

RECLAMATION OF USED LUBRICATING OILS

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Abstract

An experimental analysis was carried out by treatment of used hydraulic oil with various concentrations of fullers' earth and the results obtained were compared with fresh oil. Properties tested for include viscosity, specific gravity, absorbance and wear metals. The results obtained showed an improvement in the depleted quality of oil; in particular the viscosity falls within $\pm 15\%$ tolerance of the fresh oil value as recommended by ASTM standards. It is recommended that the reclaimed oil obtained should be re-blended with additive or fresh oil in a pre-determined ratio using ASTM blending chart for further enhancement of additive content. It is concluded that reclamation of used oil is an environmentally friendly way of dispersing waste oils which can serve as a waste to wealth method.

Key words: reclamation; absorbance; ASTM; kinematic viscosity; additive; organometallic compounds; Spectrophotometer; infra-red spectrum; transmittance; frequency; wear metals analysis.

1. Introduction

1.1 Background

The quality of the environment has been adversely affected by the activities of the petroleum industry right from the exploration, drilling, transportation and processing to storage and after use. Hence, the industry discharges waste which comes in gaseous, liquid or solid form into the environment; thus threatening the health of the population and in the long run affecting farmland and water bodies.

In Nigeria, an average of about 300 million liters of lubricating oils is consumed annually with a market potential of 5% annual growth rate. The potential waste oil level is about 80% of the annual consumption and thus the environment is prone to about 240 million liters of used lubricating which requires management and control.

It is also observed that the awareness for waste oil management and its investment potentials are not well accepted and inculcated; rather it is seen as an anti-economic issue and a necessary debt to be paid for industrialization of urban centers. In some cases, it is due to lack of adequate information on cost effective methods of oil management, for example in Canada approximately about 1 billion liters of lubricating oils are sold annually but only about 200 million liters are recovered, in other words more than half is wasted and disposed to the environment [2].

In Nigeria, despite the increase in the presence of Lube oil blending plants (both foreign and local companies), It is quite disappointing to know that the level of recycling oil is low and thus cannot meet up with the requirement of waste oil management as stipulated by the Federal Environmental Protection Agency (FEPA) that: "No oil in any form shall be discharged into public drains, rivers, lakes, seas or underground injection without permit issued by the agency or any organization so designated by FEPA" [2].

Hence it would be a worthwhile investment opportunity to establish oil reclamation plants for commercial purposes all over the country due to the increasing cost of local production and a high import value of new lubricating oils, so that in the long run not only would the environment be safe of pollution but also the overall petroleum reserves would be conserved and there would also be some economic values added through sales of such products via export.

In use, lubricating oils become dirty and contaminated with materials such as organometallic compounds particularly zinc dithiophosphate, other metals, fines, water (as a water-in-oil emulsion), and sludge, that make them useless and harmful; hence requires disposing and draining off or replacement with fresh oil.

However from a survey made, it has been observed that the methods of disposal often practiced include:

- Disposal of lubricant into drains where it eventually finds its way to seas, rivers, thereby causing pollution. The oil layers interfere with the oxygen in the sea, thus deplete the gaseous exchange between it and the atmosphere.
- The used lubricants are sold by companies to individuals who use them for other purposes asides proper reclamation.

1.2 Concept of used oils

Used oils can be referred to as semi-solid or liquid used product consisting totally or partially of mineral oil or synthesized hydrocarbons (synthetic oils), oily residues from tanks, oil-water mixtures and emulsions which arise from industrial sources where they have been used for lubricating, hydraulic, heat transfer, electrical insulating(dielectric) or other purposes and whose original characteristics have changed during use thereby rendering them "unsuitable" for further use for which they were originally intended which is as a result of contaminants or impurities [3].

Used oil primarily contains hydrocarbons; it may also contain additives such as lead and other impurities due to physical contamination and chemical reactions which occur during usage. The nature of the contaminants could be solid, liquid or gaseous; hence they tend to cause changes in the chemical and physical nature of virgin oils. The sizes of solid and liquid dispersion however are measured in micrometers and these particles in these oils can be counted using an automatic photo electronic instrument or a coulter counter [1]. The number and size of particles in fluids has been standardized by the International Standard Organization (ISO).

1.3 Effects of contaminants on lubricating oils

Contaminants can be classified into three, which differ in effects on lubricating oils. However a summary of their effects is shown below.

Table 1: Effects of Contaminants in Oils.

Solid contaminants	Liquid Contaminants	Gaseous Contaminants
Hard solids >3µm	• Promotes oil oxidation	• Causes foaming of oil
• Wear	• Forms sludge	• Promotes corrosion
• Abrasion of metals	• Reduces viscosity of the oil	• Promotes oil oxidation
• Pitting	• Promotes corrosion	• Cavitations in equipment
• Disrupted oil film	• Degrades the additives	
Soft solid <3µm		
• Promotes oil oxidation		
• Promotes acid retention		
• Increases friction		
• Helps to form sludge		

2 Experimental

2.1 Sample of used oil

A quantity of 500ml of used oil obtained from a Toyota forklift was used as sample for the analysis. This type of oil is a vintage hydraulic Oil-32 which is in a family generation of hydraulic oils, meeting the requirements of modern hydraulic output systems in machine parts, pumps, vehicles and other machineries.

2.2 Apparatus

- Laboratory glass wares, water/oil bath, viscometer, hydrometer, hot-plate, fullers' earth, FT-IR Spectrophotometer, HATCH Spectrophotometer, filter cloth, furnace, hydrochloric acid.
- Wear metal reagents: Sodium Bicinchoninate for copper wear, Phenanthroline for iron wear, Diphenyl Carbazide for chromium wear and Zincon for Zinc wear.

2.3 Procedure

- 1) Preliminary investigations of the physical properties of the oil where obtained such as specific gravity [7] measured by ASTM D-1298, color measured by ASTM D-1500,

- water content measured by a visual Crackle test method, viscosity measured by ASTM D-445, infrared spectrophotometry and a check for the wear metal concentrations measured by ASTM E-2412 [8] of the used vintage hydraulic Oil-32 was carried out for comparison with the approved specification of its freshly prepared oil.
- 2) The 500ml of used vintage hydraulic Oil-32 was poured into separate beakers A, B, C, D, and E and allowed to settle for 3 hours. This was done to allow the possible contaminants such as water, dirt, dusts, metal chips, wear particles, packing, gaskets and pipe scales to settle at the bottom of the beaker.
 - 3) The upper layer of the oil was decanted into a conical flask so as to separate the oil from the water and other contaminants which had settled at the bottom of the beaker.
 - 4) The decanted oil was filtered using the filter paper and left for 24hrs, to separate the smaller contaminants in the neighborhood of 10 μm .
 - 5) The filtered oil collected in the test tube was immersed in the oil bath so as to heat up for 45 minutes at 100°C and stirred at 5minutes intervals for agitation.
 - 6) A Visual crackle test procedure was then carried out on the oil sample to test for presence of water. Presence of water gave a popping sound on the hotplate with a presence of vapor bubbles, but its absence simply burnt off the oil [9]. However if water was detected procedure 2 was repeated.
 - 7) A weighted amount of fullers' earth was added to the heated oil forming slurry, starting with 0.05g.
 - 8) The slurry mixture was then filtered on the filter paper and left over night due to its viscous nature. This was done to allow the reclaimed oil seep from the filter cloth leaving the impurities on top.
 - 9) Portions of the sample were taken for digestion (thermal breakdown) in the furnace at temperatures between 550°C-600°C to burn off all organic matter, leaving the minerals alone. The resultant ash was mixed with dilute HCL and then heated again at above temperature. Finally, the mixture for each sample was mixed with distilled water to obtain a standard 50ml solution required for wear metal analysis.
 - 10) The properties of the reclaimed oil as done in procedure 1 were repeated for comparative analysis from the used hydraulic oil and fresh oil.
 - 11) Procedure 1-9 may be repeated if the level of reclamation is not satisfactory by not falling within the allowed tolerance of $\pm 15\%$ on or off the specification of fresh oil as allowed in the industry and International standards (ASTM).
 - 12) Procedure 7-10 were repeated for weighted amounts of fullers earth of 0.0 g, 0.10g, 0.15g, 0.2g to check on level on purity and variation with the physical properties of the reclaimed oil.

3 Results and discussion

3.1 Viscosity and specific gravity analysis

By comparison, the fresh hydraulic oil gave a kinematic viscosity of 32 cSt at 40°C, however the used lubricating oil (Sample A) gave 34.55 cSt. This increase in viscosity was as a result of insoluble contaminants such as organo-metallic compounds and emulsions; it could also be due to deterioration of the oil.

However, it was observed that after filtering the oil for the first time, there was an improvement in kinematic viscosity in sample B i.e. decreases in value from 34.55 cSt to 34.49 cSt and this was as a result of decrease in concentration of contaminants.

As the treatment of used oil progressed from Sample C to sample F, the viscosity of reclaimed oil decreased further from 32.825 cSt to 28.525 cSt. The viscosity profile gave a straight line as shown in Figure 1.

A similar trend was also observed for the kinematic viscosity at 100°C for the used lubricating oil which gave a viscosity of 6.75cSt, compared to the fresh oil at 6.0 cSt. This increase in value was due to reasons mentioned above. A gradual decrease in the viscosity from 6.75 cSt to 5.33 cSt was observed as treatment progressed, this is shown in Figure 1. Hence we can conclude that an inverse relationship existed between the concentration of Fullers' earth and the Kinematics viscosity of the hydraulic oil at 40°C and 100°C.

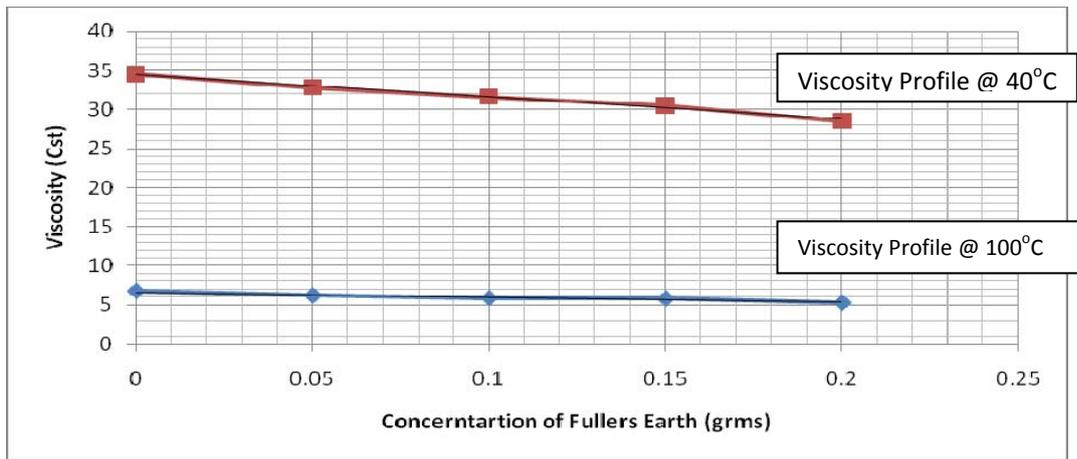


Fig.1 Kinematic viscosity profile at 40°C and 100°C with an increased fullers earth treatment

The used hydraulic oil had a higher specific gravity value of 0.90 compared to the fresh oil with a value of 0.86 at 15°C (reference temp.) This increase was also as a result of presence of contaminants such as water, solids and deterioration of used hydraulic oil. However, with a progress in oil treatment, the specific gravity improved due to gradual attainment of purity as shown in Figure 2, below.

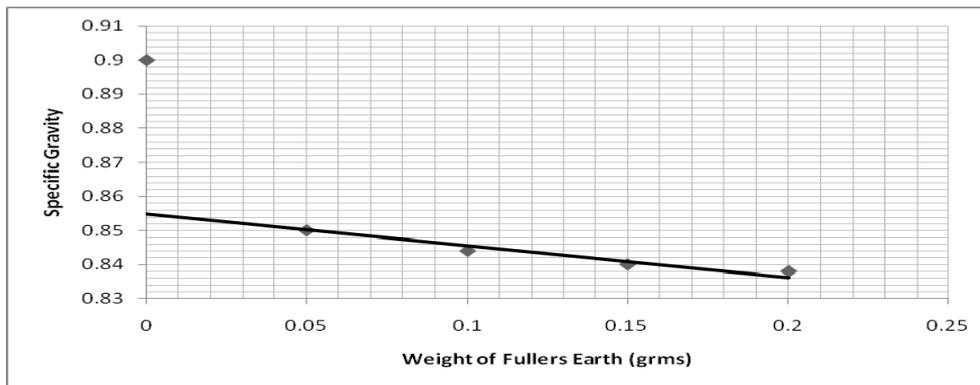


Fig. 2 Specific gravity profile with an increased fuller's earth treatment

3.2 Absorbance analysis

A dark color was observed from the sample of used oil obtained, this could be due to oxidation of the oil, contamination with dirt or contact with darker oils and metal parts; hence this accounted for the higher absorbance when ultra violet light at 510nm was passed through. However, as the treatment begun with an increased weight of fullers' earth, the filtrate became brighter and there was a corresponding reduction in absorbance from 0.77 to 0.18 as shown in Figure 3. From the results, the properties exhibited by the reclaimed oil were expected from theoretical principles.

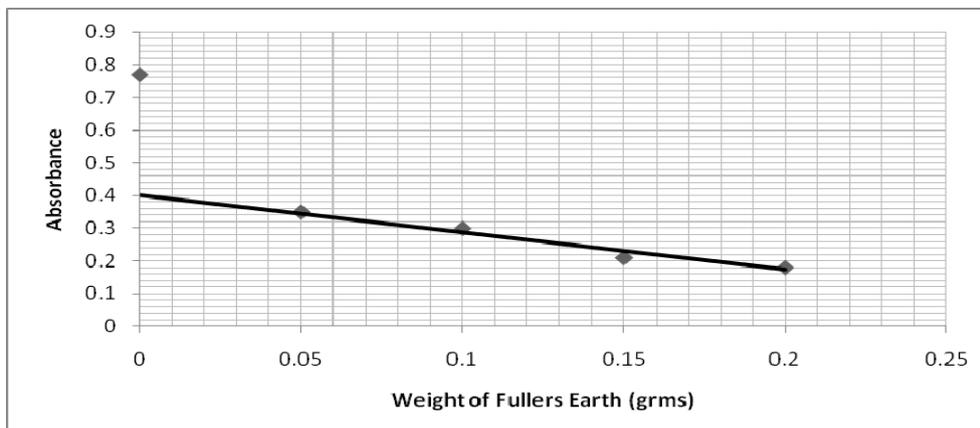


Fig. 3 Aborbance profile of Hydrualic oil with an increased fullers earth treatment

3.3 Spectrophotometry analysis

The spectrophotometric plots for a fresh oil is shown in Figure 4 below, however the samples A to F as shown in Figures 5 to 10 gave similar characteristics with that from the fresh oil in terms of prominent peaks at around vibrating frequencies 2840cm^{-1} to 3000cm^{-1} ; this region indicates the presence of alkanes with Sp -hybridization and C-H absorption bond caused by stretching. Other prominent peaks were seen around 1400cm^{-1} this due to deforming of C-H bonds. [5,6]

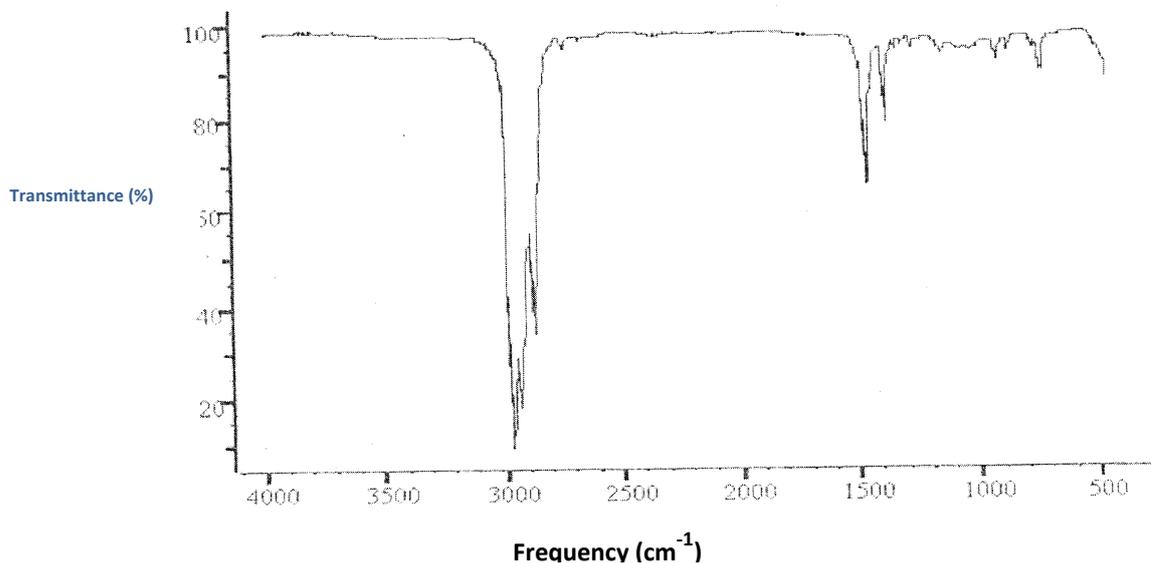


Fig. 4 The Infrared spectrum of a fresh hydraulic oil

However, a closer look at the infrared spectrum for the fresh oil in Figure 4 showed that between the regions of frequencies 3000cm^{-1} to 4000cm^{-1} there existed a relatively straight line; this shows that a 100% transmittance was relatively maintained.

This above characteristic was not evident in samples of used oil analyzed as that region exhibited rough edges. For example in the sample A (used hydraulic oil) shown in Figure 5, there were evidences of peaks around the region 3600cm^{-1} to 3895cm^{-1} due to vibration changes in the molecules of the oil ; these peaks are as a result of presence of impurities such as metals, sand stones etc.

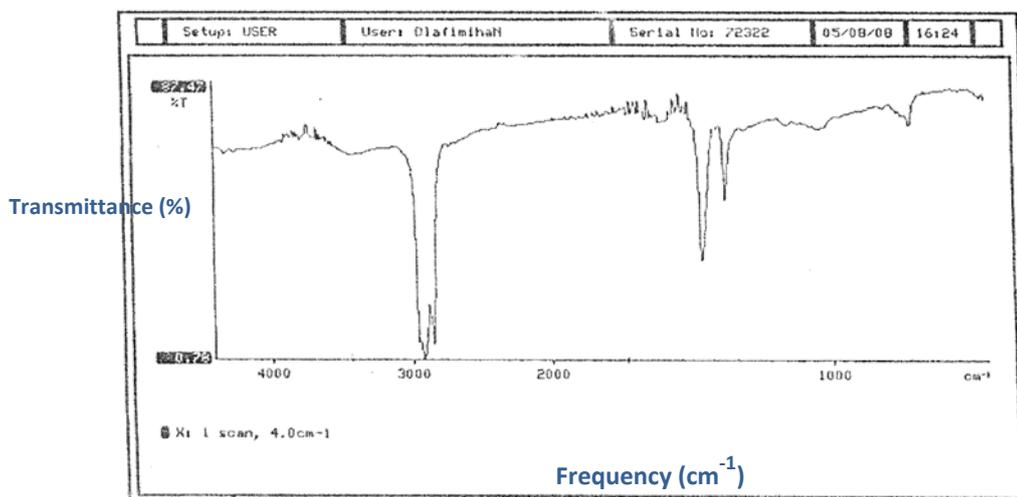


Fig. 5 Infrared spectrum of used hydraulic oil (Sample A)

However, as treatment progressed from samples B to F as shown in the infrared spectrum in Figures 6 to 10, a gradual disappearance of the peaks around the 3600cm^{-1} - 3895cm^{-1} was observed; this was prominent in sample F as shown in Figure 10

Similarly, the region 3400cm^{-1} shows the presence of O-H bonds, thus depicting the presence of water as an impurity in Sample A (used hydraulic oil). As treatment progressed, it gradually disappeared from samples A to F as shown in their respective figures.

It can be deduced that the infrared spectrum for sample F in Figure 10 gave the closest in terms of structure to fresh oil, although there still exist traces of elements of wear metals and moisture which if further treated and blended with additives would be eradicated.

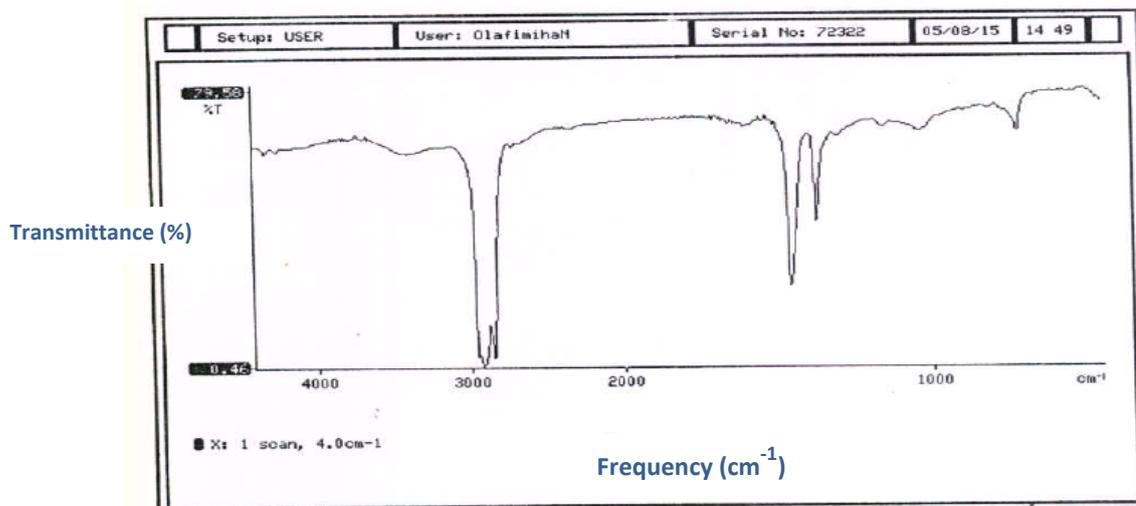


Fig. 6 Infrared spectrum of used hydraulic oil (Sample B)

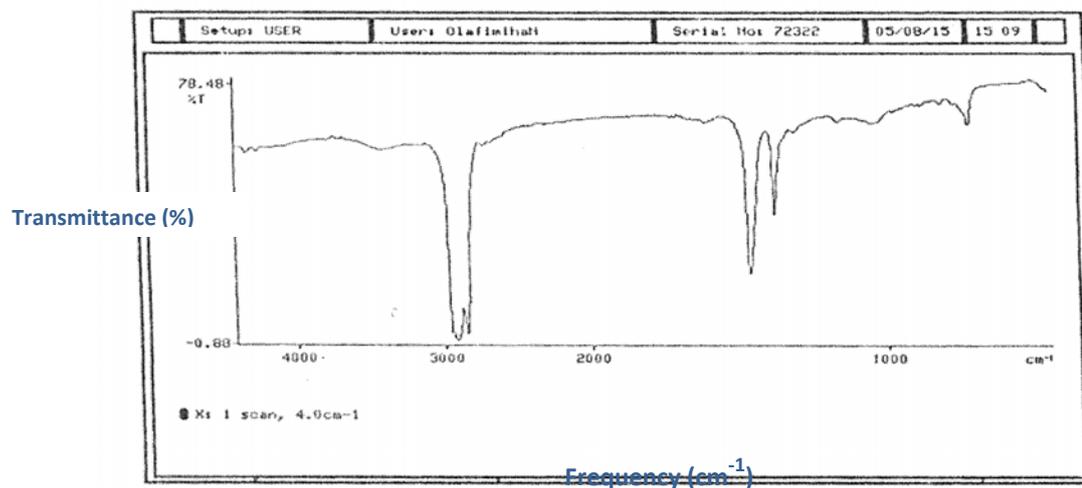


Fig. 7 Infrared spectrum of used hydraulic oil (Sample C)

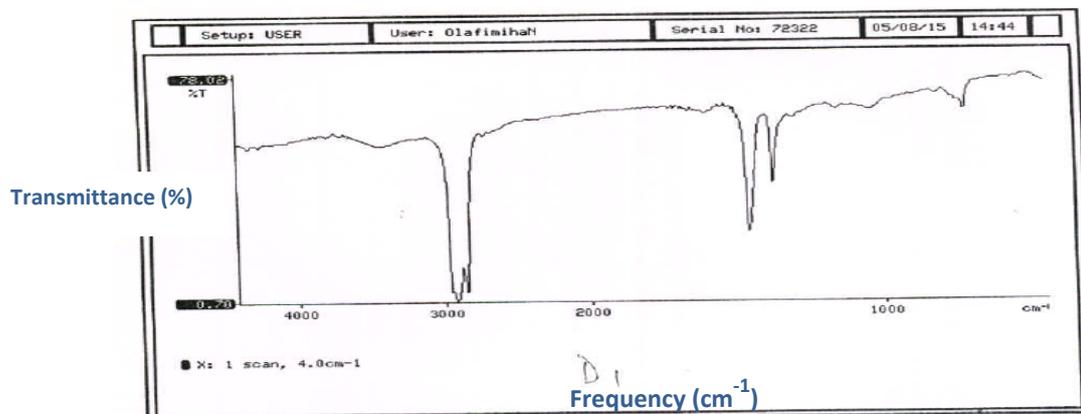


Fig. 8 Infrared spectrum of used hydraulic oil (Sample D)

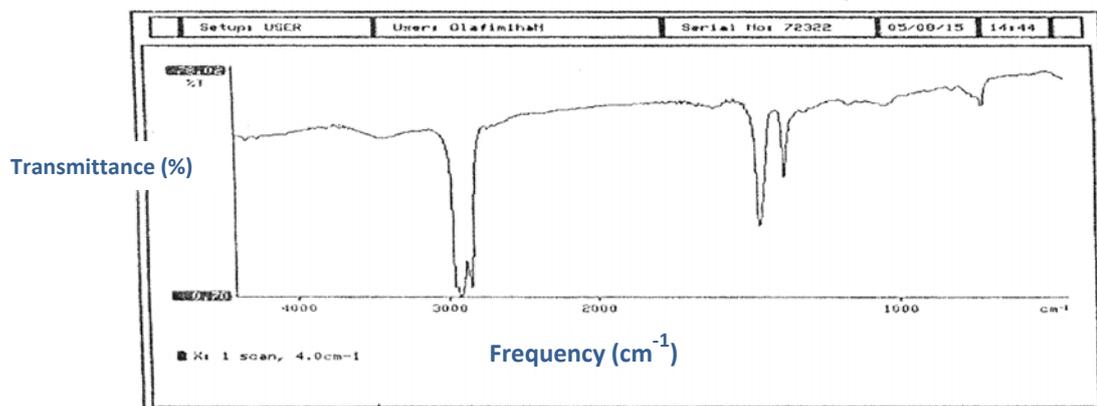


Fig. 9 Infrared spectrum of used hydraulic oil (Sample E)

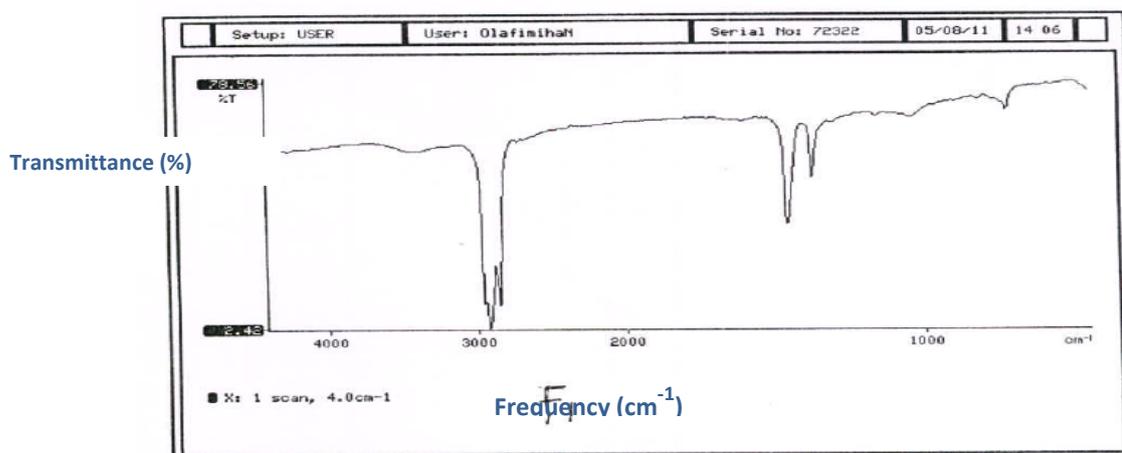


Fig. 10 Infrared spectrum of used hydraulic oil (Sample F)

3.4 Wear metal analysis

The copper wear analysis on the hydraulic oil shown in Figure 11 gave its highest concentration as 6.85ppm. However, as treatment progressed, its concentration reduced from 6.85ppm to 4.32ppm. However, a slight deviation in sample E was observed this could probably be as slight errors during experiment. The presence of copper is as a result of contact of the fresh hydraulic oil with machine parts such as bearings, bushings, air-filter meshes, etc.

The iron wear analysis shown in Figure 11, gave a concentration as high as 30.13ppm. However, as treatment progressed, the concentration reduced sharply to 4.97ppm after filtration and then gradually to 1.29ppm in sample F. A curve was exhibited as a result of a gradual reduction of the iron wear metal from sampled D to F which was 1.47ppm to 1.29ppm. The presence of iron is as a result of contact of the oil with engine parts e.g. piston rings.

For the test of chromium wear, the used oil gave its highest concentration as 0.243ppm. As treatment progressed, it gradually decreased to 0.00ppm. It is evident that treatment totally reduced the chromium wear. However, chromium exists due to contact of the fresh oil with rings, cylinder liners, crankshafts, etc. However, from analysis it is evident that chromium is least present compared to other metals analyzed.

From Zinc wear test, the used oil gave its highest concentration as 1.65ppm. However this was reduced gradually to 0.547 ppm as treatment progressed, thus giving rise to curve. The presence of zinc is as a result of contact of the oil with metal parts of machine.

Finally, from the wear metal analysis, there existed an inverse relationship between the concentration of the metal wear and concentration of fullers' earth treatment. for example in the iron analysis, as its concentration reduced from 30.13 ppm to 1.27 ppm, the concentration of fullers earth increased from 0.0g to 0.20g.

Also, it is important to note that the results from the spectrophotometry analysis obeyed the Beer-Lambert principle, which accounted for higher absorbance values for dark colors (higher intensity) and vice-versa as observed from the experimental data [1].

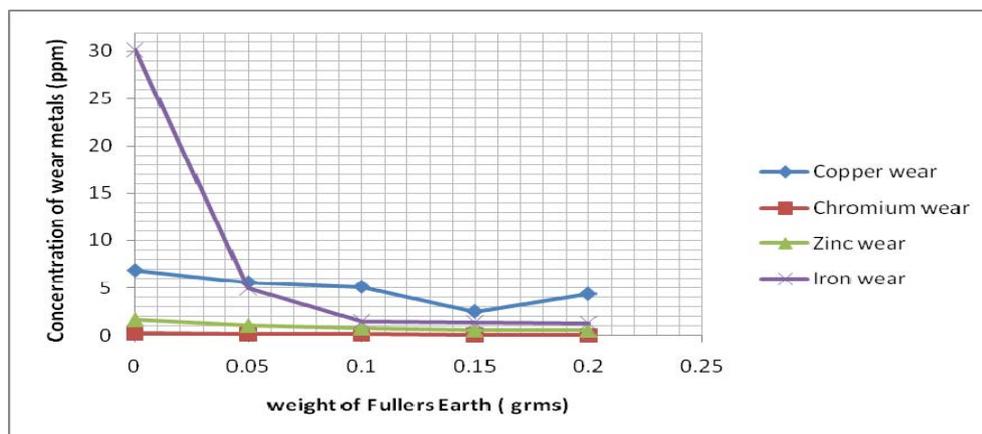


Fig. 11 Wear metal analysis profile with Fuller's earth treatment.

Table 2 Summary of hydraulic oil properties

Property	New Hydraulic Oil	Used oil before treatment (Sample A)	Used oil after treatment (Sample F)
Viscosity @ 40°C (Cst)	32	34.5	28.5
Viscosity @ 100°C (Cst)	6	6.75	5.33
Specific Gravity	0.86	0.90	0.83
Absorbance	0.36 (Clear appearance)	0.77 (Dark appearance)	0.18 (Clear appearance)
Iron wear (ppm)	-	30.13	1.29
Chromium wear (ppm)	-	0.243	0.00
Zinc wear (ppm)	-	1.65	0.54
Copper wear (ppm)	-	6.85	4.32

4 Conclusion

It was shown that an increased concentration of the fullers' earth for treatment of the used lubricating oils improved the viscosity and specific gravity because of the removal of their impurities via adsorption. With further treatment, the clarity of used oil is improved; hence the absorbance when ultra violet light at 510nm passed through it is increased.

From the infrared spectrophotometry, it was established that an increase in fullers' earth concentration helped reduce impurities and wear metals. This claim was further verified using the HATCH spectrophotometer which showed the reduction in their concentrations. Wear metals exists as a result of fresh oil contact with metal parts of various machine. The summary of the physical properties of the fresh and used hydraulic oil sample are shown in Table 2.

Finally, the need for reclamation of used oil should be paramount especially in this part of the world because of its benefits, which include environmental pollution control and management and cost savings for end users.

From comparative analysis obtained, the reclaimed oil properties were lower than those of the fresh oil; this was however expected because of depletion in its additives contents. So, in order to attain an almost 100% fresh state, it would have to re-blended with additives. It is recommended that the reclaimed oil be re-blended with fresh hydraulic oil in a predetermined ratio using an ASTM blending chart.

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