INCORPORATION OF WASTE FROM USED LUBE OIL RE-REFINING INDUSTRY IN CERAMIC BODY: CHARACTERIZATION AND PROPERTIES

Silvio R. Teixeira
Gleyson T. de A. Santos
rainho@fct.unesp.br
Tadeu_gtas@hotmail.com
Department of Physics, Chemistry and Biology, São Paulo State University (UNESP)

Abstract: In Brazil, more than 1,000,000 m3 of lube oil are consumed yearly, which generates 350,000 m3 of waste. Approximately 18.4 % of this volume is recovered as rerefined oil. Automotive use represents 70% of Brazil's motor oil consumption. The re-refining process recovers most of the lube oil that is not burned during motor use. The acid/Clay (Bernd-Meinken) recycling process is adopted in Brazil. Basically, two wastes are produced in this process: (a) acid dregs and (b) filter pie which is rich in clay (bentonite) and re-refined oil. Thermal analysis and technological tests were used to characterize pie residues and ceramic bodies. Two kinds of this waste were used: T1 (crude) and T2 (after partial chemical extraction of oil). Ceramic bodies with different waste concentration added were pressed and sintered at two different temperatures. The results show that the incorporation of 10 %- weight of T2 residue improves ceramic properties. Due to the large amount of oil in T1, sample porosity increases and worsens its properties. Nevertheless, the incorporation of 5 % of T1 still gives acceptable results in brick production. The quantity of waste to be incorporated will depend on the clay quality.

Keywords: Waste, Used lube oil, Clay, Re-refining, Bricks

1. INTRODUCTION

In the last years, the disposal of used lubricating oils has generated considerable research aimed at determining the risk to the environment that it represents. Lubricating oil constitutes about 2% of petroleum derivatives and is one of the few that is not totally consumed during its use. Automotive use represents 70% of the national consumption, mainly in diesel motors. During the lubrication of equipment, thermo-oxidative degradation of the oil and the accumulation of contaminants require that it be changed. In the process of changing the lubricant, it is drained into a collection tank for later handling (Carreteiro & Moura, 1998; RMAI, 2001; UNILUBRI, 2007; CEMPRE, 2007). Although used lubricating oil represents a small percentage of petroleum waste, its environmental impact is very great. It contains metals and highly toxic compounds, thereby being classified as a dangerous residue (class I) according to the standards of the ABNT (RMAI, 2001). Recycling has become an adequate treatment of oil through the use of specific processes, thereby allowing the recovery of the part not burned, which is separated from the residue. Among the various processes developed for recycling, the acid/Clay process (Bernd/Meinken) is one of the oldest and is adopted in Brazil. Basically, it consists of the following steps: (a) heat treatment (dehydration), (b) acidification, (c) decantation, (d) neutralization, (e) distillation, and (f) filtration. At the end of the process, a considerable amount of residues is produced, which are basically of two types: (1) acid dregs obtained indecantation and (2) the filter pie (clay impregnated with oil). Both the dregs and the filter piecan be acid or neutralized with sodium hydroxide (NaOH) or calcium carbonate ($CaCO_3$) (Carreteiro & Moura, 1998; RMAI, 2001).

The clay used in clarification and filtration is bentonite which is composed essentially of montmorillonite or other minerals of the smectite group. Sodium bentonite has many industrial applications. Non-sodium bentonite (with a predominance of Ca and Mg as exchange cations) produces active clays by treatment with acids which are utilized in the bleaching of mineral, vegetable and animal oils. In the acid/clay process, it is used in the laststep for decolorization of the recovered oil, binding free cations (Gomes, 1988; Souza Santos, 1989).

One of the possible applications of oil residues is their incorporation in ceramic bodies for the production of bricks. Various works (Silva et al., 2002; Santos et al., 2002; Souza & Holanda, 2003; Saikia et al., 2001; Zucchini et al., 1993) have been published on the incorporation of residues from the petroleum industry in ceramic bodies. Despite citing (RMAI, 2001) that filter pie has been added to ceramic bodies, no published report was found in a bibliographic search showing this incorporation of residues from the used lubricating oil re-refining industry.
Currently in Brazil, there are fourteen companies authorized by the National Agency of Petroleum (ANP), to carry out re-refining of used or contaminated lubricating oil (ANP, 2007). One of these companies, PROLUB Rerrefino de Lubrificantes, is situated in Presidente Prudente – SP.
The present work determined the influence of the incorporation of pie filter on the ceramic properties of ceramic probes prepared with clays used to produce bricks.

2. MATERIALS AND METHODS

The clay used for incorporation of the residue was from the lowlands close to the city of Indiana-SP, Brazil, which is normally used to produce solid bricks. The pie filter is one of the residues left over in the last step of the process, when the oil is re-refined and filtered. It consists of clay (bentonite), oil and residues. The samples were donated by the company PROLUB, located in Pres. Prudente-SP, Brazil.
The type and quantities of contaminants in waste oil depend on several factors including types of oil that compose the waste, detergents and dilutants added to the not used oil, management practices etc. The type and concentration of contaminants in waste oil is variable (El-Fadel et al, 2001; RMAI, 2001).
The filter pie was divided into two parts: (a) crude pie (T1) and (b) treated pie (T2) which had part of the oil (~30% of the total mass) extracted using solvents. The two samples were submitted to thermoanalytical testing (Teixeira et al., 2002): (a) thermogravimetry (TGA/DTG) in nitrogen flow, from 25 to 990 oC, (b) differential scanning calorimetry (DSC) in nitrogen flow, from 25 to 600 oC and (c) differential thermal analysis (DTA) in air flow, from 25 to 1200 oC. The equipment used was: TG-209/FTIR and DSC – 204, brand NETZSCH and DTA – 1600, brand TA - Instruments.
After thermal characterization, the residues T1 (5, 10 and 20%) and T2 (5 and 10%) were added to clay used for the manufacture of bricks (Teixeira et al., 2001, Teixeira et al., 2004). Ceramic probes (CP) were prepared with approximately 20g of mass and different concentrations of residues incorporated. The clay was ground in a blade mill and passed though a screen (< 0.50 mm). The mixtures were homogenized manually in a porcelain mortar, after the addition of 2ml (10% weight) of water. CPs (60 x 20 x 5mm) were pressed uniaxially, in triplicate, using a manual hydraulic press.
After being dried for 24 h in an oven at 110 oC, the CPs were fired at two different temperatures (900 oC and 950 oC), at a heating rate of 10 oC\min and residence time of 1h. The flexural strength (FS) was determined by three-point bending test (model DL2000, EMIC) at a loading rate of 1mm/min. Water absorption (WA) values were determined from weight differences between the dry and water saturated (immersed in water for 24 h (2h boiling)), ceramic probes. Apparent specific mass (ASM) and apparent porosity (AP) were determined from weight differences between dry, water saturated and immersed ceramic probes, Arquimedes method (Santos et al., 1989).

3. RESULTS AND DISCUSSION

3.1 Thermal Analysis

The TG data (Figure 1) for the two filter pies (T1 and T2) show that there was a loss of total mass of 47% and 38%, where approximately 30 % and 15 % equaled the burning of residual oil, respectively. The analysis of the derivative of the thermogravimetric curve (not displayed in the figure) showed that for T1 there were two peaks of mass loss at 296 and 471 oC, due to the burning of oil present and loss of hydroxyls by the clay, respectively. For T2, mass loss occurred at 60 oC, due the solvent used in the extraction of part of the oil, and there was a band of continuous mass loss between 250 and 600 oC. This band occurred due to the combustion of hydrocarbons and other residues [3] present and the loss of hydroxyls by the clay. In general, the combustion of hydrocarbons occurs between 100 and 550 oC (Saikia et al., 2001).

The differential thermal analysis (DTA) curves (Figure 2) for the samples T1 and T2 show that there is an overlapping of various exothermal peaks between 200 and 600 oC, with stronger peaks at about 380 oC (T1) and 358 oC (T2). These peaks are associated with different types of oils present in the re-refined material. The sample T2 showed a shift in the strongest peak toward a lower temperature and a 29% decrease in intensity, which represents more or less the amount of oil extracted from sample T1. Since the "burned" oil is composed of a mixture of different types of oils and additives, it is difficult to identify the reaction peaks observed in the thermograms. DTA data show that the filter pie releases energy (exothermic reaction) mainly between 280 and 428 oC and a shoulder between 428 and 600 oC, as observed also by Saikia (2001). In this cited work, the two peaks showed better resolution, but a different residue was used and, in the present study, the residue used had other contaminants, such as light products and soluble and insoluble compounds (UNILUBRI, 2007).

Figure 3 shows the results of differential scannning calorimetry (DSC), from 25 to 550 oC, for T1 (a) and T2 (b). These results indicate that there is one exothermic band where continuous release of heat occurs approximately from 150 to 550 oC. This result is overlapped by the smectite dehydroxylation that gives endothermic peaks between 100 and 800 oC. The influence of structural water lose by the clay mineral on the DSC signal is more strong in the figure to sample T2 (Fig. 3b) where the amount of oil in the pie is lesser than in the sample T1.

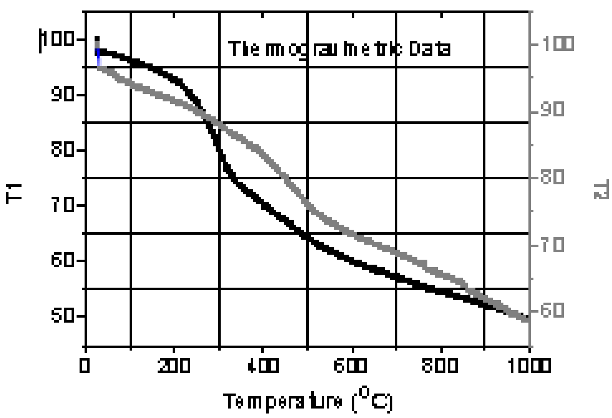

Figure 1: Sample weight variation during the treatment (TG data).

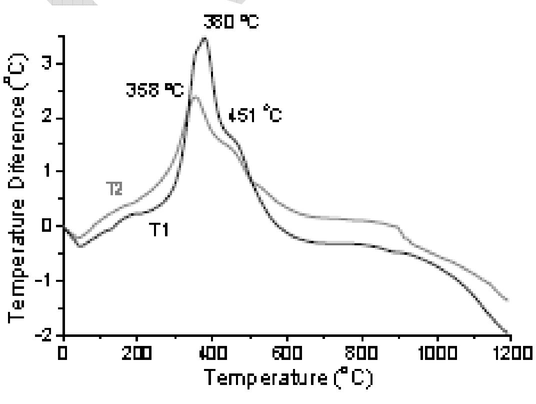

Figure 2: DTA data of the two samples (T1 and T2).

3.2 Incorporation of the Filter Pie in Ceramic Body

Since the filter pie is rich in clay, it can be mixed with a ceramic body to make solid bricks. The majority of kilns used to make bricks and hollow clay blocks in Brazil use wood as fuel. The energy released (heat of combustion) from the wood varies from 4000 to 5000 cal/g, and for used oil it is on the order of 10,000 cal/g (Zucchini et al., 1993; Carreteiro & Moura, 1998; CEMPRE, 2007). Therefore, incorporation of filter pie in the ceramic body would release heat during sintering of the ceramic pieces. This release of heat would help the firing process and contribute to economizing on energy and fuel (wood).

3.3 Ceramic Body

The results of mineralogical and textural analysis of the clay fraction, of the ceramic mass used for the incorporation of the residues, have been published previously (Teixeira ET al., 2001). These results show the presence of the following minerals: clay-minerals of the kaolinite family (major phase) with low crystalinity and kaolinite-mica inter-stratified clay, mica, smectite (montmorillonite), quartz, gibbsite, iron and titanium oxides. Textural analysis of the sample showed the following granulometric distribution: clay (38.2%), silt (27.7%) and sand (34.1%), classifying the clay mud as clay loam.

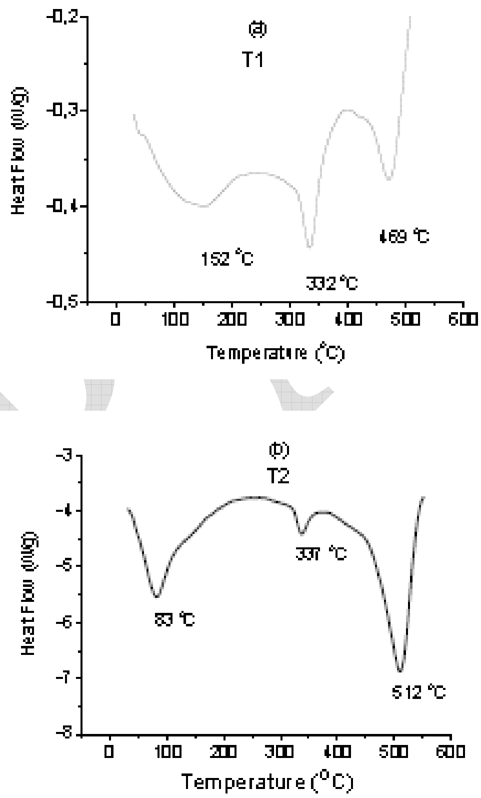

Figure 3: DSC data (a) T1 and (b) T2, with endothermic peaks associated to bentonite.

3.4 Physical Properties

Figure 4 shows the mean values for the water absorption (WA) and apparent porosity (AP), for the T1 and T2 pies, according to the percentage of residue incorporated. The results show that the addition of the T1 residue consistently increases the concentration ofpores, resulting in a greater absorption of water. The addition of the T2 pie produced a very small variation in these two parameters, due the lower concentration of oil in T2, which causes pores. Nonetheless, the WA and AP values (for T1) are still lower than the maximal limits (WA <18 % and AP < 35 %) accepted for the production of bricks (Vieira et al., 2003; Macedo et al., 1996).

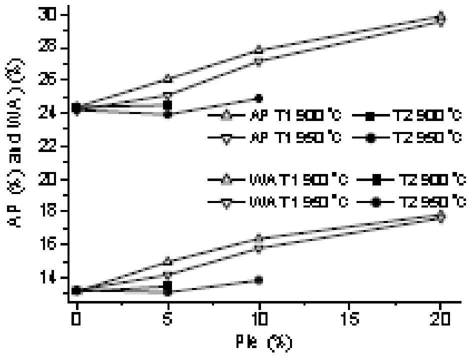

Figure 4: Absorption of water (WA) and apparent porosity (AP) mean values, as function of the residues concentration (T1 and T2 pies).

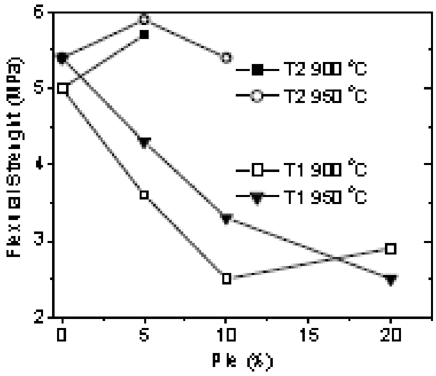

Figure 5: Flexural strength (FS) as function of the residues (pies T1 and T2) concentration.

Although total linear shrinkage (tLS) of the probes increased with the addition of the pies, the values obtained for all samples were less than 1%, showing that the pieces undergo little variation in size during firing. The apparent specific mass (ASM) decreased slightly with the addition of the T1 pie, but staying above the minimal value recommended (1.7 kg/cm3), for the addition of up to 10 % of this residue. The addition of the T2 pie had practically no effect on the ASM of the probes (1.83 g/cm2), which remained higher than the minimal value.

3. CONCLUSIONS

The results of this work allow us to draw the following conclusions. 1) The quantity of oil present in the pie incorporated is a determinant factor in the physical characteristics of the ceramic material. The addition of the crude pie (T1) consistently worsens the properties of the ceramic pieces, due to the greater concentration of oil which results in greater porosity in sintered pieces. Despite this, for the clay used in this work, these properties were still within the limits established for the addition of up to 20 % (in weight). 2) The addition of pie T2 had practically no affect on some properties (ASM, WA, AP) and improves the mechanical resistance of probes for the addition of up to 10 % filter pie (which was highest concentration studied).

From an environmental and economic point of view, the incorporation of this filter pie in a ceramic body will be constructive, because it presents an option for the use of the residue which would usually be discarded into the environment, and in economizing on fuel (wood) used in the firing of the ceramic pieces.

The amount of oil in the pie, firing temperature and type of clay used as matrix, Will determine the quantity of residue to be incorporated and the final properties of the ceramic material. Therefore, the results of this work show that this waste can be incorporated to ceramic mass to produce bricks.

Acknowledgements

The authors wish to acknowledge the contribution of Eng. Eduardo Chesine (PROLUB Company) for the samples and information about them and to Dr. Aldo E. Job for thermal analysis lab availability. Special thanks to PROPe/UNESP and FAPESP for financial support to the meeting participation.

REFERENCES

ANP - Agência Nacional do Petróleo, Ministério de Minas e Energia, Portaria ANP 128/1999, www.anp.gov.br, viewed on June 21, 2007.

Carreteiro R. P. & Moura C. R. S., 1998. Lubrificantes e Lubrificação, Makron Books, São Paulo - SP, Brasil.

CEMPRE, Fichas Técnicas: Óleo Lubrificante Usado, www.cempre.org.br (in fichas técnicas, óleo usado), viewed on on June 22, 2007.

El-Fadel, M. & Khoury, R., 2001. Strategies for vehicle waste-oil management: a case study, Resources, Conservation and Recycling 30, pp. 75-91.

Gomes, C. F., 1988. Argilas: O que são e para que servem, Fundação Calouste Gulbenkian, Lisboa-Portugal.

Macedo, R. S., Galdino, A. G. S., Morais, C. R. S. & Ferreira, H. F., 1996. Estudo Preliminar de Argilas do Estado da Paraíba para Utilização como Matérias-Prima em Cerâmica Vermelha - Parte I, Cerâmica 42(275) p. 259.

RMAI, Reciclagem de Óleos Lubrificantes, Revista Meio Ambiente Industrial 31, 30 (2001) www.ida.org.br/artigos/reciclagemoleo.htm, viewed on June 21, 2007.

Saikia, N. J., Sengupta, P., Gogoi, P. K. & Borthakur, P. C., 2001. Physico-chemical and cementitious properties of sludge from oil field effluent treatment plant, Cement and Concrete Research 31, pp. 1221.