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[Technical Report]

Proposal of Lubricant Maintenance by Monitoring Peroxide Value

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This preliminary study on the maintenance of industrial lubricants for chemical plant investigated appropriate maintenance through condition monitoring of the lubricants, in particular autoxidation of base oil as the major degradation process. Changes in chemical and physical properties caused by the autoxidation of hydrocarbons were considered in terms of reaction sequence. The roles of antioxidants for maintaining the quality of lubricants were also considered. The reaction mechanism suggested the importance of antioxidants in lubricants during service. Therefore, a new method to diagnose consumption of antioxidant was required. Organic peroxides are reactive species generated during the autoxidation of hydrocarbons at the initial stage and can be quantitatively analyzed by iodometric titration. The peroxide value (POV) is proposed as a new parameter to monitor conditions of lubricants. The POV trace was examined by a model oxidation test of lubricant in the laboratory. Subdivided addition of antioxidants to lubricant before an increase in POV was found to prolong the lifetime of the lubricants. POV in lubricants for compressors in chemical plant was monitored during the regular maintenance process for two years. Increased POV was observed during machine operation. Oil refill reduced the POV of the lubricant to some extent. Changes in total acid number (TAN) of lubricant were closely related to change in POV, whereas other parameters such as viscosity, insoluble contaminants and water contaminants seemed independent of the changes in POV. The utility of the POV trace depended on the conditions of machine operation, but provided early diagnostics of lubricant degradation in some cases.

Keywords
Lubricant maintenance, Peroxide value, Autoxidation, Lubricant degradation, Industrial lubricant, Antioxidant

1. Introduction

Lubricants undergo degradation during service, so require regular renewal when their functions became inadequate. Shutdown maintenance may be necessary for recovery of all systems, which allows both replacement of aged oils and defective parts, but also cleaning of the machines. However, shutdown maintenance is usually expensive. Therefore, partial maintenance on demand is desirable to reduce the cost. Replacement of all the lubricating oil in the reservoir is usually expensive and time consuming. Therefore, replacement of only the oil lost through evaporation or leakage is a common procedure in lubricant maintenance. Similarly, replenishment of lubricant additives consumed during service is sometimes applied in the maintenance of industrial lubricants. This technique, the so-called "make up of lubricant," can prolong the lifetime of the lubricant if the maintenance is correctly programmed.

Antioxidants are one of the major components of industrial lubricants, which are added to prevent lubricant degradation caused by autoxidation during service. The additives are consumed during the decomposition or removal of the active intermediates such as radicals and peroxides that are formed during the autoxidation process. Replenishment of antioxidants is widely recognized as very important in the make-up of industrial lubricants. We previously pointed out that the effect of antioxidants in make-up oil strongly depends on the stage of aging[1)]. Our results indicated that the make-up procedure should be performed before the initiation of the autoxidation of the base oil.

The chemical process of the autoxidation is illustrated in **Fig. 1**. The autoxidation mechanism of hydrocarbons involves carbon radicals and organic peroxides as active intermediates[2)]. The active intermediates are unstable substances generated at the initial stage of the autoxidation. The organic peroxides are then converted to organic oxides such as aldehydes, ketones, alcohols, and carboxylic acids. In particular, the carboxylic acids cause the corrosion of metallic materials. The formation of carboxylic acids can be detected by

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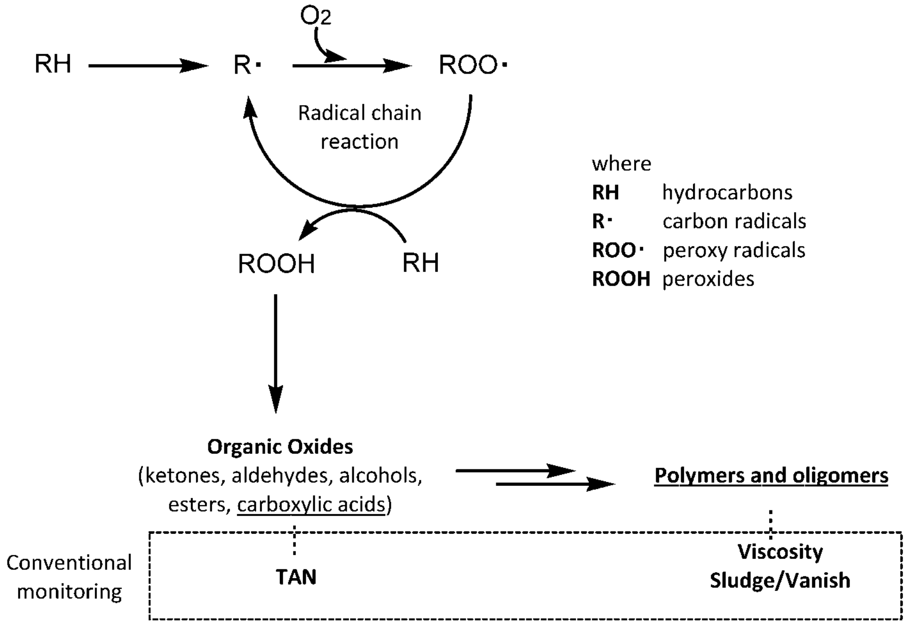

Fig. 1 Degradation Process Caused by Autoxidation

increases in the total acid number (TAN) of lubricants. Some organic oxides undergo further reactions that cause changes in the physical and chemical properties of the lubricant. For example, the aldol condensation of carbonyl compounds forms oligomers and/or polymers that increase the viscosity of the lubricant. Certain polymers are considered to be precursors of varnish or sludge. These changes can be observed sequentially in model laboratory experiments[3].

The autoxidation process involves an induction period during which the presence of antioxidants is effective to remove the active organic peroxide intermediates. However, the antioxidants are consumed by the removal of the active intermediates during the induction period, so when depleted, the level of peroxides starts to rise. The end of the induction period is marked by the final depletion of the effective levels of antioxidants. At this stage, few if any changes have occurred in the physical and chemical properties of the aged oil[1]. Therefore, we considered that the initial increase in the peroxide levels in aged oil may provide an early indicator of lubricant degradation. Such early diagnosis of autoxidation would be very beneficial to schedule the timing of the maintenance program. In addition, replenishment of antioxidants should be performed just before the completion of the induction period. Fortunately, quantitative analysis of peroxides is easily performed by iodometric titration at reasonable cost[4].

The present study proposes the measurement of the peroxide value (POV) as an indicator of the need for antioxidant replenishment in lubricating oil, which was tested in a model study in the laboratory and a field study in a chemical plant. We hypothesized that subdivided addition of antioxidants would prolong the lubricant lifetime. Model oxidation of the sample oil found that autoxidation was prevented if the antioxidants were replenished before an increase in POV was detected. The POV and other conventional parameters were then measured in lubricants in service for compressors in a chemical plant for two years to determine the relationships between POV and other parameters of lubricants in terms of the operating conditions of machines.

2. Experimental

2. 1. Model Oxidation Test in the Laboratory

Practical lubricants consist of the base oil and several additives to satisfy the tribological requirements and to prevent degradation. The complexity of additive systems is sometimes considered to make fundamental research difficult. Therefore, we first designed a model system for this study. The major desirable functions of lubricants are improvement in the tribological properties and prevention of degradation. Usually, lubricant additives are responsible for these functions, and include ZnDTPs as one of the most versatile additives that both reduce the wear of surfaces as well as prevent the autoxidation of base oils[5],[6]. Therefore, both functions can be monitored simultaneously by tracing one component. In addition, a model lubricant containing two additives may involve some interaction between them. The bifunctionality of ZnDTP eliminates any undesirable interaction of additives that would complicate the results.

Procedure A: To a solution of ZnDTP in squalane

Table 1 List of Machines and Lubricants Monitored in This Work

Machine		Lubricant contents
ID	Type	
#1	Turbo-compressor	Paraffinic mineral oil with 1 maass% of additives (antioxidants, rust inhibitors and foam control additives)
#2	Turbo-compressor	
#3	Rotary screw compressor	
#4	Gear turbo-compressor	Paraffinic mineral oil with additives (specified antioxidants, rust inhibitors and foam control additives)
#5	Gear turbo-compressor	
#6	Reciprocating compressor	Paraffinic mineral oil with 5 mass% of additives (antioxidants, rust inhibitors and foam control additives)

Table 2 Methods of Oil Analysis

Parameter	Method	Regulation
Contamination	Filtration	JIS B 9931
Water content	Karl-Fischer titration	JIS K 2275
Viscosity	Viscometer	JIS K 2283
TAN	Neutralization titration	JIS K 2501
POV	Iodometric titration	ASTM D 1832

(1 mmol·kg^{-1}, 200 g), dry air was introduced at 0.2 dm^3·min^{-1} maintaining the temperature at 120℃. The oxidation was continued for 50 h. 50 g of mixture was sampled and fresh ZnDTP solution in squalane (4 mmol·kg^{-1}, 50 g) was added. The resultant solution was oxidized by the same procedure for additional 50 h. The TAN and POV of the oxidized samples were obtained by titration according to JIS K 2501 and ASTM D 1832, respectively. The tribological properties of the oxidized samples were evaluated by the four-ball type wear test according to ASTM D 4172. In this procedure, the total amount of ZnDTP was 0.4 mmol.

Procedure B: This is a similar procedure, but with modified interval of sampling and ZnDTP re-addition. To a solution of ZnDTP in squalane (1 mmol·kg^{-1}, 200 g), dry air was introduced at 0.2 dm^3·min^{-1} maintaining the temperature at 120℃. Every 10 h, 10 g of oxidized oil was sampled and fresh solution of ZnDTP in squalane (2 mmol·kg^{-1}, 10 g) was added. This sampling-addition procedure was repeated 9 times, during total oxidation time of 100 h. In this procedure, the total amount of ZnDTP was 0.38 mmol.

2. 2. Oil Monitoring in a Chemical Plant

Lubricants for machines in a chemical plant were analyzed as part of the regular maintenance procedure. Addition to the conventional parameters, the POV of the lubricants was measured. The types of machines and methods for lubricant analysis are listed in **Tables 1** and **2**, respectively.

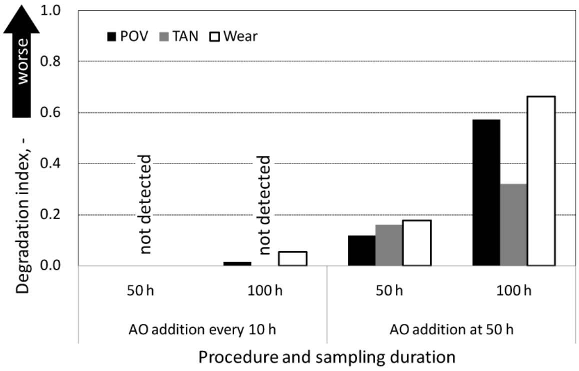

Fig. 2 Results of Laboratory Oxidation Test

3. Results and Discussion

3. 1. Model Oxidation Test in the Laboratory

Procedure A caused both POV and TAN to increase within 50 h, indicating that autoxidation occurred under these conditions (**Fig. 2**). Therefore, the anti-wear properties of the lubricant evaluated by the four-ball test were poor. Another portion of ZnDTP was added to the aged oil and the model oxidation was continued for a further 50 h, showing that the rate of rise in POV during the second 50-h period was higher than that during the first 50-h period. These results indicate that the function of ZnDTP as antioxidant during the second 50-h period is inferior to that during the first 50-h period. The findings of the four-ball wear test also indicated increased additive depletion during the second 50-h period. Considerable rises in the three degradation indices (POV, TAN and wear) during the second 50-h period suggested that further addition of ZnDTP did not improve the function of the lubricant. In contrast, procedure B resulted in few changes in the degradation indices, although the total amount of ZnDTP was slightly lower than that for procedure A.

Obvious differences in the anti-oxidation function of ZnDTP between procedure A and the procedure B can be explained by the reaction mechanism. The primary function of ZnDTP as antioxidant is to remove the reactive species such as organic peroxides that are generated

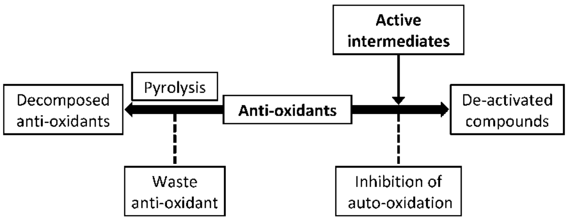

Fig. 3 Major Pathways for Antioxidant Reaction

by the autoxidation of hydrocarbons. In addition, several side reactions (or simultaneous reactions) have to be considered, including pyrolysis of the antioxidants which probably occurs under these conditions. Such side reactions may be important if excess amounts of antioxidants for removing the active intermediates are present in the system (**Fig. 3**). The subdivided addition of antioxidant provides the appropriate amount of antioxidants for removing the active intermediates if timing of the addition was successfully programmed. We propose that this is the main reason why procedure B is superior to procedure A.

The TAN increased after the first 50-h period in procedure A, suggesting the formation of certain organic oxides. The findings accord with the previous report demonstrating that organic oxides have detrimental affects on the function of antioxidants.

Pyrolysis causes unnecessary consumption of antioxidants, so prevention of side reactions is important to optimize the anti-oxidation properties that prolong the lifetime of lubricants. The laboratory oxidation test suggested that subdivided addition of antioxidants has the best potential for practical applications. The most effective procedure is addition of antioxidants just before the generation of organic oxides by autoxidation. Therefore, the timing of the re-addition of antioxidants is very important. As explained in **Fig. 1**, we evaluated the POV as an indicator of autoxidation in the early stages of lubricant degradation.

3. 2. Monitoring in a Chemical Plant

The degradation of lubricants in practical application is complicated. Autoxidation and other mechanisms have to be considered. Therefore, we investigated the POV change in practical lubricants during service. Comparison of POV with other conventional parameters for lubricant maintenance was also of interest. Therefore, sample oils obtained through regular oil maintenance procedures were evaluated by iodometric titration according to ASTM D 1832. Results of the POV trace and TAN trace are presented as **Figs. 4-9**. Changes in other parameters are explained briefly.

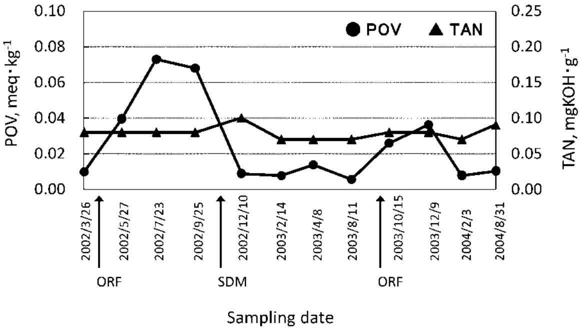

Fig. 4 POV and TAN Traces: chemical plant machine #1

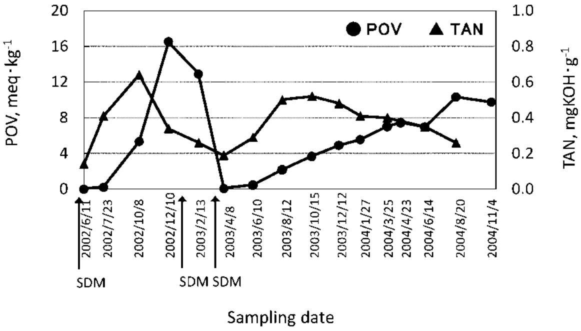

Fig. 5 POV and TAN Traces: chemical plant machine #2

Machine #1 (**Fig. 4**): POV increased during machine operation, but slightly decreased after 2002/7/23. POV increase is an indicator of the initiation of the autoxidation. POV reached the point of inflection around 2002/7/23. At that time, no changes in TAN and viscosity were detected. Fortunately regular shutdown maintenance (SDM) was scheduled after 2002/10/15. Our hypothesis based on the laboratory oxidation test suggests that this is the ideal timing for lubricant maintenance. The machine was re-started on 2002/12/10 and the monitoring was continued. POV increased again after 2003/8/11 and reduced after 2003/12/9. An increase in TAN was observed on 2004/8/31, just after the POV drop. These changes indicate the initial stage of autoxidation. The observations agree with the model oxidation process. Insoluble contamination and water contents in the lubricant were also monitored during machine operation, but showed no obvious relationships with POV.

Machine #2 (**Fig. 5**): Results obtained from machine operation were confusing. TAN increased before POV rose, which cannot be explained by the mechanism of autoxidation. Careful analysis of the operating conditions of the machine revealed that introduction of acidic contaminants into the oil during service. The acid contaminants might promote the autoxidation of oil and result in POV increase. POV decreased after SDM on 2002/12/10 and on 2003/2/13. The reductions in TAN and POV by additives in fresh lubricant are expected. In this case, POV measurement was strongly supported for monitoring of lubricant condition. Similar to the findings for machine #1, no obvious change in viscosity was detected. Insoluble contamination and water con-

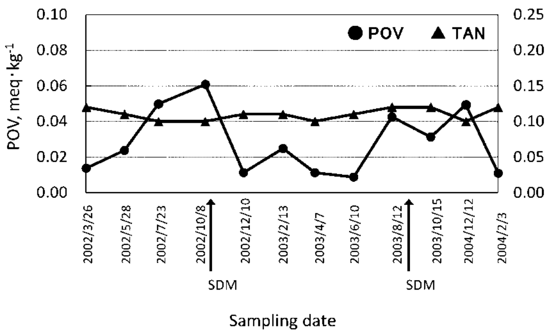

Fig. 6 POV and TAN Traces: chemical plant machine #3

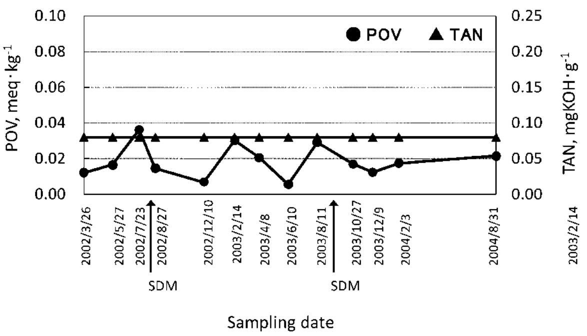

Fig. 8 POV and TAN Traces: chemical plant machine #5

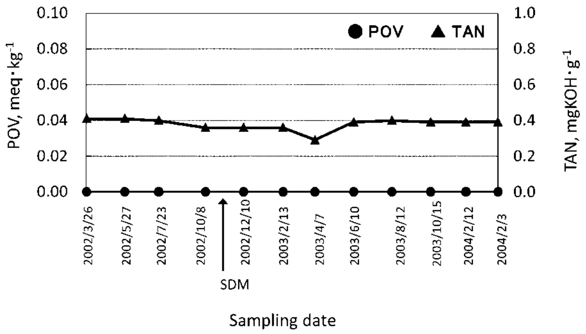

Fig. 7 POV and TAN Traces: chemical plant machine #4

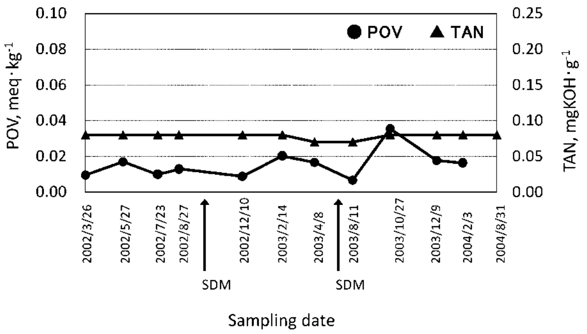

Fig. 9 POV and TAN Traces: chemical plant machine #6

tents seemed to be independent of changes in POV and TAN.

Machine #3 (**Fig. 6**): POV increased during machine operation and decreased after SDM on 2002/10/8 and 2003/8/12. POV decreased on 2004/2/3 and TAN subsequently slightly increased. This might be a signal that whole antioxidants had consumed. No changes in viscosity and water contaminants were detected, however insoluble contamination was scattered in this case.

Machine #4 (**Fig. 7**): No detectable changes in POV were observed throughout machine operation. The machine was a nitrogen compressor, so autoxidation was unlikely. Therefore, low POV was expected. The lubricant might undergo degradation by other causes. No changes in viscosity and water contaminants were detected, but insoluble contamination was present.

Machine #5 (**Fig. 8**): POV increased during machine operation and decreased after SDM. However, no obvious changes in TAN and viscosity were detected throughout the service. These results suggest initiation of autoxidation. Insoluble contamination and water contents seemed independent of changes in POV.

Machine #6 (**Fig. 9**): The findings were very similar to those of machine #5.

POV increase during service was observed in all machines except for machine #4. Increase in TAN was also observed subsequently for machines #1 and #3, which is in good agreement with the reaction mechanism. Changes in POV but not TAN were detected for machines #5 and #6 before the regular maintenance. Therefore, the conventional maintenance seems to adopt appropriate timing. Machine #4 was run under nitrogen, so autoxidation did not seem to be significant. On the other hand, machine #2 was run under acidic NO_x gas, so both POV and TAN increased significantly even during short duration of service. In this case, promotion of autoxidation by NO_x is most likely$^{7)}$. No obvious change in lubricant viscosity was observed for all machines monitored. Insoluble contamination and water had no direct relationships to the autoxidation. In summary, POV should be monitored carefully for machine #2. POV in addition to the conventional parameters should be monitored for machines #1 and #3, if an early diagnostic is required. Lubricant maintenance is best done for machines #4, #5, and #6 by monitoring the conventional parameters. Application of the proposed POV-TAN monitoring for lubricant maintenance in the chemical plant is now in progress.

4. Conclusions

Subdivided re-addition of antioxidant was proposed to preserve the functions of industrial lubricants. The timing of the re-addition can be optimized by monitoring the stage of autoxidation. POV and TAN are convenient parameters to indicate the early stage of the autoxidation. These parameters and the conventional parameters of practical lubricants were monitored for two years in a chemical plant. The conventional parameters for monitoring of lubricants were effective maintenance of machines for chemical plant. POV measurement provided early diagnosis of lubricant degradation in some machines run under particular conditions.

Acknowledgments

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Nomenclatures

ASTM : American Society for Testing Materials
JIS : Japan Industrial Standards
ORF : oil refill
POV : peroxide value
SDM : shutdown maintenance
TAN : total acid number
ZnDTP : zinc bis(dialkyldithiophosphate)
Degradation index,
for POV : POV rise/10 [meq·kg^{-1}]
for TAN : TAN rise [mgKOH·g^{-1}]

$$\text{for wear : } \frac{(\text{WSD by an oxidized sample}) - (\text{WSD by the fresh oil})}{(\text{WSD by the fresh oil})}$$

where WSD = wear scar diameter obtained by four-ball wear test.

References

1) Minami, I., *Lubrication Science*, **7**, (4), 319 (1995).
2) Zuidema, H. H., *Chemical Reviews*, **38**, (2), 197 (1946).
3) Minami, I., Mimura K., *J. Synth. Lubrication*, **21**, (3), 193 (2004).
4) Mair, R. D., Graupner, A. J., *Anal. Chem.*, **36**, (1), 194 (1964).
5) Burn, A. J., *Tetrahedron*, **22**, 2153 (1966).
6) Spikes, H. A., *Tribology Lett.*, **17**, (3), 469 (2004).
7) Johnson, M. D., Korcek, S., *Lubrication Science*, **3**, (4), 95 (1991).

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要　旨

過酸化物価変化に注目した潤滑油メンテナンス方法の提案

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本研究は化学プラント機器用工業潤滑油のメンテナンスを目的とした探索的研究である。その主目的は潤滑油の状態分析を通して適切な潤滑油管理を行って潤滑油の寿命を延ばすことである。潤滑油劣化要因の一つとして基油の自動酸化に注目した。また，自動酸化の進行に伴う潤滑油の物理的性質と化学的性質の変化および反応機構を考慮して系中に残存する酸化防止剤とその機能の重要性に注目した。そこで，酸化防止剤の劣化や消耗を診断するための新たな指標が必要となった。酸化防止剤が消耗すると，炭化水素の自動酸化反応初期段階で生成する活性な有機過酸化物が生じる。これはヨウ素還元滴定で定量できる。我々は潤滑油の状態分析のパラメーターとして新たに過酸化物価（POV）を提案し，その有用性を実験室内のモデル酸化試験で示した。これにより，潤滑油中のPOVが上昇する前に酸化防止剤を分割して添加することで潤滑油の長寿命化に有効であることが分かった。次に，化学プラントで実働している圧縮機の潤滑油を2年間にわたって追跡調査した。機械の運転条件次第でPOVは上昇し，その挙動は全酸価の上昇と関連する。POVが実機に使用している潤滑油の劣化を早期に診断するパラメーターとなりうることを示した。

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