

# CONTRIBUTION ULTRA VIOLET RADIATION ON DEGRADATION OF BIODEGRADABLE BASE OIL

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## ABSTRACT

*Increasing environmental awareness led to the development of environmentally harmless lubricants made by biodegradable materials. Biodegradable lubricants are suitable for various kinds of application, one of the promising usages is for railways. Oils or greases are applied for railways or points to keep sufficient friction coefficient or to avoid wear damage. These lubricants are "once-through" lubricants, and never recovered but defused into the earth's surface. The oxidation of lubricants on the railways will take place because of the sunlight effect. The solar radiation at the top of earth's atmosphere contains a significant amount of UV radiation of shorter wavelength, and therefore higher energy. This study shows that the UV-B radiation can deteriorate rapeseed oil immediately. It is showed by the results of peroxide value, total acid number and molecular weight distribution are increased with oxidation time.*

*Key words : Biodegradable lubricants, vegetable oil, UV radiation, antioxidant.*

## I. INTRODUCTION

Biodegradable lubricants have a minimum impact on the environment and are suitable for various kinds of application, such as agricultural, woodworking, road and tunnel construction machines, hydroelectric power plant, etc. Lubricants can enter the environments either through normal use ("total-loss" or "once-through" lubricants), or by leakage and spillage (e.g. hydraulic fluids). This fact and ever increasing environmental awareness led to the development of environmentally harmless lubricants<sup>[1]</sup>.

One of the promising usages of biodegradable lubricant is for railways. Oils or greases are applied for railways or points to keep adequate friction coefficient or to avoid wear damage. These lubricants are "once-through" lubricants, and never recovered but defused into the *earth's surface*.

Although animal oils are also considered biodegradable, the most common mineral oil substitute consist of vegetable oils (natural esters) and synthetic esters. Vegetable oils have been proposed to substi-

tute the mineral base oil because of their superior biodegradability even though they have poor oxidation stability. Therefore, the improvement of the anti oxidation performance of vegetable oils is a key technology for their usage<sup>[2]</sup>.

The oxidation of lubricants on the railways will take place because of the sunlight effect. The solar radiation at the top of earth's atmosphere contains a significant amount of UV radiation of shorter wavelength, and therefore higher energy. The shortest of these wavelengths is ultra violet C (UV-C, 200-280 nm), it is completely blocked (absorbed) by atmospheric oxygen (O<sub>2</sub>) and ozone (O<sub>3</sub>). The ultra violet B (UV-B, 280-315 nm) is absorbed not completely by O<sub>3</sub>, while ultra violet A (UV-A, 315-400 nm) is less absorbed by O<sub>3</sub> and are therefore more easily transmitted to the earth's surface<sup>[3]</sup>.

This study describes the effect of antioxidants (AO) for long lubrication life of vegetable oil as biodegradable base oil under the UV radiation at moderate temperature.

**II. EXPERIMENTAL DETAILS**

**A. Materials**

The sample used in this study is commercially available rapeseed oil (RO). Three kinds of phenolic type antioxidants AO-A [penta erythritol tetrakis (3-(3,5-di-tert-butyl- 4-hydroxyphenyl)propionate)], AO-B [octadecyl- 3-(3,5-di-tert-butyl-4- hydroxyphenyl) propionate], and DBMP [2-6-di-tert-butyl-4-methylphenol] were used.

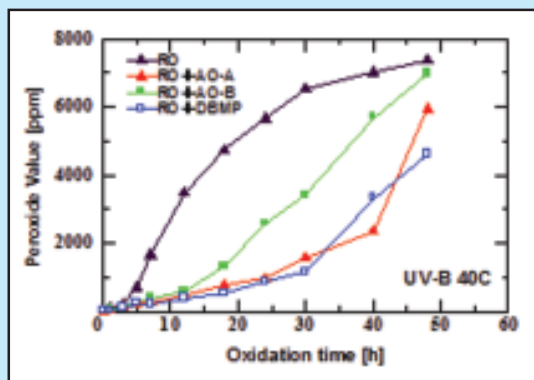
**B. Sample Preparation**

Formulations of sample prepared are presented in Table 1. The oxidation of the samples was carried out by two different methods that are UV-B radiation at 40°C and high temperature oxidation at 120°C.

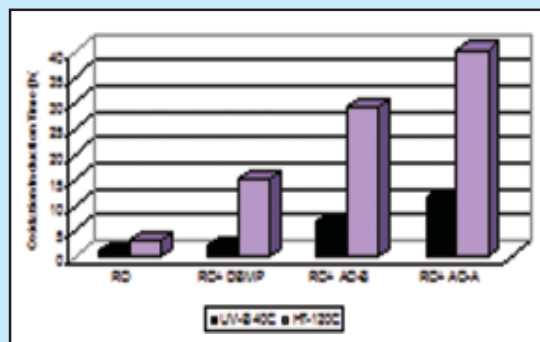
Irradiation was carried out using a UV-lighting box, which contained an ultraviolet light source and hot plate (40°C). The UV light source was UV-B lamp emitting in the range of 280-320 nm (maximum at 315 nm). The oxidation at high temperature was car-

**Table 1**  
**Formulation of RO samples**

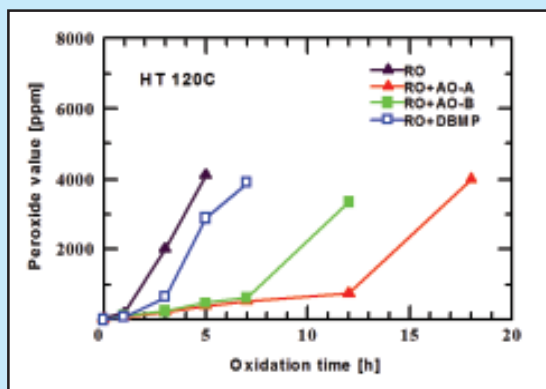
Formulation	AO-A	AO-B	DBMP
	(mass%)	(mass%)	(mass%)
RO	-	-	-
RO+AO-A	0.95	-	-
RO+AO-B	-	1.0	-
RO+DBMP	-	-	1.0



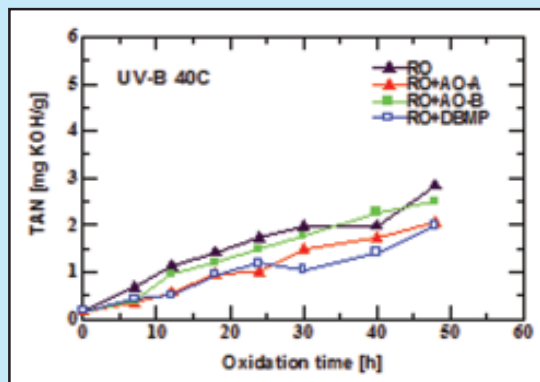
**Figure 1**  
Peroxide value of RO and RO+AO under UV-B



**Figure 3**  
Oxidation Induction Time of RO and RO+AO under UV-B radiation and HT oxidation



**Figure 2**  
Peroxide value of RO and RO+AO at HT



**Figure 4**  
Total acid number of RO and RO+AO under UV-B

ried out using an oven at 120°C. For these experiments, fixed amount of sample (350 mg) is poured into a steel pan, then irradiated by UV-B light or heated on the oven under varied of times, respectively.

### C. Method

Oxidation stability evaluation was conducted by Peroxide Value (PV) (ASTM D-3703), Total Acid Number (TAN) (ASTM D-664), and Molecular Weight Distribution (MWD) by High Performance Liquid Chromatography (HPLC).

## III. RESULTS AND DISCUSSION

### A. Peroxide Value (PV)

The results of peroxide value analysis of rapeseed oil (RO) and rapeseed oil plus antioxidant (RO+AO), after the oxidation with UV-B radiation, or at high temperature (HT), are shown in Figures 1 and 2, respectively. As shown in these figures, the peroxide value of original rapeseed oil immediately increased in both oxidation methods. Therefore, the oxidation induction time of rapeseed oil is very short.

The effect of antioxidant on the oxidation induction time of rapeseed oil at UV-B radiation and high temperature oxidation is summarized in Figure 3. The oxidation induction time (OIT) is calculated from onset time in Figures 1 and 2. The oxidation induction time of rapeseed oil oxidation under UV-B radiation, increased from 3 to 15 hours by adding of 1 mass% AO-B, to 29 hours by 1 mass% DBMP, and 40 hours by 0.95 mass% AO-A. On the other hand, the oxidation induction time of rapeseed oil high temperature oxidation increased from 1 to 2.1 hours by adding of 1 mass% DBMP, to 6.8 hours by 1 mass% AO-B and 11.3 hours by 0.95 mass% AO-A. It appears that the most effective antioxidant among three antioxidants on oxidation stability of rapeseed oil at UV-B radiation and high temperature oxidation is AO-A.

### B. Total Acid Number (TAN)

The results of total acid number analysis of rapeseed oil from both two oxidation methods of UV-B radiation and high temperature oxidation are shown in Figures 4 and 5, respectively. The original rapeseed oil as sample in this study has a total acid number value of 0.15 mg KOH/g.

The total acid number value of rapeseed oil (RO) and rapeseed oil plus antioxidant (RO+AO) after

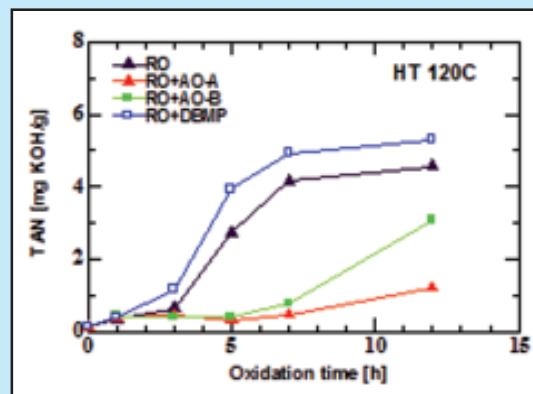


Figure 5  
Total Acid Number of RO and RO+AO at HT

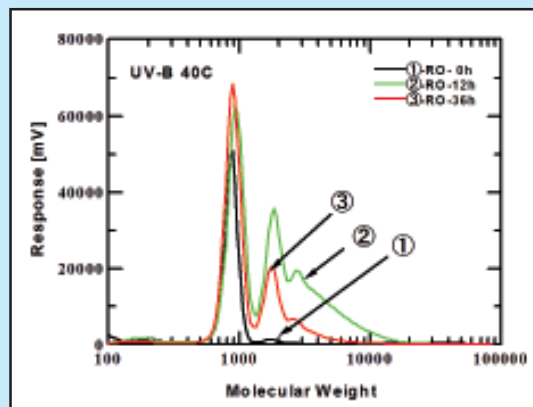


Figure 6  
Molecular weight distribution of RO under UV-B radiation for each oxidation time

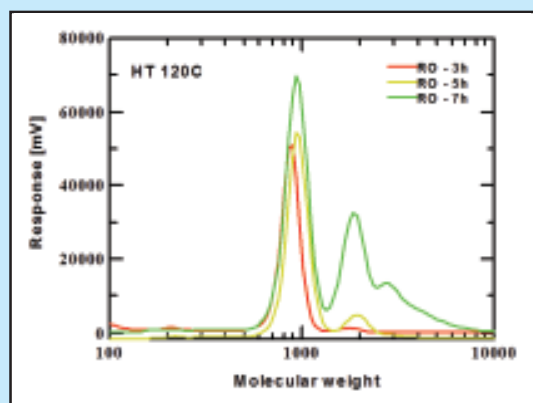


Figure 7  
Molecular weight distribution of RO at HT Oxidation for each oxidation time

oxidation at UV-B light gradually increased with oxidation time as shown in Figure 4. It is shown that UV-B light effect on total acid number value of rapeseed oil and rapeseed oil plus antioxidant are not significantly different.

On the other hand, total acid number value at high temperature oxidation of rapeseed oil and rapeseed oil plus antioxidant DBMP increased sharply after 3 hours, for rapeseed oil and rapeseed oil plus AO-B increased sharply after 7 hours, but for rapeseed oil and rapeseed oil plus antioxidant AO-A gradually increased. This result shows that the most effective antioxidant among three antioxidants on total acid number value of rapeseed oil at high temperature oxidation, is AO-A.

### C. *Molecular Weight Distribution (MWD)*

Representative HPLC chromatograms of rapeseed oil (RO) from both two oxidation methods of UV-B radiation and high temperature oxidation obtained by UV-detector, are compared with that of the original rapeseed oil as presented at Figure 6 and 7. As shown in these figures, HPLC chromatograms show that the growth of high molecular weight material depends on the oxidation time. High molecular weight materials are formed increasingly as the oxidation time becomes longer.

## IV. CONCLUSION

- This study shows that the UV-B radiation can deteriorate rapeseed oil immediately. It is showed by the results of peroxide value (PV), total acid number (TAN) and molecular weight distribution (MWD) are increased with oxidation time.
- Among three antioxidants used in this study, AO-A is the most effective to preserve long life lubrication of rapeseed oil.

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## REFERENCES

1. Loderer D., (1995) "Lifetime Lubrication of Rolling Bearing with Rapidly Biodegradable Lubrication Grease", NLGI spokesman, Volume 59, page 16-20.
2. Goyan, R.L, et al. (1998) "Biodegradable Lubricants", Technical Paper, Journal Lubrication Engineering, p 10-17.
3. Madronich, S., et al. "Changes in biologically active ultraviolet radiation reaching the Earth's surface", Journal Photochemistry Photobiology B: Biol. Volume 46, 5-19. ✓