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RECLAMATION OF WASTE LUBRICATING OILS USING GROUND PERIWINKLE SHELL ADSORBENTS

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Acid treated ground periwinkle (*Fuscatus tympanotonu*) shell adsorbents were used in the reclamation of used hydraulic oil by both the continuous elution and bed filtration techniques.Quantitative yields of oils were obtained by both techniques. The bed filtration technique gave clear oils but was slower than the continuous elution technique. Comparison with conventional adsorbents showed that the ground shell adsorbent was comparable to fullers earth and better than silica or alumina. Elevated temperature oxidation of the reclaimed oils in the presence of atmospheric oxygen gave resins, which could be used in the production of paints, leather polishes and wood varnishes.

Key words. Lubricating oils, Ground periwinkle shell, *Fucatus tympanotonu.*

Introduction

Handling and disposal of used lubricating oils are increasingly becoming a matter of concern to environmentalists, governments, industries and research scientists (Swain 1978). Indiscriminate disposal of used oils on the soil around automobile maintenance garages and into waste water streams by many industries constitute serious pollution hazards to both terrestial and aquatic environments (Nemerow 1978; CONCAWE 1987). Also burning of used oils as a means of disposal is identified as a source of atmospheric pollution through widely dispersed distribution of heavy metal oxides and damaging gases (Becker 1982). Besides the pollution hazards, these methods of disposal of used oils are considered a waste of valuable resources as most used oils still contain substantial amounts of recoverable base oil.

Therefore, taking into account the stringent environmental regulations leading to higher cost of disposal coupled with the generally rising costs of petroleum products and recycling of used oils is now considered a viable option for a non-polluting disposal and at the same time conservation of oils (Swain 1978). Various processes available for used oil reclamation are reported in comprehensive reviews by Cotton (1979) and Brinkman *et al* (1987). Of the available reclamation processes, adsorption purification using various adsorbents such as bleaching clay, bauxite, silica gel, activated carbon, char bone, etc is the oldest and had remained one of the most effective and cheapest methods. An earlier study (Ofunne *et al* 1989) showed that the use of the naturally available, easily purified and regenerable sharp sand was as effective as fullers earth as an adsorbent for the reclamation of used hydraulic oil.

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In the present study, the effectiveness of another readily available material as an adsorbent for used hydraulic oil reclamation is investigated. The material, periwinkle (*Fuscatus tympanotonu*) shell is a food process waste and litters most of Nigeria's coastal towns. Chemical compositional analyses showed that it contains mainly calcium carbonate and silicates which are similar to the constituents of some of the well- known adsorbents such as the bentonites and florisil. Thus the investigation of its potentials as an adsorbent was thought worthwhile technically and as an environmental sanitation measure.

Practically oil can be reemployed in its former service once its equivalency with the original base oil has been established and necessary reformulations are made (Jacobs 1977). However, the engine tests required to establish the equivalency of a reclaimed oil with the original base oil that are usually very expensive. Moreover, refining is not always feasible because highly specialized and expensive facilities are involved. Therefore, it was sought to find other uses for the reclaimed oils in the study, by converting to resins, which could be useful to other industries.

Experimental

Materials. The used mineral based hydraulic oil was obtained from the D.R. shaft hydraulic systems at the Delta Steel Company Limited, Aladja, Nigeria. Chromatogrpahic alumina and silica gel (70 - 230 mesh) were products of Merck. The periwinkle shells were obtained from the roadsides in Port Harcourt. N-Hexane (BDH) was the eluting solvent.

Treatment of the periwinkle shell. The shells were washed, dried, ground and sieved with a 500 μm mesh sieve.

Table 1
The physicochemical characteristics of the used, formulated and bare hydraulic oils

Parameter & appearance	Used oil white emulsion	Formulated oil golden yellow	Bare oil golden yellow
Kin. Visc. (cst) at 40 °C	78.40	65.600	65.5
100 °C	13.20	8.200	8.2
Flash point (°C)	284.00	230.000	230.0
Water content (wt %)	4.20	Nil	Nil
Ash content (wt %)	0.14	0.001	Nil
Zinc (ppm)	34.60	10.500	N.D
Manganese (ppm)	30.80	N.D	N.D
Iron (ppm)	41.30	N.D	N.D
Nickel (ppm)	23.10	N.D	N.D

Key: N.D. = Not detected.

Table 2
The physicochemical characteristics of the oils reclaimed by the continuous elution technique

Parameters	Silica gel	Alumina	Fullers earth	Periwinkle (untreated)	Periwinkle (treated & activated)
Appearance	Golden yellow	Golden yellow	Golden yellow	Thick yellow	Golden yellow
Kin. Visc (cst) at 40°C	66.200	66.600	65.100	69.400	65.800
100°C	8.400	8.300	8.100	10.100	8.300
Flash point (°C)	231.000	234.000	230.000	252.000	230.000
Water (wt %)	Nil	Nil	Nil	Nil	Nil
Ash (wt %)	<0.001	<0.001	<0.001	0.002	<0.001
Zinc (ppm)	0.009	0.011	0.011	0.006	0.009
Manganese (ppm)	N.D	N.D	N.D	N.D	N.D
Iron (ppm)	0.023	0.022	0.008	0.047	0.010
Nickel (ppm)	N.D	N.D	N.D	N.D	N.D
Yield (%)	92.000	90.400	87.800	91.300	86.400

Key : N.D. = Not detected.

200 g of this was packed into a column and 300 cm^3 of benzene followed by 300 cm^3 of diethyl ether were passed through the column to wash off all organic matters. The adsorbent was removed from the column, dried and repacked. Then 500 cm^3 of 3M HNO_3 was passed through it followed by distilled water until it was neutral to litmus. The adsorbent was dried and further activated at 300°C for 12 h .

Reclamation procedure. The reclamation processes followed, were the continuous elution and bed filtration techniques as previously described (Ofunne *et al* 1989). The continuous elution technique involved recycling of the eluting solvent through a column of the adsorbent and oil in a soxhlet extractor. The bed filtration technique involved the percolation of the oil through a column of adsorbent.

Quality of reclaimed oil. The quality of the reclaimed oils was assessed by standard ASTM analyses procedure (ASTM 1982) for kinematic viscosity, Flash point, water content, and metal content by AAS.

Oxidation of reclaimed oil. The elevated temperature oxidation of the reclaimed oil was carried out according to the method described in (Ofunne *et al* 1989). The oxidation was conducted at 250°C and continued until the oil oxidate solidified.

Recovery of resins. The resinous oxidation products were recovered as *n*-hexane insoluble, in accordance with ASTM method D893.

Results and Discussion

The physicochemical characteristics of the used oil, the base oil and the unused fully formulated oil are shown in Table 1. The used oil had the appearance of a whitish emulsion due to the relatively high contamination by water which was 4.2%. This high contamination by water also appears to be the cause of the high flash point and kinematic viscosities of the oil (Hudgens and Feldhans 1978). The metals in the used oil are the results of the wears of the hydraulic systems which are made of the alloys of iron, zinc, manganese and nickel (Steelbergen 1978). The presence of zinc in the fully formulated oil is due to the zinc dialkyl dithiophosphate incorporated as antioxidant and antirust additives.

The physicochemical characteristics of the reclaimed oils using various adsorbents by the continuous elution and the bed filtration techniques are shown in Tables 2 and 3, respectively. In general, all the metals measured were below detection limit in the oils reclaimed by the bed filtration technique. In the continuous elution process, manganese and nickel were not detected while small amounts of zinc and iron in the range of 0.01 to 0.09% of the amounts in the used oil were detected in the reclaimed oils.The greater absorbability of nickel and manganese may be the result of their higher complexation ability than zinc or iron. Also the better performance of the bed filtration process relative to the continuous elution process in removing the metals could be explained by the method of introduction of the samples. In the continuous elution process, the used oil was mixed with the adsorbent to form a paste prior to insertion in the soxhlet extractor, while the used oil was introduced unto the top of the adsorbent in the bed filtration

Table 3
The physicochemical characteristics of the oils reclaimed by the bed filtration technique

Parameters	Silica gel	Alumina	Fullers earth	Periwinkle (Un-treated)	Periwinkle (treated & activated)
Appearance	Golden yellow	Golden yellow	Color-less (Initial) Golden yellow	Thick yellow Golden	Colorless (Initial) yellow
Kin.Visc (cst) at 40˚C	65.7	65.9	65.0	67.2	65.2
100˚C	8.2	8.2	8.1	8.9	8.1
Flash point (˚C)	230.0	231.0	230.0	233.0	230.0
Water content	Nil	Nil	Nil	Nil	Nil
Ash (Wt %)	Nil	Nil	Nil	Nil	Nil
Zinc (ppm)	N.D	N.D	N.D	N.D	N.D
Manganese	N.D	N.D	N.D	N.D	N.D
(ppm)	N.D	N.D	N.D	N.D	N.D
Iron (ppm)	N.D	N.D	N.D	N.D	N.D
Nickel (ppm)	N.D	N.D	N.D	N.D	N.D
Yield (%)	84.2	86.2	82.4	88.6	81.7

Key: N.D. = Not detected.

process, and allowed to percolate slowly down the adsorbent bed. Thus, it was easier for all the metals to be held up in the bed filtration process relative to the continuous elution process.

Visual inspection also showed the oils reclaimed by the bed filtration technique to be clearer and brighter than those from the continuous elution process. Moreover, the initial eluates from the bed filtration reclamation using fullers earth and the treated / activated periwinkle shell were colorless, signifying that these adsorbents were able to separate and elute the oil according to hydrocarbon types. The initial colorless eluate would correspond to super refined white mineral oil, composed mainly of saturated straight chain paraffins, and could be suitable for application in cosmetics formulations. However, no attempt was made to collect it separately since this study was not directed at the fractionation of the bare oil. The thick yellow color observed for the oil reclaimation using the untreated periwinkle shell appears to come from organic matters still present in the adsorbent. Apart from this, the untreated adsorbent was nearly as efficient as the treated one in the bed filtration process. However, the treatment seemed to make a significant difference in the continuous elution reclamation as shown by the relative amounts of metals eluted.

Production of resins. High temperature auto-oxidation of engine oils is known to result in the production of high molecular weight insoluble resins through aldol type condensation of the primary oxidation products (Gunsel *et al* 1988). Although these processes are a nuisance and totally undesirable in any engine, they are the processes for the synthesis of a wide range of basic chemicals in industry (Lebedev 1984).

Oxidation of the reclaimed oils at 250˚C in the presence of air, gave a very shiny and waxy solid in 72 to 96 h. The average yield of dry resins recovered was 32 wt% of the oils, and this is reasonably high. Nevertheless, it is expected that with better understanding of the mechanism and optionization of the polymerisation conditions by the use of catalysts, it would be possible to achieve higher percentage conversions. Further work on the utilization of the resins in the formulation of paints, polishes and varnishes is in progress.

Conclusion

Ground periwinkle shell adsorbent was shown to be as effective as the well-known adsorbents like fullers earth for the reclamation of used hydraulic oil by both the continuous and bed filtration techniques. Elevated temperature oxidation of the reclaimed oils gave resins which could be useful base materials to industries for the production of paints, polishes and varnishes.

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