CHAPTER - 3

MATERIALS AND METHODS

This chapter deals with the used lubricating oil, its characterization, the treatment methods, testing of very pertinent properties and the blending of additives to restore the quality of recycled lubricating oils in order to make it fit for further applications.

The samples of used lubricating oils were collected from Aligarh Auto Centre, Near New Bus Stand, Aligarh and Hero Honda Workshop, Marris Road, Aligarh. To carry out this research work, various solvents and chemicals of fine quality and purity were used. The main chemicals are n-Hexane, 2-Propanol, 1-Butanol, Keiselguhr, Sodium hydroxide Pellets, Conc. Hydrochloric acid, Fuller’s Earth, Methyl ethyl ketone, Methyl iso butyl ketone, Conc. Sulphuric acid, Zincdithiophosphate, Molybdenum disulfide and Polyisobutylene.

3.1 EXPERIMENTAL METHODS

First of all the used lubricating oils from various sources were characterized in order to ensure their characteristics. For this purpose, these were subjected to various tests like flash point, ash content, viscosity and viscosity index, pour point, total acidity, inorganic acidity, saponification number and copper corrosion test.
3.1.1 Physico-Chemical Characteristics

The following physico-chemical characteristics have been studied during the present experimental research work:

3.1.1.1 Flash Point

Flash point is the lowest temperature at which application of test flame causes the vapour above the oil to ignite. Flash point measures the tendency of the fuel to form a flammable mixture with air under controlled laboratory conditions.

Procedure: The flash point of the samples (used engine oil, gear oil, compressor and hydraulic oils) was determined by using Cleveland (open) cup method. The sample was poured in the test cup. The temperature of the sample was increased fairly rapidly at the initial stage and then at a slow constant rate as the flash point of the sample approached (at specified intervals). After this, small test flame was passed across the cup. The lowest temperature at which application of the test flame caused the vapors above the surface of the liquid to ignite momentarily was taken as the flash point. It is very important property of a pet. product as it gives indication of vaporization. Higher flash point hydrocarbons/ pet. products catch the fire with difficulty when ignited. So it is important w.r.t. safety aspects.

3.1.1.2 Ash Content

Ash can result from oil, water-soluble metallic compounds, or extraneous solids, such as dirt and rust. The Knowledge of the amount of a product’s ash forming material can provide information on whether the product is suitable for use in a given application.
Procedure: The silica crucible was heated at 800°C for 10 minutes and cooled to room temperature in a suitable container not containing a desiccating agent and weighted to the nearest 0.1 mg. The sufficient sample of oil was weighted into the crucible to give approximately 20 mg of ash. The sample in the crucible was heated until the contents became capable of being ignited with a flame and maintained at such a temperature to burn the sample at a uniform and moderate rate until only ash and carbon was left when the burning ceased. The residue was incinerated in a muffle furnace at 800°C until all carbonaceous material disappeared. Thereafter; it was cooled in the crucible to room temperature and weighed to the nearest 0.1 mg. The heating and weighing of crucible containing ash was repeated until consecutive weightings did not differ by more than 0.5 mg.

The weight of the ash was calculated as a percentage of the original of the sample as follows:

\[
\text{The ash percent (by weight)} = 100 \frac{w}{W}
\]

Where; \(w\) = Weight in g of ash, and \(W\) = Weight in g of sample.

3.1.1.3 Viscosity and Viscosity Index

Kinematic viscosity is the measure of the resistance to gravity flow of a fluid. The pressure head is proportional to the density. The time of flow of a fixed volume of fluid is directly proportional to its kinematic viscosity. The unit of kinematic viscosity is stoke. Kinematic viscosity may be measured as an absolute property of the fuel, or alternately as a conventional property that is
dependent on the instrument and the method used. Viscosity index is the most widely used way of characterizing the effect of change of temperature on the viscosity of any oil.

**Procedure:** The viscosity index was calculated by Redwood Viscometer No.1. It comprises a sample cup fitted with a standard-sized orifice in the base and surrounded by a water jacket containing a heating device. When the temperature reaches the test level, the orifice is unsealed a heating device. When the temperature reaches the test level, the orifice is unsealed and the time of flow is determined for 50ml volume of the sample. The viscosities of lubricating oils were determined by Red Wood Viscometer No.1 at 40°C and 100°C. Viscosity index were calculated by the following formula:

\[ \text{Viscosity index} = \left[ \frac{L-U}{L-H} \right] \times 100 \]

Where;  
\( L \) = Kinematic viscosity at 40°C of an oil of 0 viscosity index  
\( U \) = Kinematic viscosity at 40°C of the oil whose viscosity index is to be calculated.  
\( H \) = Kinematic viscosity at 40°C of an oil 100 viscosity index

3.1.1.4 Pour Point

Pour point is a well-established test to estimate the temperature at which a sample of oil becomes sufficiently solid to prevent its movement. It is the lowest temperature expressed in multiple of 3°C at which the oil is observed to flow when cooled and examined under prescribed conditions. The pour point
temperature depends to a large extent on the thermal history of the sample. Also, the pour point indicates the waxy nature of the oils.

**Procedure:** The pour point of the lubricating oils, are important properties related with the flow of lube oil. The oil sample was poured into the test jar to the specified level and closed with the cork fitted with the thermometer. The position of the cork and thermometer was adjusted so as the cork was fitted in tightly and the thermometer and the jar were coaxial, moreover, the thermometer bulb was immersed so that the beginning of the capillary was 3 mm below the surface of the oil. The disk was placed in the bottom of the jacket and ring gasket around the test jar, 25mm above the bottom. The disc, gasket, and inside of the jacket should be clean and dry. The test jar was inserted in the jacket. The bath temperature was maintained at -1°C to +2°C. After the oil was cooled enough to allow the formation of paraffin wax crystals, great care is to be taken to disturb the mass of the oil nor permit the thermometer to shift in the oil; Any disturbance of the spongy network of wax crystals, will lead to low and fictitious results. Beginning at a temperature 9°C above the expected pour point in case of oils with pour point above 39°C and for other oils at a temperature 12°C above the expected pour point, at each test thermometer reading which was a multiple of 3°C, the jar was removed from the jacket carefully and was tilted enough to ascertain whether there was a movement of the removal and replacement should not take more than 3 seconds. If the oil has not ceased to flow when it has been cooled to 9°C, the test jar has to be transferred to another jacket in a second bath maintained at a temperature of -18 to -15°C. If the oil has not ceased to flow when it has been cooled to -6°C , the jar has to be transferred to another jacket in a third bath maintained at a temperature range of -35 to -32°C. The test is continued in this manner until a point reached at which
the oil in the test jar shows no movement when the test jar was held in a horizontal position for exactly 5 seconds. The accurate temperature with the help of the test thermometer was recorded and 3°C was added to this temperature as the pour point.

3.1.1.5 Total Acidity

New and used petroleum products may contain acidic constituents present as additives or as degradation products, such as oxidation products, formed during service. Total acidity is a measure of the combined organic and inorganic acidity. Total acidity is an indication of the corrosive properties of the product.

**Procedure:** In total acidity, toluene 60 ml and alcohol 40 ml were neutralized using alkali-blue solution as an indicator with alcoholic potassium hydroxide (KOH) solution. This mixture was added to approximately 10 g of sample was completely dissolved until the colour of the mixture turned purple blue. It was titrated with KOH and at the end-point, the purple blue colour changed to red colour comparable to that of 10% solution of cobalt nitrate. The total acidity was calculated from the following formula:

\[
A_T = \frac{56.1 \times [N \times V]}{W}
\]

Where;

- \( A_T \) = Total acidity in mg potassium hydroxide / g of sample
- \( V \) = Volume of potassium hydroxide solution in ml,
- \( N \) = Normality of the potassium hydroxide solution,
3.1.1.6 Inorganic Acidity

Inorganic acidity is a measure of the mineral acid present. Organic acidity is obtained by deducting the inorganic acidity from the total acidity.

**Procedure:** 25 g of the sample was diluted with 75 ml toluene and thereafter 100 ml boiled distilled water was added. The mixture was then heated for 15 min followed by cooling. The inorganic acidity was calculated from the following formula:

\[
\text{Inorganic Acidity} = 4.5 \times N \times T
\]

Where; \( N \) = Normality of potassium solution,

\( T \) = Volume of potassium hydroxide solution in ml

3.1.1.7 Saponification Number

**Procedure:** A known weight of the sample was dissolved in 25 ml methyl ethyl ketone and heated for 30 min with 25 ml of 0.1 N alcoholic potassium hydroxide. Thereafter, 50 ml of naphtha was added immediately and the solution was titrated with 0.1N hydrochloric acid using neutralized phenolphthalein as indicator. The blank reading was taken without using oil sample. The saponification value was calculated from the following formula:

\[
\text{Saponification Number} = \frac{56.1 \times N \times (V_1 - V_2)}{W}
\]

Where; \( N \) = Normality of the hydrochloric acid,

\( V_1 \) = Volume in ml of acid used in titrating blank,
$V_2 =$ Volume in ml of acid in titrating the sample,
$W =$ Weight of the sample in grams

3.1.1.8 Copper Corrosion Test

Petroleum products contain sulphur compounds, most of which are removed during refining. Of the sulphur compounds remaining in the petroleum products, however, some can have a corroding effect on various metals. The corrosivity is not necessarily directly related to the total sulphur content. The effect can vary according to other chemicals and types of sulphur compounds present. This test serves as a measure of possible difficulties with copper, brass or bronze parts of the fuel systems.

Procedure: A cleaned and smoothly polished copper strip is immersed in a given quantity of sample, which is then maintained at the specified temperature for the specified length of time. The strip is removed from sample, washed with aromatic and sulphur free petroleum spirit and examined for evidence of etching, pitting or discoloration it is then compared with ASTM copper-strip corrosion standard colour code. The classification code indicates that the numbers 1, 2, 3 and 4 designate slight tarnish, moderate tarnish, dark tarnish and corrosion, respectively.

3.2 RECLAMATION OF USED LUBRICATING OILS

Used lubricating oils were collected from different local garages and service stations in Aligarh city and mixed in a single container. Used lubricating oil was stored for seven days to allow large suspended particles to settle under gravity. As the samples were obtained from many locations, it was assumed that it could represent a typical feedstock for recycling the used lubricating oil. Used
oils (engine, gear, compressor and hydraulic) were regenerated by physical as well as chemical methods e.g. dehydration, solvent treatment, clay treatment and filtration. Different additives were blended in sufficient amount to prepare finished oils of different grades. The whole procedure of the regeneration of used oils has shown in a flow diagram.

3.2.1 Reclamation of Used Engine Oils

3.2.1.1 Dehydration

Used engine oils were taken in a two-necked round bottom flask equipped with arrangements for heating and stirring under vacuum. The used lubricating oils were heated at 100°C for one hour to remove water. After dehydration, the temperature was raised to 250°C to remove light ends and after their removals; the dehydrated oils were allowed to cool to room temperature and filtered.

3.2.1.2 Solvent Treatment

The dehydrated oils thus obtained were then solvent treated with 1-butanol using 50 percent and 60 percent (v/v) at room temperature with constant stirring for 30 min. and centrifuged. The solvent treated oils were also allowed to settle over night after 24 h, solvent sludge was removed and supernatant solvent treated oils were recovered.

3.2.1.3 Clay Treatment and Filtration

To prepare different samples, the solvent treated oils were heated under vacuum with constant stirring to 100°C and the fuller’s earth was added in 8 to 10 percent (w/v) for 50 and 60 percent solvent treated oils and then the temperature
was raised to the bleaching temperature (250°C, 280°C and 300°C ). Thereafter, the clay treated oils were allowed to cool and filtered.

3.2.2 Reclamation of Used Gear Oils

3.2.2.1 Dehydration

Used gear oils were subjected to dehydration for removal of water at 100°C under vacuum with constant stirring for one hour and then allowed to cool to room temperature and then filtered.

3.2.2.2 Solvent Treatment

The dehydrated oils thus obtained were then solvent treated with 1-butanol solvent using 30 to 50 percent (v/v) at room temperature with constant stirring for 30 min. The solvent treated oils were allowed to settle overnight. After 24 h solvent sludge was removed and supernatant solvent treated oils were recovered.

3.2.2.3 Clay Treatment and Filtration

Solvent treated oils were heated under vacuum to 100°C and the fuller’s earth was added in 4 to 6 percent (w/v). The temperature was raised to 300°C for 30 min then cooled and filtered.
3.2.3 Reclamation of Used Compressor Oils

3.2.3.1 Dehydration

Used compressor oils were dehydrated at 100°C for removal of water under vacuum with constant stirring for 1 h, thereafter, the oil was allowed to cool at room temperature and filtered to remove impurities.

3.2.3.2 Solvent Treatment

Dehydrated oils thus obtained were solvent treated with 1-butanol using solvent 30 to 40 percent (v/v) at room temperature with constant stirring for 30 min. The solvent treated oils were then allowed to settle overnight. After 24 h, solvent sludge was removed and supernatant solvent treated oils were recovered.

3.2.3.3 Clay Treatment and Filtration

Solvent treated oils were heated under vacuum to 100°C and the fuller’s earth was added in 4 to 6 percent (w/v). The temperature was raised to 200°C and the oil was bleached at this temperature for 30 min. After bleaching, the oil was cooled and filtered.

3.2.4 Reclamation of Used Hydraulic Oils

3.2.4.1 Dehydration

Used hydraulic oils were subjected to dehydration for removal of water at 100°C under vacuum with constant stirring for 1h and then allowed to cool to room temperature and filtered.
3.2.4.2 Solvent Treatment

Dehydrated oils thus obtained were then solvent treated with 1-butanol using solvent 30 to 50 percent (v/v) at room temperature with constant stirring for 30 min. The solvent treated oils were allowed to settle overnight. After 24 h, solvent sludge was removed and supernatant solvent treated oils were recovered.

3.2.4.3 Clay Treatment and Filtration

Solvent treated oils were heated under vacuum with constant stirring to 100°C and the fuller’s earth was added in 4 to 6 percent (w/v). The temperature was raised to 250°C and the oil was bleached at this temperature for 30 min and then cooled thereafter, the oil was filtered.

3.2.5 Blending of Additives

Different percentages of additives were blended in such proportion which could result in yielding the reclaimed and blended lubricating oils so as they meet their respective Indian specification. Sufficient amount of Zincdithiophosphate, Polyisobutylene and Molybdenum disulfide was blended in suitable base stocks to prepare different mono and multigrade of engines oils for automotive purposes.

3.2.6 Percent Sludge Removal

The percent sludge removal represents the quantity of dry sludge removed from the used oil after mixing with solvent. The sample of used oil is mixed with the solvent in a test tube for 25 minutes under continuous stirring (400- 430 r.p.m.).
The steps consist of removing the sludge from the bottom of the settling flask after the settling period has lapsed into a weighted glass tube. First the separated sludge is redispersed by adding 10 cm³ of 2-propanol which immediately produces large flakes. After 24 hr of gravity settling, the liquid is discarded using vacuum filtration and the bottom sludge cake was collected. The washed sludge is then placed into an oven for 20 minutes at 100°C for drying purposes. The hot dry sludge is then cooled to room temperature and weighted \( W_2 \). The percent of sludge removal can then be calculated as follows.

\[
\text{PSR} = \frac{W_2}{W} \quad (1)
\]

where \( W \) is the mass of used oil in the solvent/oil mixture.

3.2.7 Percentage Oil Losses

The oil loss represents the amount of oil that did not dissolve in the solvent but rather settles with the sludge but rather settles with the sludge. Percent oil loss is defined as the amount of oil in sludge phase per 100 grams of used oil. This factor was calculated from the same washing process stated above and calculated as follows.

\[
\text{POL} = \frac{(W_1 - W_2)}{W} \quad (2)
\]
3.3 EQUIPMENTS USED IN RECLAMATION OF LUBRICATING OILS

[Redwood Viscometer]

Manufactured by: S.M. Scientific Instruments (P) Ltd, Delhi-92
[Redwood Viscometer]

Manufactured by: S.M. Scientific Instruments (P) Ltd, Delhi-92
[Cleveland (Open) Cup]

Manufactured by: D. K. Scientific Industries, Ahmedabad, Gujarat,
[Colorimeter]

Manufactured by: R. K. Scientific & Engineering Works, Roorkee
[Portomin Deluxe Centrifuge]
Manufactured by: R. K. Scientific & Engineering Works, Roorkee
[Copper Strip Corrosion Apparatus]
Manufactured by: Petroleum Instruments (India) Pvt. Ltd., Calcutta - 13
[Oven]

Manufactured by: S.M. Scientific Instruments (P) Ltd, Delhi-92
[Motorized Oil Test]
Manufactured by: Rectifiers and Electronics Instruments Pvt. Ltd., New-Delhi
[Rust Preventive Tester]

Manufactured by: Petroleum Instruments (India) Pvt. Ltd., Calcutta - 13
[Experimental Set-up]
3.3.1 Parts of experimental set-up

**Apparatus** - The experimental apparatus consisted of a glass flask heated by suitable means and provided with a reflux condenser discharging into a trap and connected to the flask. The connections between the trap and the condenser and the flask should be interchangeable ground glass joints. The trap serves to collect and measure the condensed water and to return the solvent to the flask. The various components are described below:

a) **Flask** - A 250 to 500 ml flasks made of hard resistance glass, well annealed was used during this research work.

b) **Condenser** - A glass made water - cooled reflux type condenser was used during this research work.

- Socket - 24/29
- Cone - 24/29
- Effective length - 200 mm

c) **Receivers Adapter** - otherwise called the trap, made of hard resistance glass, well annealed provided with ground glass joints.

- Socket - 24/29
- Cone - 24/29

d) **Thermometer Mercury filled** - Range 0- 360°C
Fig 3.1 Flow diagram of Reclamation of Used Lubricating Oils