METAL CONCENTRATIONS OF FRESH, USED AND TREATED CRANKCASE OIL

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ABSTRACT

The levels of iron, copper, lead, chromium, barium, zinc and calcium were determined in fresh, used and treated crankcase oil using standard technique. The three methods of treatment used gave different level of metal in the oil. The used sample from diesel engine (lorry) gave a high level of metals than that of gasoline oil (car). Butanol/Hydrocarbon method of treatment gave a relatively low level of iron and copper compared to other two methods (caustic soda/hydrogen peroxide and propanol/butanol) while propanol/butanol gave a very low level of lead. Crankcase oil should not be discharged indiscrimately, recycling is preferable because of its environmental hazard to human beings through bioaccumulation and biotransfer from terresial and aquatic plants and animals.

Keywords: Crankcase, Butanol/Hydrocarbon, Propanol/Hydrogen peroxide, Propanol/Butanol, Environmental.

INTRODUCTION

Waste oils collect contaminant in many ways, depending upon the original use of the oil. In general waste oils contain oxidation products, sediment, water and metallic particles resulting from machine wear. In addition to these, waste automotive oil also contain gasoline fuel, organic and inorganic chemicals used in oil additives and metals which were present in gasoline and transferred to the crankcase during combustion^{1,2}. Lead is the principal metallic contaminant found in waste automotive oils being present in amounts which sometimes exceed 1% by weight².

It is estimated that waste oil generated from automotive and industrial sources in Nigeria at the rate of well over one billion of gallon each year³. Waste oil recovery and possibly its disposal are of interest both for conservation of resources and for protection of the environment, as well as for economic advantages. The advancement in population have led to high levels of industrialization and urbanization which in turn have led to environmental pollution arising from the indiscriminate discharge of industrial effluents. These effluents may contain most common heavy metals, such as Hg, Zn, Cu, Sb, Co, Pb, Cr^{4,5}. It is know that pollution through trace heavy metal has become increasingly more in recent years, not only because people are more sensitive on this subject but also because the amount of pollution has increased markedly. Therefore, there is need for research and public information less these unknown dangers create irreparable environmental damage. Since 1999, thousands of cars, lorries, motor cycles are coming into Nigeria and the numbers of mechanic villages are increasing at a very high rate and the amount of crankcase oil being disposed everyday is enormous.

The source of waste oil are classified primarily by point of generation. The quantity of waste oils generated can be deduced from the data available on number of registered vehicles in Nigeria as shown in Table -1

Other sources of waste oil are from generating plant used in industries to generate power and at home etc. The number of drain depends on the use of the vehicle, Oliver and Anderson⁶ reported that engine oil should be drained after traveling for a distance of between 3,000-5,000 km. From 1999 to this time, it is obvious that the number would have increased at least in more than five folds of this 1995 as a result of population growth and industrial development.

To reduce the environment pollution as a result of indiscriminate disposal of used crankcase oils, this paper report metal concentration of used, virgin and treated crankcase oils. This type of work is important since edible plants, terrestrial and aquatic animals around the mechanic villages have the ability to bioaccumulation and biotransfer harmful minerals to ruminants that serve as protein sources to human beings or direct consumptions of the plants or animals as source of food around the mechanic village. Also, these minerals are soluble in water and it can be transferred through soil by a well or river that are being used directly by human beings.

EXPERIMENTAL

Sampling

Samples of used oil were collected from

two main service stations, used engine oil from gasoline (Car) was collected from mechanical village at Sabo-yaba Lagos labelled 'A'. Sample 'B' was collected at service station, Sango eleyele road, Ibadan, this sample is from heavy duty lorry (Diesel engine). Unused (Virgin) oil Mobil super XHP with engineering designation of SAE 20w50 and API SJ/CF. was obtained from a filling station.

Sample treatment

The used oils were treated by three different methods; Gulick⁷ in which caustic soda and Hydrogen peroxide (30% v/v) were used for the treatment of 'A' and 'B' samples followed by centrifugation and decantation, the product was label A₁ and B₁.

Propanol/Butanol mixture was used to treat another portion of used sample labeled A_2 and B_2 after centrifugation and decantation following the method of Feinman⁸. Also the method of Hess² in which mixture or low boiling point range pentane/Butanol mixture was used to treat another portion of the sample followed by centrifugation and decantation to give sample A_3 and B_3 .

Elemental analysis

2.5 ml of sample was taken using hypodemic syring and dissolve with toluene in 25 ml standard flask. The diluted sample was aspirated into atomic absorption spectrometer. The blank was prepared from the mixture of Hydrocarbon base oil and toluene. The flushing reagent is pure toluene.

| Type of motors | Total no. of vehicles | Estimate of used lubricating oil in Litres/annum |
|--------------------------------|-----------------------|---|
| Saloon cars & Station wagon | 605015 | 3005656 |
| Vans, Pickup & Kt cars | 150072 | 485580 |
| Buses | 110788 | 668560 |
| Lorries, Trucks & Tippers | 52236 | 722280 |
| Trailers Total | 8268 968770 | 165132 575854 |

Table -1: Registered motor vehicles by type (between 1980 – 1995) in Nigeria³

| | Table | e -2: Some metal | determined in th | le -2: Some metal determined in the fresh, used and treated oil samples (ppm) | treated oil samp | les (ppm) | |
|-------------------------------------|---|-------------------|--------------------|---|------------------|------------------|-----------------|
| Sample | Fe | Cu | Pb | Cr | Ba | Zn | Ca |
| 0 | 1.04±0.02 | 0.31±0.02 | 5.70±0.01 | 0.20±0.01 | 604.90±9.01 | 1630.20±1.13 | 1200±0.32 |
| A | 98.95±0.02 | 29.09±0.01 | 604.90±0.01 | 1.27±0.02 | 608.04 ± 9.1 | 1724.19±9.94 | 1300.21±0.04 |
| В | 166.20±0.02 | 30.34±0.01 | 751.80±0.64 | 2.24±0.03 | 701±6.20 | 1801±4.20 | 1380±0.6 |
| , A | 21.09±0.04 | 4.82±0.03 | 105.60 ± 0.03 | 0.66±0.03 | 302.02±0.13 | 809.06±6.02 | 650±0.20 |
| Ē | 86.18±2.01 | 8.21±0.01 | 301.02±6.01 | 1.82 ± 0.01 | 347.05±1.02 | 967.24±1.02 | 732.17±0.61 |
| , e | 44.95±0.60 | 4.51±0.04 | 39.10±0.11 | 1.12±0.11 | 201.03±1.11 | 1001.20 ± 0.04 | 790.00±0.18 |
| 'n | 102.11±0.04 | 9.24±0.05 | 58.77±0.21 | $1.89.09\pm0.06$ | 297.18±0.06 | 997.87±1.11 | 830.72±0.01 |
| ٩. | 17.21±0.02 | 3.48±0.07 | 71.90±0.18 | 0.73±0.01 | 104.03 ± 0.04 | 725.05±0.02 | 200.32 ± 0.05 |
| ്ല് | 75.13±0.01 | 6.33±1.02 | 211.12±1.02 | 1.21±0.01 | 217.97±2.18 | 897.24±0.01 | 380.11±3.12 |
| Means of th | Aeans of three sample ± SD | C – fresh oil san | nple; A – used | C - fresh oil sample; A - used oil (car); B - used oil (lorry); | ed oil (lorry); | | |
| A ¹ & B ¹ – (| A ¹ & B ¹ – caustic/peroxide t | treated gasoline | engine oil of us | treated gasoline engine oil of used A & B sample | | | |
| A ² & B ² – t | A ² & B ² – butanol/propanol treated gasoline engine oil of used A & B sample | treated gasoline | engine oil of us | ed A & B sample | | | |
| A ³ & B ³ – h | A^3 & B^3 – hydrocarbon/butanol treated gasoline engine oil of used A & B sample | nol treated gasc | oline engine oil o | f used A & B san | nple | | |

ppm for Fe, Cu, Pb, Cr, Ba, Zn and Ca respectively, this reveals that even fresh oil have metal level that can contaminate the environment. The high level of metal in oil is as a result of additives like zinc dialkyldithiophosphate, barium and calcium sulphonates⁹. these elements, Zn, Pb, Cu, Ba are present in the build up of additives which range between 0 - 20% of the fresh formulated oil. Most of these elements are known to be toxic at level even below 1 ppm (WHO)¹⁰.

RESULTS AND DISCUSSION

for fresh, used and treated oils. The fresh oil contain 1.04 ± 0.02 , 0.31 ± 0.02 , 5.70 ± 0.01 , 0.02 ± 0.01 , 609.90 ± 9.00 , 1630.20 ± 1.13 and 1200 ± 0.32

Table -2 depicts the metal concentration

The used oil from car and lorry gave a higher value of elemental composition than virgin oil for example virgin oil gave 1.04 ± 0.02 ppm of Fe and used car oil gave 98.95 ± 0.02 ppm and that of lorry is 166.20 ± 0.02 ppm. In general the value of the elemental composition of the lorry is more than that of car, this may due to the size of the car engine and also the power of the engine. The degree of the elemental composition of the used oil depends on the kilometer covered by a vehicle, that is to say the level of metal in used oil depends on kilometer covered and the age of the engine, the older it is, the easier for the engine to wear. The three methods of oil treatment used gave different value of Fe content with the least value by Hydrocarbon/Butanol treatment method with 17.21 ± 0.02 ppm compared to 98. 95 ± 0.02 ppm of untreated oil. However, Fe, which is widely distributed in nature with varying concentrations, has not been associated with any proven health hazards even at concentration well above the permissible level¹⁰, but could cause brown coloration in water, some cosmetic effect such as skin or tooth discoloration¹¹.

The value of copper in virgin oil is very low, 0.31 ± 0.02 ppm compared to the used oil which are 29.09 ± 0.01 ppm and 30.34 ± 0.01 ppm for used car and lorry oil respectively, this means that copper is one of the major constituent of motor parts like Fe. Also, Hydrocarbon/butanol treated method gave the least value of 3.48 ± 0.07 ppm. Copper is a necessary element in animal metabolism. Cu also required for the growth and reproduction of lower plant form such as algae and fungi. Cu has been identified as toxic metal in a large amount¹² and can also impact an unpalatable taste on water¹³.

The lead (Pb) concentration in engine oil was found to be 5.70 ± 0.01 , 604.90 ± 0.01 and 751.50 ± 0.64 ppm for virgin, used car and used lorry oil respectively. Also all the three methods of treatment used reduced the pb concentration of used oil with Butanol/propanol giving the least value of 39.10 ± 0.11 ppm. Lead ingestion could cause damage to the central nervous system, including miscarriage in pregnant woman and anemia by causing a shortening of the line of red blood cells due to disruption of the red blood cell¹⁴.

The chromium in the virgin oil is 0.20 ± 0.01 ppm and 1.27 ± 0.02 , 2.24 ± 0.03 for used car and lorry used oil respectively. Caustic/peroxide method of treatment is more efficient in Cr removal than other method of treatment. Cr is essential to life. Trivalent chromium (cr³⁺) is essential for glucose and lipids metabolism, its deficiency results in diabetic mellitus and increases the toxicity of lead¹⁵. It is very poorly absorbed in skin to form a superficially stable insoluble conplex¹⁵.

The value of Barium is high in the virgin 604.90 ± 0.01 ppm this high value is due to the Barium sulphate used as additive in the oil. The increase in the value of used oil is as a result of part of the engine made with barium metal. Hydrocarbon/Butanol treatment method has the highest reduction value of elemental composition. Zinc has the highest value of elemental composition in virgin and used oil, the zinc content in virgin is as a result of additive zinc dialkyldithiophosphate used during the

formulation⁹. Zinc is essential metal and plays important roles in enzyme activity. It protects the body against lead and cadmium poisoning¹¹. However too much of zinc oxide in the body usually blocks ducts of sebaceous glands. Symptoms of zinc toxicity in human include abnormal pain, dizziness, vomiting, dehydration, lethargy and lack of muscular coordination¹⁶. Calcium sulphate used as additive is responsible for the high value of the calcium in the virgin oil, wear and tear of the engine part makes the value to increase in used oil. The three methods used for the treatment reduced the value of calcium used oil with Hydrocarbon/Butanol with the least value.

Many research works has been carried out and is still continuing in assessing the pollution level of metals (minor and major elements) in soil, water, plant and animal ^{17,18,19}, but the source of this pollution has not been thoroughly looked into the way it should be. Many factors could be responsible for water, soil pollution which can later transfer to man by drinking the water or eating the plant that have accumulated those metals from soil. Industrialization and population growth in Nigeria is rapid and used oil are discharge indiscriminately in towns to river and soil up till now government has not done anything tangible apart from making law that all mechanic workshop and industry should be cited outside the town and villages but this law is not properly monitored and citing a mechanic workshop outside the town cannot even solve the problem because these metal elements present in the oil can be transferred through running water, plants etc, with the knowledge of the concentration and adverse effect of this materials in our environment which is deleterious to man, the need to find ways of proper recycling/disposal of our waste oil is inevitable.

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