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Development of an Amine Antioxidant Depletion Diagnosis Method Using Colorimetric Analysis of Membrane Patches

Tomomi Honda[1] and Daisuke Hamano[2]

[1] *Graduate school of engineering, University of Fukui, Bunkyo 3-9-1, Fukui-shi, 910-8570, Japan*
honda@u-fukui.ac.jp

[2] *Powertrain and EV Engineering Division, Nissan Motor Co., Ltd., 1-1, Takashima 1-chome, Yokohama-shi, Kanagawa, 220-8686, Japan*
hamano@mail.nissan.co.jp

ABSTRACT

The degradation of lubricating oils can be roughly classified into two types, one is caused by solid particles and the other is caused by oil oxidation products. In electric power plants, a main cause of oil degradation is oxidation. As oxidation progresses, oxidation products are formed. These are polymerized and generate varnish and sludge, which cause serious problems such as sticks of valves in critical systems, plugging filter media, and lowering the cooling effects. This study examines the degradation compounds of amine antioxidants and investigates the relationship between oxidized products of amine antioxidants that have been captured by the membrane filter and the color of the membrane patch. A new diagnosis method for the depletion of amine anitoxidants was discussed based on the experimental results. As a result, we found that amine antioxidant oxidation products in ester-based oils are deposited by mixing with non-polar solvents and that they affect the color of the membrane patch. Furthermore, we found that there is a strong correlation between ΔE_{RGB} and the residual ratio of amine antioxidants.

1. INTRODUCTION

Various factors contribute to the degradation of lubricating oils, which then leads to mechanical failure. To prevent mechanical failures of this type, attention has recently been focused on proactive, condition-based maintenance that can prevent mechanical failure by detecting the root causes of oil degradation and then control them within specific reference values. The degradation of lubricating oils can be roughly classified into two types, one is caused by solid particles and the other is caused by oil oxidation products. In electric power plants, a main cause of oil degradation is oxidation. As oxidation progresses, oxidation products are formed. These are polymerized and generate varnish and sludge, which cause serious problems such as sticks of valves in critical systems, plugging filter media, and lowering the cooling effects (Sasaki, et. Al., 2008), (Day, 2008), (Livingstone & Oakton, 2010). Generally, antioxidants are added to turbine oils to prevent the formation of sludge; antioxidants terminate the chain reaction of autoxidation and gradually consume. However, as soon as an antioxidant is depleted, the oxidation of its base oil progresses rapidly. Thus, on-site antioxidant depletion diagnosis is important in allowing us to monitor the root causes of oil degradation during the initial stages and begin executing proactive maintenance. Several diagnosis methods measure an antioxidant's residual ratio (such as chromatography (Keller & Saba, 1987) and ASTM D2272: Rotary Pressure Vessel Oxidation Test (RPVOT) (ASTM, 2014), but none can be used on site, and most require both time and experience. On the other hand, ASTM D6971: Remaining Useful Life Evolution Routine (RULER) (ASTM, 2009) is an electrochemical method that can measure antioxidant degradation in a short amount of time. RULER is good for measuring the residual ratio of antioxidants, but it cannot detect oxidation compounds in turbine oil. We have previously reported that there is a strong relationship between the degradation of lubricating oil and the color of the membrane patch (Yamaguchi, et. al., 2002). Furthermore, we have developed a degradation diagnosis method for lubricating oils that focuses on the coloration of contaminated membrane patches. However, when amine antioxidants is added to ester oil, purple compounds affect the effectiveness of that method. Here, we examined the degradation compounds of amine antioxidants and investigated the relationship between oxidized amine antioxidant products that have been captured by the membrane filter and the color of the membrane patch. The possibility of a new diagnosis method for the depletion of amine antioxidants was also discussed.

2. EXPERIMENTAL APPARATUS

2.1. Production method of the sample oil

We used RPVOT to produce oxidized lubricating oil in order to obtain degraded turbine oil, such as is used in power plants, as shown in Fig. 1. This method utilizes an oxygen-pressured vessel to evaluate the oxidation stability of new and in-service turbine oils in the presence of water and a copper catalyst coil at 150°C; thus, the color of the membrane patch is influenced by oxidation products from the copper catalyst. Therefore, for this study we used RPVOT to degrade sample oils by oxidation in stages without a copper catalyst. Values were then set for each oxygen pressure change, as shown in Fig. 2. We set the change in pressure at 1–9 PSI (6.9–62 kPa) in order to simulate gradual contamination.

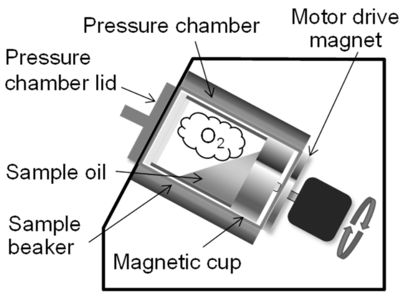


Figure 1 Schematic of the RPVOT apparatus.

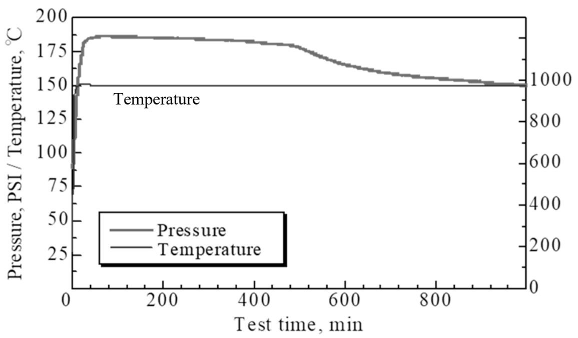


Figure 2 Example of RPVOT and change in pressure on sampling time.

2.2. Filtering equipment

The filtration equipment comprised of a dustproof cover, a filter support of vacuum flask, a filter funnel, and a vacuum pump. Figure 3 gives a schematic of the filtering equipment. Figure 4 shows a surface and a cross-section structure of the membrane filter. The membrane filter (with a pore size of 0.8 µm, a diameter of 25 mm, and a thickness of 0.125 mm) was placed between the filter support of vacuum flask and the filter funnel and then clamped. The mixture of sample oil and petroleum ether was filtered with reduced flask pressure. To prepare the mixture, the sample oil was first poured into petroleum ether in a beaker using a burette; the mixture was then stirred with a glass rod. After filtration, the oil on the membrane patch was removed with petroleum ether, and the membrane filter that filtered the sample oil was dried; the dried membrane filter is called the "membrane patch."

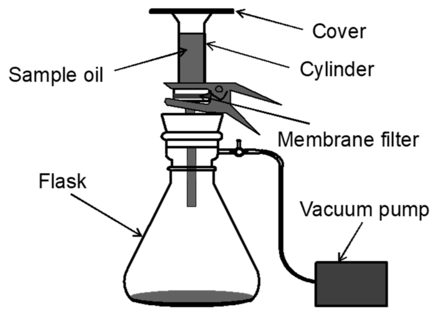


Figure 3 Filtering equipment.

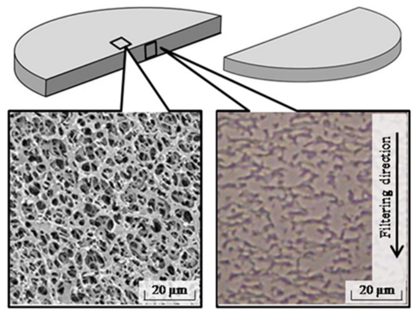


Figure 4 Magnified images of the membrane filter.

2.3. Filtering equipment

We measured the color parameters (maximum color difference and ΔE_{RGB}) of the membrane patch using a colorimetric patch analyzer (CPA). Figure 5 shows the CPA's measurement principle. The CPA measures the RGB values of contamination, which were captured on the surface and interior of the membrane patch by transmitting and reflecting light. Therefore, all the information we need about the oxidation product captured by the filter can be obtained by transmitting light. RGB values were indicated in 256 levels. For example, white has 255 at R, G, and B, and black has 0. Color parameters were calculated from RGB values. The maximum color difference is defined as the maximum difference between any two values of R, G, and B. ΔE_{RGB} is defined as the distance from white to the membrane patch color; it is obtained from formula (1), which follows.

$$\Delta E_{RGB} = \{(255 - R)^2 + (255 - G)^2 + (255 - B)^2\}^{0.5} \quad (1)$$

In this study, we used RGB values that were measured by transmitting light.

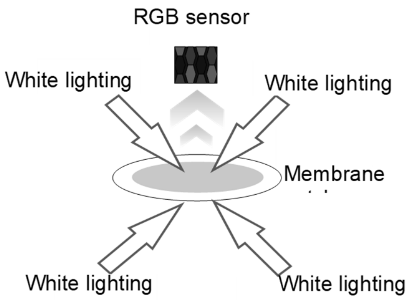


Figure 5 Measurement principle of the CPA.

3. Results and discussion

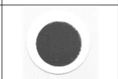
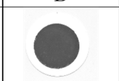
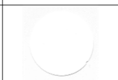
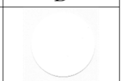
3.1. Relations between various solvents and color of membrane patches

We prepared membrane patches with various organic solvents, as listed in Table 1. The polarity of solvents ranged from low to high in the order A to D. The solvents were mixed with sample oil with a change in pressure of 9 PSI. Table 2 shows images of the membrane patch; results were measured by the CPA's transmitting light. The membrane patch color with petroleum ether became a dark purple, and the ΔE_{RGB} value was large. However, no great change in membrane patch color occurred with toluene or diethyl ether, and the ΔE_{RGB} value was small.

Table 1 Properties of the solvents.

	Solvent	Permittivity	Dipole moment
A	Petroleum ether	1.84	0
B	Hexane	1.89	0
C	Toluene	2.38	1.20
D	Diethyl ether	4.30	3.83

Table 2 Membrane patch images and RGB value.

	A	B	C	D
Image				
R	11	10	247	202
G	6	6	255	215
B	10	10	255	245
ΔE_{RGB}	424	428	8	67

When high-polar and low-polar solvents are mixed, the polarity of the solution becomes lower than that of the high-polar solvent. In this case, polar solute that dissolves in the high-polar/low-polar solution cannot dissolve in the lubricating oil. As a result, polar solute is deposited (Otaki, 1987). Tsurugi says that aromatic amine forms Wurster's salt when mixed with peroxide radicals (Tsurugi & Murakami, 1970). In this experiment, we assumed that Wurster's salt was deposited due to the solution's decreased polarity, which was caused by the mixture of low-polar solvent and higher-polar sample oil.

3.2. Optimum filtration quantity

Two experiments were used in order to set the optimum filtration quantity for diagnosis. First, the mixing quantity of the sample oil was changed; in this experiment, the mixed liquid had a constant mixing ratio of (sample oil):(petroleum ether) = 1:100. Then, the mixing quantity of petroleum ether with the 0.1 ml sample oil was changed. Images of the membrane patch that filtered each solution in these two experiments are shown in Tables 3 and 4. Furthermore, the relationship between ΔE_{RGB} and the amount of sample oil / amount of petroleum ether are shown in Figs. 6 and 7, respectively.

Table 3 Membrane patch images (mixture ratio = 1:100).

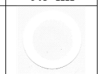
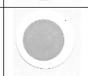
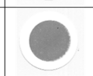
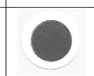
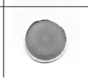
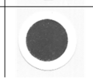
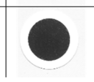
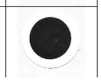
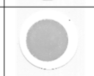
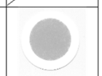
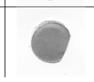
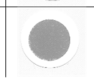
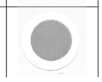
	0.1 ml	0.2 ml	0.3 ml	0.4 ml	0.5 ml
1 PSI					
3 PSI					
5 PSI					

Table 4 Membrane patch images (sample oil = 0.1 ml).

	10 ml	20 ml	40 ml	60 ml
1 PSI				
3 PSI				
5 PSI				

In the first experiment, the color of the membrane patches darkened and the value of ΔE_{RGB} increased with changes in pressure and the amount of sample oil. In the second experiment, there was no great change in membrane patch color or ΔE_{RGB}. These results suggest that the amount of deposits captured by the membrane patch is affected by the amount of sample oil but not by the amount of petroleum ether if the mixing ratio of sample oil and petroleum ether is large enough and constant. Therefore, we propose an optimum filtration quantity in which the amount of sample oil is less than 0.1 ml and the mixing ratio of sample oil and petroleum ether is more than 1:100.

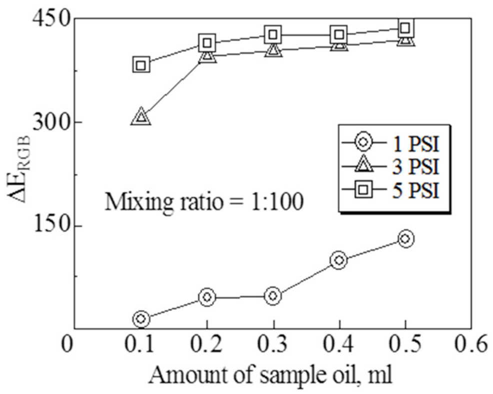


Figure 6 Relationship between the amount of sample oil and ΔE_{RGB}.

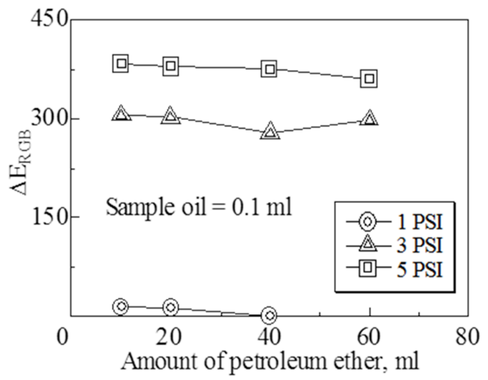


Figure 7 Relationship between the amount of petroleum ether and ΔE_{RGB}.

3.3. GC-MS analysis of sample oils

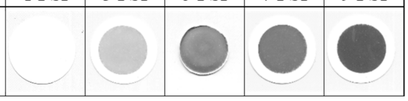
We used gas chromatography mass spectrometry (GC-MS) to identify the antioxidant additives in the turbine oil and analyzed the presence of the antioxidant's residual ratio in sample oils (1, 3, 5, 7, and 9 PSI). Table 5 shows images of the membrane patch that filtered mixtures of each sample oil (0.1 ml) and petroleum ether (10 ml). The membrane patch colors became a deep purple with an increase of the change in pressure. Figure 8 shows the GC-MS chromatograms of new oil and sample oil of 9 PSI. Two amine antioxidants, such as phenyl-1-naphtylamine (PANA) and 4,4'-dioctyldiphenylamine (DODPA), were identified by comparing the old oil with new oil. Peaks of low-molecular-weight compounds increased in the sample oil with hydrolyzing ester.

The residual ratio of these antioxidants decreased as the change in pressure increased. This result confirms that these amine antioxidants were oxidized by the RPVOT. Figure 9 shows the relationship between the residual ratio of these amine antioxidants and the ΔE_{RGB} value of the membrane patches. ΔE_{RGB} increased as the amine antioxidant residual ratio decreased. In particular, PANA oxidation products had dominant membrane patch colors.

Based on the results in Table 5 and Fig.9, by investigating the relationship between the degree of oxidative deterioration and the color of the lubricating oil in the actual

Table 5 Membrane patch images with the change in pressure.

	1 PSI	3 PSI	5 PSI	7 PSI	9 PSI
Image					



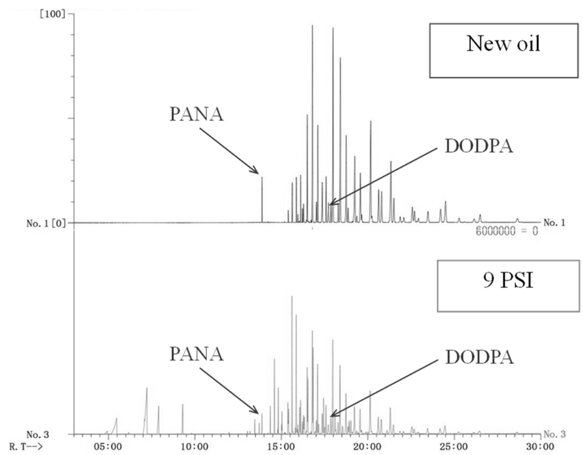


Figure 8 Total ion chromatogram.

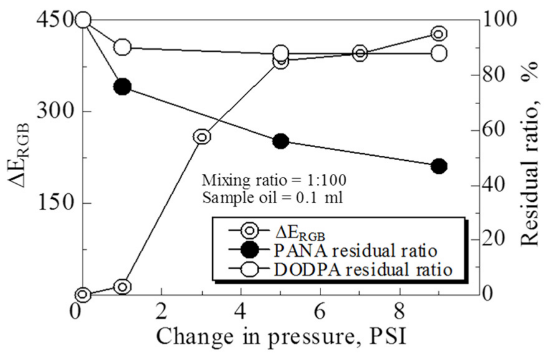


Figure 9 Relationship between the residual ratio of antioxidant and ΔE_{RGB}.

machine, it is possible to monitor the degree of oxidative deterioration of the lubricating oil in the actual machine using only the color of the membrane patch. This method can know the deterioration of lubricating performance due to the deterioration of lubricating oil and is useful for determining the optimum oil change timing. Conventionally, diagnosis was performed using expensive analysis equipment for each sampling, but by using this method, daily trend management can be performed at an extremely low cost, leading to a significant reduction in maintenance costs.

As the next issue, we believe that it is most important to clarify the relationship between lubricant deterioration and machine life, and we are currently conducting research on the effects of lubricant deterioration on tribological characteristics.

4. Conclusion

We found that amine antioxidant oxidation products in ester-based oils are deposited by mixing with non-polar solvents and that they affect the color of the membrane patch. Furthermore, we found that there is a strong correlation between ΔE_{RGB} and the residual ratio of amine antioxidants. These results indicate the possibility of a new amine antioxidant depletion diagnosis method for on-site diagnoses.

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Tomomi Honda received his Doctorate degree from Tohoku University in 1993. Since 1993, he has been working for University of Fukui, Japan. His research interests include tribology and condition monitoring. He is a member of the Society of Tribologists and Lubrication Engineers (STLE), the Japan Society of Mechanical Engineers (JSME) and the Japanese Society of Tribologists (JAST). He won the JSME Best Paper Award in 2018.

Daisuke Hamano received his M.S degree from University of Fukui in 2016. Since 2016, he has been with Nissan Motor Co., Ltd., Japan. His research interests include powertrain and electric vehicle engineering.