,

   **METHODS:**

   The time is measured in seconds for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer.


   This test method covers the determination of total sulfur in liquid hydrocarbons, boiling in the range from approximately 25°C to 400°C, with viscosities between approximately 0.2 and 10 cSt (mm²/S) at room temperature.

   **METHODS:**

   A hydrocarbon sample is directly injected or placed in a sample boat. The sample or boat, or both, enters into a high temperature combustion tube where the sulfur is oxidized to sulfur dioxide (SO₂) in an oxygen rich atmosphere. Water produced during the sample combustion is removed and the sample is next exposed to ultraviolet (UV) light. The SO₂ absorbs the energy from the UV light and is converted to excited sulfur dioxide. The fluorescence emitted from the excited SO₂ as it returns to a stable state is detected by a photomultiplier tube and the resulting signal is a measure of the sulfur contained in the sample.

Characterization of the various fractions of petroleum can be done by the use of the n.d.M method (n= refractive index, d = density, M= molecular weight. This method enables determination of the carbon distribution and thus indicates the percentage of carbon in aromatic structure (% CA), the percentage of carbon in naphthene structure (% CN), and the percentage of carbon in paraffin structure (% CP).

B) Antioxidant Study
Sterically hindered Phenolic and aminic antioxidants from the major manufacturers (e.g. BASF, Rhein Chemie, Van derbilt, and Chemtura will be selected. Antioxidant additives will be dissolved in the selected base oil and solutions of different molar concentration will be made. These blends will be tested with following test equipments/methods for assessing the performance.

1. Oxidation Induction Time by Pressure Differential Scanning Calorimetry (PDSC) using ASTM standard D6186 [28]
2. Oxidation Stability by Rotating Pressure Vessel using ASTM D 2272 test procedure [44]
5. Oxidation characteristics using BS 2000-48 (IP-48) test procedures. [47]

The test data will be analyzed to build the relation between structure of antioxidant additives and their performance.

The brief introduction of these tests is as below,

Oxidation induction time as determined under the conditions of this test method may be used as an indication of oxidation stability. This test method covers the determination of oxidation induction time of lubricating oils subjected to oxygen at 3.5 MPa and temperature between 130 and 210°C. This test method is faster than other oil oxidation tests, and requires a very small amount of sample.

METHODS:
A small quantity of oil is weighed into a sample pan and placed in a test cell. The cell is heated to a specified temperature and then pressurized with oxygen. The cell is held at a regulated temperature and pressure until an exothermic reaction occurs. The extrapolated onset time is measured and reported as the oxidation induction time for the lubricating oil at the specified test temperature.

This test method utilizes an oxygen pressured vessel to evaluate the oxidation stability of new and in-service turbine oils having the same composition (base stock and additives) in the presence of water and a copper catalyst coil at 150°C.

METHODS:
The test oil, water, and copper catalyst coil, contained in a covered glass container, are placed in a vessel equipped with a pressure gage. The vessel is charged with oxygen to a gauge pressure of 620 kPa, placed in a constant temperature oil bath set at 150°C, and rotated axially at 100 r /min at an angle of 30° from the horizontal. The number of minutes required to reach a specific drop in gauge pressure is the oxidation stability of the test sample.

Oxidation onset temperature is a relative measure of the degree of oxidative stability of the material evaluated at a given heating rate and oxidative environment of oxygen; the higher the OOT value the more stable the material. The OOT values can be used for comparative purposes and are not an absolute measurement, like the oxidation
induction time (OIT) at a constant temperature. The presence or effectiveness of antioxidants may be determined by these test methods.

4. **CEC-L-85-T-99**:
   The CEC L-85-T-99 pressure differential calorimetry (PDSC) test was developed in Europe for ACEA E5 specification for heavy duty diesel oils. This test differentiate between base oils, additives, indicates synergies between antioxidants and correlates with other oxidation tests. This tests the measures the oxidation onset temperature on small quantity of sample in pressure DSC cell. This gives relative oxidation effectiveness of antioxidants.

**METHODS:**
2mg of sample is heated between 50° and 210°C then held at that temperature for up to 2 hour in a closed system at 100 psi (6.9 bar) overpressure. The oxidative Induction time, expressed in minutes, is the onset time observed from achieving the isothermal temperature.

This test method indicates the tendency of lubricating oil to deteriorate on oxidation under specified conditions. A measure of the deterioration is obtained by comparison of the viscosity and carbon residue before and after oxidation. The test is not suitable for additive-type oils (other than those containing ash less additives) or those which form solid products or lose more than 10% by evaporation during the test.

The peak area increase (PAI) is representative of the quantity of all the compounds containing a carbonyl function that have formed by the oxidation of the lubricant (aldehydes, ketones, carboxylic acids, esters, anhydrides, etc.). The PAI gives representative information on the chemical degradation of the lubricant which has been caused by oxidation.
METHODS:
FT-IR spectra of the fresh and the used oils are recorded in a transmission cell of known pathlength. Both spectra are converted to absorbance mode and then subtracted. Using this resulting differential spectrum, a baseline is set under the peak corresponding to the carbonyl region around 1650 cm$^{-1}$ and 1820 cm$^{-1}$ and the area created by this baseline and the carbonyl peak is calculated. The area of the carbonyl region is divided by the cell pathlength in mm and this result is reported as peak area increase.

C) Antiwear & EP additives

Different antiwear and extreme pressure additives of sulphur compounds, sulphur – nitrogen compounds, phosphorus-nitrogen compounds, Nitrogen compounds will be selected from various commercially available sources (such as BASF, Rhein Chemie, Van derbilt, Chemtura, Arkema, Elco, etc). These will be blended with different base oils in various treat levels. These blends will be tested for

1. Wear preventive characteristics on four ball wear test apparatus as per ASTM D4172 [49]
2. Extreme pressure performance as per ASTM D2783 [50]
3. Antiwear performance using Universal material Tester (UMT)
4. Antiwear performance using High Frequency reciprocating rig (HFRR) [51],

Data collected will be analyzed for establishing structure performance relation in selected additives.


This test method covers a procedure for making a preliminary evaluation of the anti-wear properties of fluid lubricants in sliding contact by means of the Four-Ball Wear Test Machine.

METHODS:
Three steel balls are clamped together and covered with the test lubricant. A fourth ball is pressed with a force of 147 or 392 N into the cavity formed by the three clamped balls for three-point contact. The lubricant temperature is maintained at 75°C, and the fourth ball is rotated at 1200 r/min for 60 min. Lubricants are compared by using the average size of the scar diameters worn on the three lowered clamped balls.


This test method is used for specification purposes, differentiates between lubricating fluids having low, medium, and high levels of extreme pressure properties. Two determinations are made: load-wear index, and weld point by means of four-ball extreme pressure tester.

METHODS:
The tester is operated with one steel ball under load rotating against three steel balls held stationary in the form of a cradle. Test lubricant covers the lower three balls. The rotating speed is 1760 ± 40 r/min. The machine and the lubricant are brought to 65–95°F and then a series of tests of 10-s duration are made at increasing loads until welding occurs.

7. Universal Material Tester (UMT)

The UMT Tribometer is specifically designed for comprehensive macro-mechanical tests of lubricants, metal and ceramic materials, with a load range of 0.1N to 1kN. It performs automated synchronized control of several specimen motions with linear speeds from 0.1µm/s to 30m/s, and angular speeds ranging from 0.001 to 7,000rpm. All motions are independently programmable (for custom wear tracks), and automatic coefficient of friction versus load/velocity curves are generated (tribological finger print).

8. ASTM D6079-11: Standard Test Method for Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig (HFRR)

A 2-mL test specimen of fuel is placed in the test reservoir of the HFRR and adjusted to either of the standard temperature 60°C. When the sample temperature has
stabilized, a vibrator arm holding a nonrotating steel ball and loaded with a 200-g mass is lowered until it contacts a test disk completely submerged in the fuel. The ball is caused to rub against the disk with a 1-mm stroke at a frequency of 50 Hz for 75 min. Then the ball is removed from the vibrator arm and cleaned. The dimensions of the major and minor axes of the wear scar are measured under 100 magnification and recorded.