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Development of a turbine oil contamination diagnosis method using colorimetric analysis of membrane patches

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Abstract

Lubricating oils are used in various machines and devices; however, they degrade during operation because of their usage environment. The causes of lubricating oil contamination are roughly classified into two types: the contamination caused by solid particles and that caused by oil oxidation products. Much research into diagnosing solid particles in lubricating oils has been conducted and many standards have been achieved; however, few diagnosis methods exist for oil oxidation products. Moreover, the oxidation of turbine basis oils has recently become a serious problem in power generation plants. Therefore, an on-site deterioration diagnosis method capable of detecting turbine oil oxidation in its early stages is desirable for proactive maintenance. We have developed a lubricating oil contamination diagnosis method that considers the coloration of contaminated membrane patches. Sample oils for testing the method have been oxidized in a laboratory using a rotary pressure vessel oxidation test apparatus, and the colors of the resulting membrane patches have been determined using the colorimetric patch analyzer. The relation between the colors and the Fourier transform infrared spectroscopy analysis has been investigated. The results verify that the proposed method is capable of an early detection of changes in the oxidation products of turbine oil.

Keywords : Maintenance, Colorimetric analysis, Lubricant contamination, Oil oxidation products, Turbine oils

1. Introduction

Lubricating oils are used in various machines and devices; however, they degrade during operation because of their usage environment. The causes of lubricating oil contamination are roughly classified into two types: the contamination caused by solid particles and that caused by oil oxidation products. Diagnosis methods for solid particles in lubricating oils have several useful standards—for instance, NAS1638(Aerospace industries association, 1964), ISO4406 (International Organization for Standardization, 1999), and SAE AS4059(SAE International, 1988) are based on particle count. However, few diagnosis methods exist for oil oxidation products. Most lubrication engineers know that when contaminated oils are filtered through a membrane filter, the filter will be colored. However, no standard for judging oil contamination using colors existed until 2012 when ASTM D7843(ASTM international, 2016) was established.

Meanwhile, since 1998, we have investigated the use of colorimetric analysis for detecting oil contamination(Yamaguchi et al., 2002), (Sasaki et al., 2013), (Kon et al., 2016) and have recently developed a state-of-the-art colorimetric analysis device and method that uses the red–green–blue (RGB) color system to study the color of contaminants in used oils collected by membrane patches; patents for this device and method have been obtained in the United States(Honda et al., 2013), European Union and Japan. The device has been named the colorimetric patch analyzer (CPA). The first CPA model examined the color of contaminants trapped on the surface of membrane patches by reflecting light in a similar manner as other currently available colorimetric analyzers. It also was good to examine the color of contaminants collected on the surface of membrane patches. When the membrane patches

through which hot turbine oils have been filtered were examined with light from the back, they showed light brown colors, although their surfaces were white in color. This suggests that membrane patches trap contaminants. To confirm this, we have developed a state-of-the-art CPA that can examine contaminants on the surface of membrane patches by reflecting light and contaminants in the membrane patches, themselves, by transmitting light.

For energy efficiency, a combined cycle power generation system that uses both gas and steam turbines has become general. However, fuel efficiency of gas turbines also improves with higher inlet gas temperature. For these reasons, the average operating oil temperature of gas turbines has increased, leading to more serious problems with varnish (Day, 2008), (Livingstone and Oakton, 2010). In the case of modern gas turbine oils, the working oil temperature is high and oil oxidation products with relatively small molecular weight are soluble in the working oil. Thus, the new contamination diagnosis method is of vast importance.

To solve varnish problems, it is important to understand how oxidation progresses in the oil prior to the production of oxidation products. In this study, sample oils were oxidized in stages by using a rotary pressure vessel oxidation test (RPVOT) in order to develop a specific diagnostic technique for oxidation analysis. The color parameters of the membrane patch produced from the sample oils were measured using the newly developed CPA. The relation between the color of the membrane patch and oxidation was then examined. Furthermore, the properties of the sample oils were analyzed by using Fourier transform infrared spectroscopy (FT-IR), and changes in the properties of the sample oils were examined in detail according to the progress of the oxidation.

2. Test equipment

2.1 Filtration equipment and membrane filter

The filtration equipment used in this test consisted of a dust-proof cover, cylinder, flask, and vacuum pump. A membrane filter with a diameter of 25 mm and a thickness of 0.125 mm was installed between the cylinder and the flask. Twenty-five millimeters of sample oil were put into the cylinder and then filtered with the vacuum pump. The surface and cross section of the filter used in the filtration process are shown in Fig. 1. The membrane filter pore size was 0.8 μm , and a flow channel was irregularly formed in the filtering direction. After filtration, the residual oil was removed from the membrane filter, which is designated as the membrane patch, using petroleum ether and the membrane patch was dried. The color parameters were then measured by the CPA. Each component of the RGB reading was represented using 256 gradations, where white was represented by 255, 255, 255 and black by 0, 0, 0. The maximum color difference indicates the maximum difference between two of the RGB reading colors. ΔE_{RGB} indicates the distance from white to a specific membrane patch color and is represented by the following equation,

$$\Delta E_{\text{RGB}} = \{(255-R)^2 + (255-G)^2 + (255-C)^2\}^{0.5}$$

Previous studies have reported that both depth filtration and cake filtration are used by the membrane filter to process oil that has been contaminated by oxidation. In depth filtration, the contaminants are captured within the membrane filter; in cake filtration, the contaminants on the filter surface act as their own filter. Therefore, in this study, we measured RGB using transmitted light with which color information could be obtained from both the surface and the interior of the membrane patch. Furthermore, we used FT-IR to conduct infrared spectroscopic analysis of each of the sample oils; measurements were conducted using the attenuated total reflection method. Light was reflected through the prism 10 times.

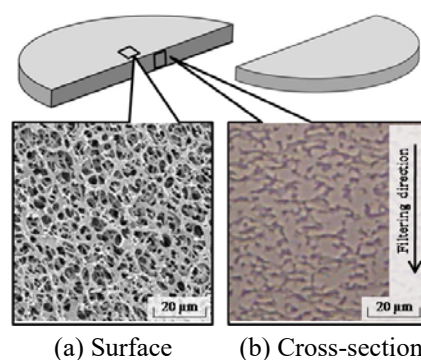


Fig. 1 Membrane filter

2.2 Oxidation test of turbine oil using the RPVOT

New turbine oil used in thermal power plants was oxidized using RPVOT, which is specified in ASTM D2272-14a (ASTM international, 2014). They are commercially available mineral oils with antioxidants. The viscosity grade is 32 with a kinematic viscosity of 5.9 mm²/s at a temperature of 100 °C. The viscosity index is 131. Figure 2 shows a schematic of RPVOT, and Table 1 summarizes the test conditions. The time taken to reach a prescribed change in pressure from the original maximum pressure was measured and is referred to as the “RPVOT time”. Furthermore, the oxidation stability was evaluated by accelerating oxidation through the use of a copper coil, which has a catalytic effect, RPVOT enables oxidation stability to be evaluated in a short amount of time. However, with regular RPVOT, the copper oxide deposits left in the oil influence the color of the membrane patch. Therefore, a copper coil was not used in this study. We prepared several sample oils that were oxidized in stages by pressure changes.

Figure 3 shows an example of RPVOT and sampling times. The sudden pressure drop that occurs within a testing time of 1200 min indicates rapid oxidation caused by waste from the oxidation inhibitor in the turbine oil. Because this study aims to detect signs of contamination in its initial and middle stages within a usable range of lubricating oil, we prepared sample oils that were oxidized prior to the rapid pressure change within the oxidation induction period. We set the pressure change at 1–9 PSI (6.9–62 kPa) in order to simulate gradual contamination in the initial and middle stages of the process. Table 2 shows images of the sample oils prepared inside liquid cells. Small sample sizes of oil make visual observation of the contamination progress difficult.

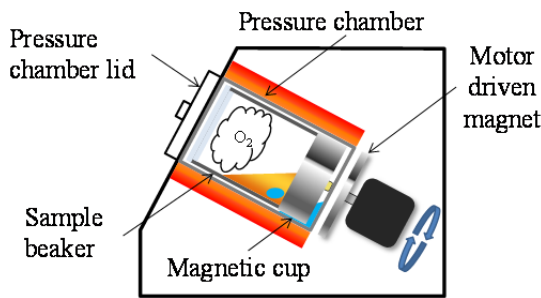


Fig. 2 RPVOT apparatus

Table 1 RPVOT test conditions

Lubricating oils, g	50 ± 0.5
Distilled water in sample beaker, ml	5
Distilled water in pressure vessel, ml	5
Initial pressure, PSI	90 ± 0.2
Test temperature, °C	150
Rotational speed, rpm	150 ± 5

Table 2 Sample oil images

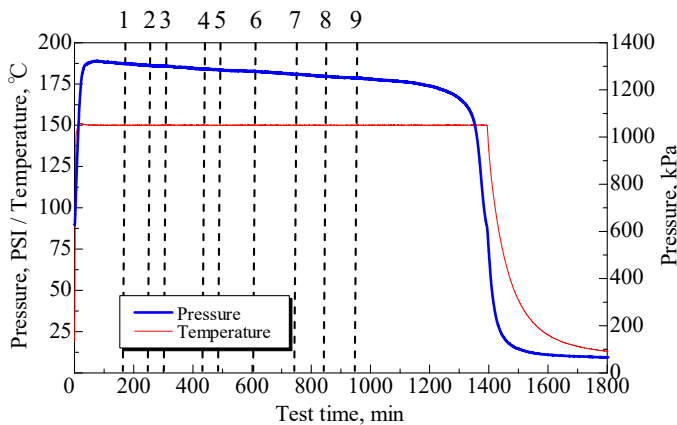


Fig. 3 Example of RPVOT and change in pressure

Change in pressure, PSI	1	2	3	4
Images				
	5	6	7	8

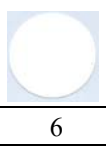

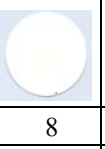

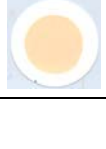
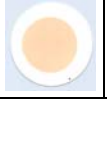


3. Experimental results and discussion

3.1 Membrane patch color

Images of the membrane patches are shown in Table 3. At a change of 1–3 PSI in pressure, only slight membrane patch coloration was observed; it was therefore difficult to distinguish differences in color. At 4 PSI, the characteristic brown color of the oxidized lubricating oil was apparent. Furthermore, a variation in testing time between each pressure change was apparent with differences in excess of 120 min for pressure change of 3–4, 5–6, and 6–7 PSI. However, a drastic color change was apparent only between 5 and 6 PSI. We can conclude from these results that the production of the oxidation product is accelerated between 5 and 6 PSI.

Figure 4 shows the relation between the change in pressure and RGB readings. Up to 6 PSI, the R reading for each membrane patch reached its maximum value of 255; once the pressure reached 7 PSI, the R reading gradually began to decrease. From 1 PSI, the G reading exhibited a steady decline and the B reading significantly decreased. Furthermore, the RGB value exhibited a significant decrease at 4 PSI, the point at which coloration was visible, and at 6–8 PSI, the point at which coloration deepened. However, the rate of decrease slowed from 9 PSI onward. By using the RGB readings for the membrane patches created from each of the sample oils, it was possible to distinguish between the color of the membrane patches when pressure changed 1–3 PSI, even though such slight pressure changes are difficult to visually discern color differences. Moreover, the use of these values enabled accurate identification of the initial stage of oxidation.

Table 3 Membrane patch images

Change in pressure, PSI	1	2	3	4
Images				
	5	6	7	8
				

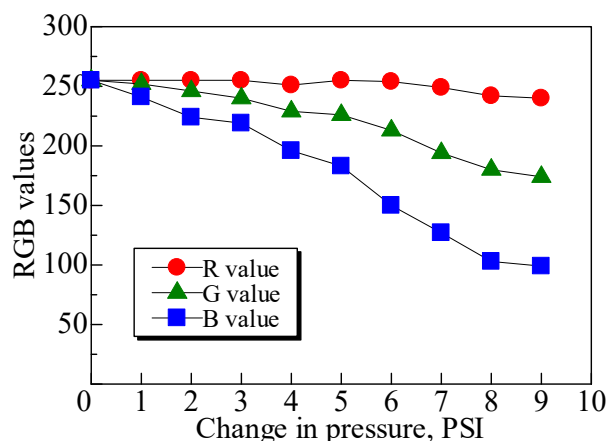


Fig. 4 Relation between change in pressure and RGB values

Figure 5 shows the relations among change in pressure, maximum color difference, and ΔE_{RGB} . The maximum color difference and ΔE_{RGB} both increased as oxidation progressed. ΔE_{RGB} represents the level of contaminants in the oil and can therefore be expected to increase even when the oxidation rapidly progresses beyond the oxidation induction period. However, previous studies have reported that the color difference reaches its maximum value during oxidation and then decreases. Thus, when we prepared membrane patches from the sample oils simulating initial- and middle-stage oxidation within the oxidation induction period, we determined that the maximum color difference and ΔE_{RGB} exhibited an increasing tendency in accordance with the progression of oxidation.

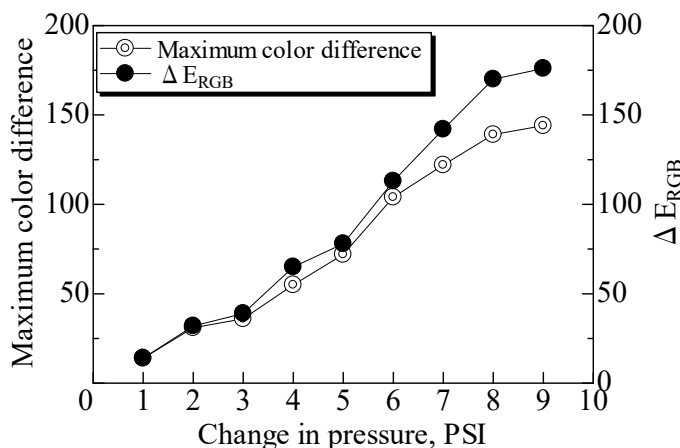


Fig. 5 Relation among change in pressure, maximum color difference and ΔE_{RGB}

3.2 Infrared spectroscopic analysis of sample oils

Figure 6 shows the results of the infrared spectroscopic analysis of the base oil and each of the sample oils. A full-scale comparison of the spectra revealed no difference between the base oil and each of the sample oils. However, as shown in Fig. 7, in the results for the infrared spectroscopic analysis of the turbine oil, which was considerably oxidized, a peak that is believed to be an oxidation product near 1713 cm^{-1} appeared at full scale when RPVOT was

conducted for longer than 1600 min. Oxidation products that belong to the carbonyl group C(=O)-, such as carboxylic acid, had an absorption band of 1800–1650 cm^{-1} . The band intensity of organic compounds that incorporated a carbonyl group is represented as carboxylic acid > ester > ketone \approx aldehyde \approx amide (Kiemle, 1983). Therefore, because the absorption band of carboxylic acid existed in 1725–1700 cm^{-1} , the peak near 1713 cm^{-1} is believed to represent carboxylic acid.

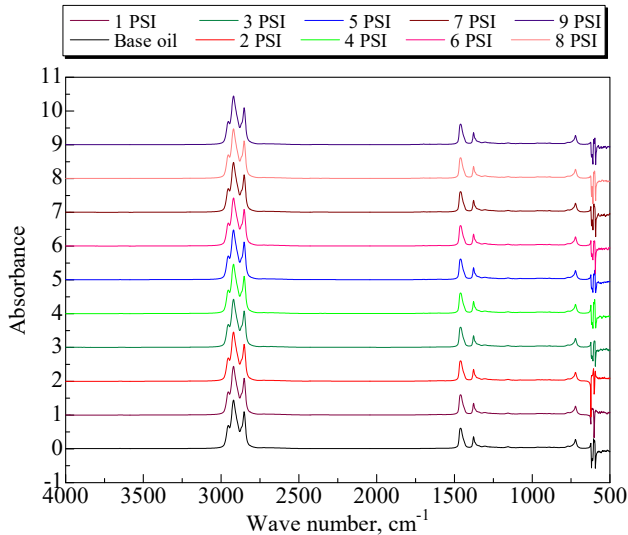


Fig.6 IR spectrums of sample oils as absorbance

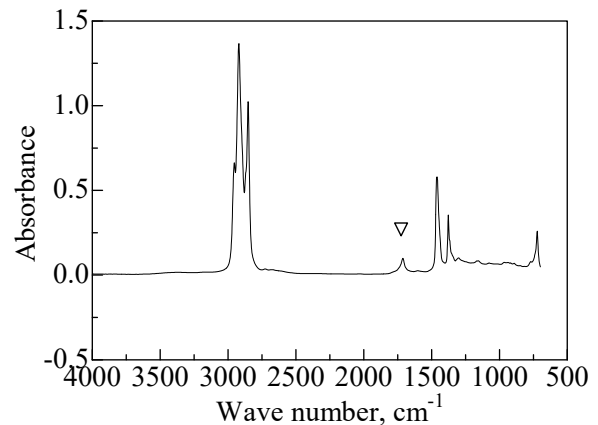


Fig. 7 IR spectra of the turbine oil with the most oxidative contamination

Because no apparent differences were detected in the spectra, as shown in Fig. 6, we expanded the absorption band of the carbonyl group C(=O)-, such as carboxylic acid, and studied the peaks for the oxidation products. Figure 8 shows the results after the carbonyl group absorption band for each of the sample oils was expanded. The figure was adjusted such that the spectrum for each of the sample oils had an absorbance of 0.005 at approximately 1740 cm^{-1} . A peak existed near 1697 cm^{-1} , which increased in intensity in accordance with the progress of oxidation. For this reason, it is believed that the oxidation substances that absorbed the wavenumber infrared light were oxidation products belonging to the carbonyl group. However, as illustrated in Fig. 6, since the carboxylic acid peak that is visible in the spectrum of the turbine oil, which underwent considerable oxidation, existed near 1713 cm^{-1} , the oxidation product was not likely carboxylic acid.

It was therefore necessary to examine the relation between oxidation products that exhibit absorption near 1697 cm^{-1} and carboxylic acid that exhibits absorption near 1713 cm^{-1} . Therefore, we prepared a sample oil at 15 PSI to represent oxidation that had progressed beyond 1–9 PSI, upon which we conducted infrared spectroscopic analysis. Figure 9 shows the analysis results when the spectra for the sample oils at 6, 9, and 15 PSI in the vicinity of 1740–1660 cm^{-1} had an absorbance of 0.005 at approximately 1740 cm^{-1} . The peak intensity of the 15 PSI sample oil in the vicinity of approximately 1697 cm^{-1} was lower than that of the sample oil at 9 PSI. Furthermore, in Fig. 9, the absorbance is shown to increase at 1740–1700 cm^{-1} until it peaks in the vicinity of approximately 1697 cm^{-1} , in accordance with the progression of oxidation. These results indicate a possible relation between the decrease in peak intensity near 1697 cm^{-1} on the 15 PSI spectrum and the increase in absorption band at 1740–1700 cm^{-1} . Moreover, the oxidation product near 1697 cm^{-1} likely converted into carboxylic acid.

When the turbine oil was oxidized using RPVOT without a copper catalyst, an oxidation product exhibiting a peak near 1697 cm^{-1} was produced from 1 to 8 PSI. Then, from 9 PSI onward, peaks near 1697 cm^{-1} that appeared because of the progression of base oil oxidation, oxidation products, and carboxylic acid were produced at the same time. It is highly likely that the oxidation product produced at the peak near 1697 cm^{-1} was oxidized to form carboxylic acid. Previous studies have reported that oxidation products that convert to carboxylic acid are primary alcohol, secondary alcohol, aldehyde, and ketone. However, the oxidation product on this occasion was not consistent with primary or secondary alcohol because the absorption band for alcohols is in the range of 1260–1000 cm^{-1} owing to the C–O stretching vibration (Kiemle, 1983). Therefore, the oxidation product indicated by the peak near 1697 cm^{-1} is likely to

be aldehyde or ketone. It has been previously determined that aromatic ketone has an absorption band of 1700–1680 cm^{-1} . However, aldehydes with conjugated unsaturated bonds have an absorption band of 1705–1680 cm^{-1} because such bonds shift the absorption of the carbonyl group to a wavenumber of 15–40 cm^{-1} , which is lower than normal. Consequently, the existence of a peak near 1697 cm^{-1} likely appeared because the oxidation product that converted to carboxylic acid is either aromatic ketone or aldehyde with a conjugated unsaturated bond (Hesse et al., 2000). We can conclude from these results that when the sample oil is oxidized through RPVOT without a copper catalyst, an oxidation product believed to be aromatic ketone or aldehyde with a conjugated unsaturated bond is produced in the first stage. Moreover, carboxylic acid is produced by the oxidation of these products in the second stage.

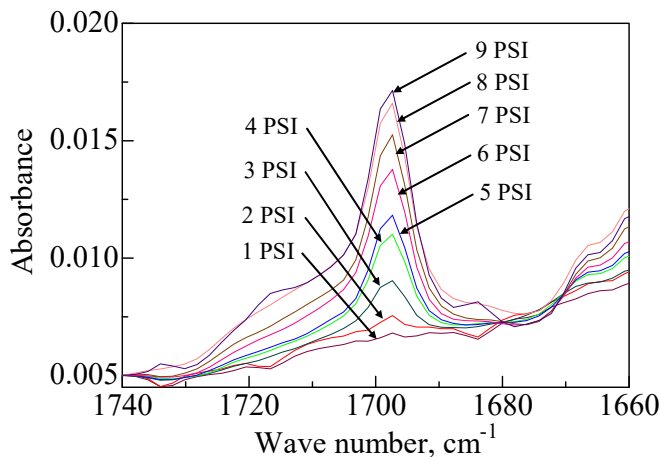


Fig. 8 IR spectra of sample oils to 1800–1650 cm^{-1}

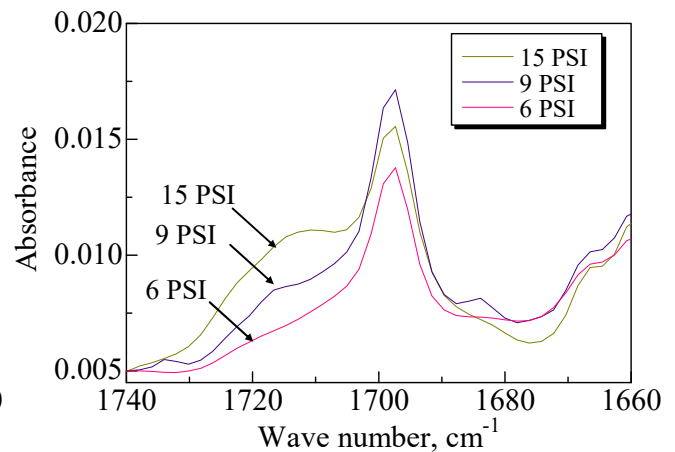


Fig. 9 IR spectra of sample oils with pressure changes of 6, 9, and 15 PSI to 1800–1650 cm^{-1}

3.3 Relation between the color parameters and peak intensity of the oxidation products

Figure 10 shows the relations among change in pressure, peak intensity near 1697 cm^{-1} , and maximum color difference. Figure 11 shows the relations among change in pressure, peak intensity near 1697 cm^{-1} , and ΔE_{RGB} . We determined that the tendency of the maximum color difference to increase as the oxidation contamination progresses correlates well with the tendency of the peak intensity to increase near 1697 cm^{-1} . On the contrary, a strong correlation was apparent between the increasing tendency of ΔE_{RGB} and that of the peak intensity near 1697 cm^{-1} in the initial stage of oxidation, 1–5 PSI. However, from 6 PSI onward (i.e., the point at which the membrane patch color rapidly deepened), the rate of increase for ΔE_{RGB} increased. It is clear from these trends that when the initial and middle stages of oil oxidation are simulated using RPVOT, the maximum color difference and ΔE_{RGB} exhibit an increasing tendency because of the increased amount oxidation products in the oil. Furthermore, the increasing tendency of the oxidation product peak intensity may be used to broadly identify the maximum color difference at the initial and middle stages of oil oxidation. Moreover, this increasing tendency can be used to indicate the peak intensity of oxidation product from the increasing tendency of ΔE_{RGB} for oxidation as a whole and to manage the degree of contamination.

From 4 PSI onward, the membrane patch was tinged brown; the color deepened at 6 PSI. However, the peak intensity near 1697 cm^{-1} indicates a tendency for oxidation to increase from the initial stage. Even though the rate of peak intensity increase for 3 PSI is proportional to that for 4 and 6 PSI, the membrane patch for 3 PSI was not tinged brown. Furthermore, even though the rate of peak intensity increase for 5 PSI was lower than that for 3 PSI, the rate of color difference and ΔE_{RGB} increases for 5 PSI were greater than those for 3 PSI. We can conclude from these results that, for the membrane patch to become brown in color, at least a certain amount of oxidation product must be captured, and that if this amount is exceeded, the captured amount of oxidation product is then sensitively reflected by color. The increasing tendency of the ΔE_{RGB} value for the membrane patch, which indicates the degree of contamination in the sample oil, and the increasing tendency of the oxidation product peak intensity both increased from 6 PSI onward. Therefore, it is believed that the properties of the sample oil significantly changed owing to rapid oxidation between 5 and 6 PSI.

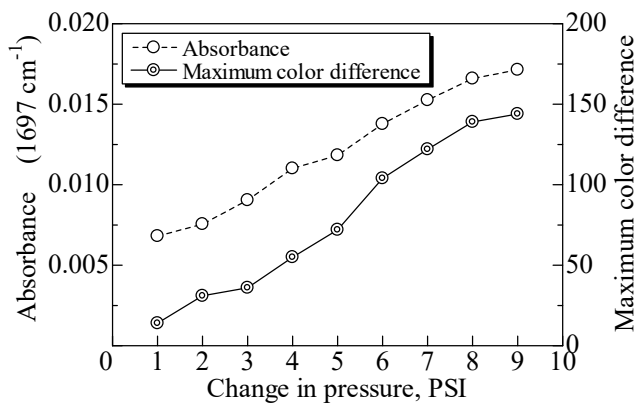


Fig. 10 Relation among change in pressure, absorbance and maximum color difference

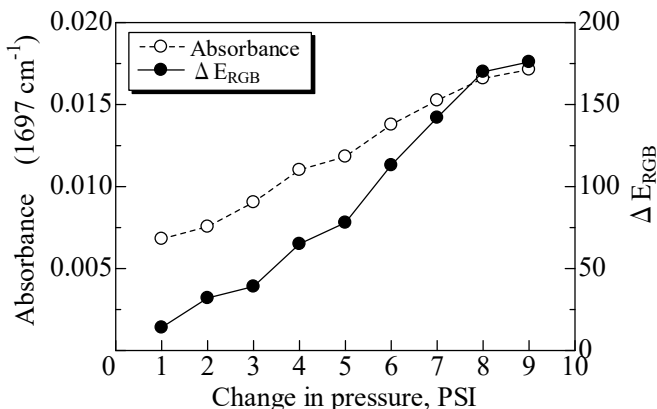


Fig. 11 Relation among change in pressure, absorbance and ΔE_{RGB}

4. Conclusion

The results of this study are summarized in the following points:

(1) When the initial and middle stages of oxidation within the oxidation induction period of turbine oil were simulated in a laboratory, the membrane patch became brown in color and the maximum color difference and ΔE_{RGB} increased together as oxidation progressed.

(2) When the initial and middle stages of oxidation within the oxidation induction period of turbine oil were simulated in a laboratory, aromatic ketone or aldehyde with conjugated unsaturated bonds were produced when the pressure changed between 1 and 8 PSI. It is believed that these oxidation products were also produced at 9 PSI along with the carboxylic acid produced by their oxidations.

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