

Study on Estimation Method of Anti-oxidation Performance for Engine Oil Deterioration Monitoring System

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ABSTRACT

The research discussed in this paper demonstrated the existence of a strong correlation between the anti-oxidation performance of engine oil and the production of sludge. Analysis of the deterioration mode of anti-oxidation performance in component tests and engine bench tests of engine oil indicated that the reaction mechanisms causing engine oil deterioration could be approximated by the superpositioning of zero- and first-order reactions. The results of these tests also demonstrated that heat, air, NOx and unburnt fuel are major factors in the deterioration of anti-oxidation performance. Detailed analysis resulted in the proposal of a general equation for the deterioration of oil anti-oxidation performance, which enabled the degree of deterioration to be estimated.

Actual vehicle tests showed that the use of the equation enabled accurate estimation of the deterioration rate of anti-oxidation performance, indicating that the method has potential for onboard use.

1. Introduction

Increasing efforts are today being made to protect the environment, spurred by issues such as global warming. This trend has extended to the area of automotive lubricating oils, generating demands for reductions in the volume of waste oil⁽¹⁾. In the case of engine oil, in particular, the high volume of waste oil, high frequency of oil changes, and high degree of public awareness of the product make the extension of the period between engine oil changes an important factor to consider for automotive manufacturers^{(2), (3)}.

However, engine oil quality issues have emerged in Europe and the U.S., including the production of black sludge. Because of this, simply extending the period between engine oil changes might result in damage to the engine⁽⁴⁾.

An engine oil deterioration monitoring system would represent an effective method of protecting the engine while extending the period between engine oil changes. If such a system could indicate the appropriate time to change the oil to the user, engine protection could be balanced with environmental protection.

The key to judging when engine oil needs to be changed is determining whether the oil is continuing to fulfill its functions of lubrication, cleaning, rust protection, corrosion protection, and sealing. In addition to additives that enable these functions to be fulfilled, engine oil contains additives to help prevent oxidation and control the progress of deterioration. It is known that as the depletion of anti-oxidant additives progresses, oxide polymerization reactions occur, and there is a rapid decline in the performance of the oil. There are indications that this may cause major engine issues, such as low lubrication performance and clogging of the oil channels due to the production of varnish and sludge.

The anti-oxidation performance of the oil therefore has an important effect on the degree of oil deterioration, and the remaining usable life of the oil can be judged from the remaining anti-oxidation amount⁽⁵⁾⁻⁽⁷⁾. An engine oil deterioration monitoring system that judges the remaining usable life of the oil on the basis of cleaning performance has been developed⁽⁸⁾. The combination of two indicators, anti-oxidation performance and cleaning performance, could be expected to provide a more accurate means of judging the remaining usable life of the oil. However,

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analysis of both these indicators calls for the use of special equipment, and vehicle users could not be expected to independently employ them to judge the usable life of their engine oil.

The research discussed in this paper developed a technology of estimating the remaining anti-oxidation performance of engine oil, based on data from engine sensors, without the necessity of actually measuring remaining performance indicators. The project also verified the fact that the new technology could be employed in an on-board anti-oxidation performance monitoring system.

2. Analysis of Depletion of Anti-oxidant Additives

2.1. Mechanism of Prevention of Oxidation Deterioration of Engine Oil

As Fig. 1 shows, when $RO\cdot$ radicals and $ROO\cdot$ radicals are produced in the base oil of an engine oil, a chain oxidation reaction begins to proceed. Anti-oxidants and extreme pressure agents are additives that are known to help prevent this oxidation reaction^{(9), (10)}. Anti-oxidants function by means of a mechanism called chain termination, which renders $RO\cdot$ and $ROO\cdot$ radicals inactive. The mechanism of functioning of extreme pressure agents is called peroxide decomposition. These additives function to help prevent the inactive substance $ROOH$ from being reconverted into $RO\cdot$ and $ROO\cdot$.

2.2. Experimental Oil Compositions and Engine Bench Tests

An engine oil was formulated using a phenol-based anti-oxidant (selected as a representative type) and secondary zinc dialkyl dithiophosphate (sec-ZnDTP) as an extreme pressure agent, and subjected to engine bench

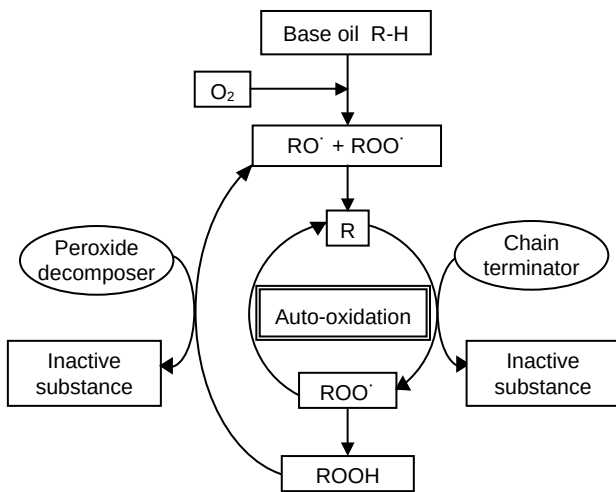


Fig. 1 Mechanism of engine oil auto-oxidation and terminal reaction

Table 1 Engine specification and test conditions

Engine specification	Water-cooled 4-cylinder 2.4L gasoline	
Mode	Medium speed mode	
Engine oil formulation	Antioxidants	0.2 wt%
	Sec-ZnDTP	0.5 wt%
	Detergents	3 wt%
	Succinic imide	5 wt%
	Base oil	PAO

tests (Table 1). The oil was removed at fixed intervals and analyzed to determine the mode of depletion of each of the additives. The anti-oxidant was analyzed using gas chromatography, and the sec-ZnDTP was analyzed using phosphorous-31 nuclear magnetic resonance ($^{31}\text{P-NMR}$).

The results of this analysis of the mode of depletion of the anti-oxidant additive and the sec-ZnDTP are shown in Fig. 2. Differential calculus was used to determine the reaction rates of the additives. The anti-oxidant additive demonstrated linear depletion, which can be approximated by the zero-order reaction shown in Eq. (1). The sec-ZnDTP, by contrast, demonstrated exponential depletion, which can be approximated by the first-order reaction shown in Eq. (2).

$$[AH] = -k_{AH}t + [AH]_0 \quad (1)$$

$$[Zn] = [Zn]_0 e^{-k_{Zn}t} \quad (2)$$

$[AH]$: Concentration of chain terminator

$[Zn]$: Concentration of peroxide decomposer

k_{AH} : Reaction rate constant of chain termination mechanism

k_{Zn} : Reaction rate constant of peroxide decomposition mechanism

t : Time

$[AH]_0$: Initial concentration of chain terminator

$[Zn]_0$: Initial concentration of peroxide decomposer

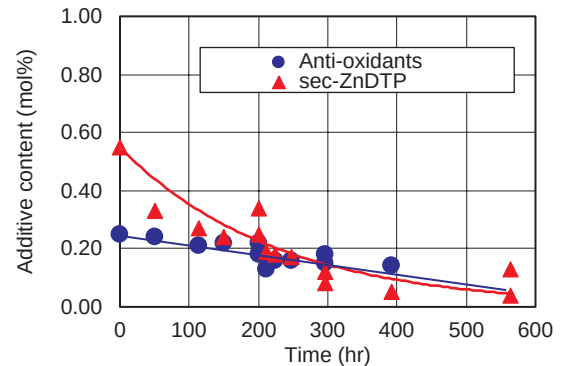


Fig. 2 Deterioration mode of anti-oxidants and sec-ZnDTP in engine bench tests

3. Analysis of Relationship between Remaining Anti-oxidation Performance and Production of Sludge

3.1. Estimation Method of Remaining Anti-oxidation Performance

A number of indicators of the anti-oxidation performance of engine oils have been proposed to date. Pressure differential scanning calorimetric (PDSC) was employed in the research discussed here, from considerations of the correlation between anti-oxidation performance and the production of sludge, and the convenience of the method in enabling analysis of infinitesimal quantities of test oil⁽¹¹⁾. In this method, test oil and a reference substance are subjected to high temperatures and high pressures, and the difference in heat balance between the oil and the reference substance is measured. As Fig. 3 shows, PDSC measurements enable determination of oxidation induction time (OIT), a parameter that provides an index of anti-oxidation performance.

3.2. Relationship between Sludge, OIT and Insolubles

Insolubles are known to normally be produced in engine oil before sludge is produced. Figure 4 shows the

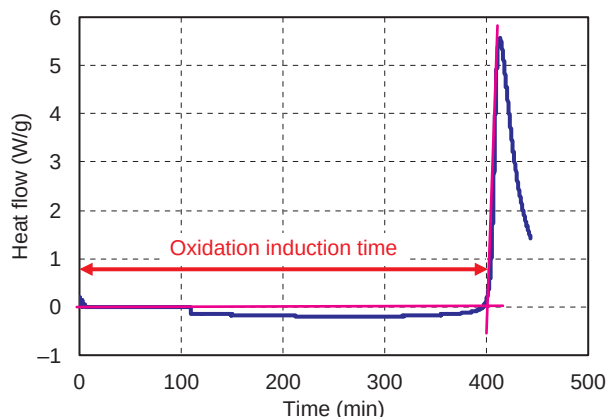


Fig. 3 PDSC analysis chart for fresh API SG grade oil

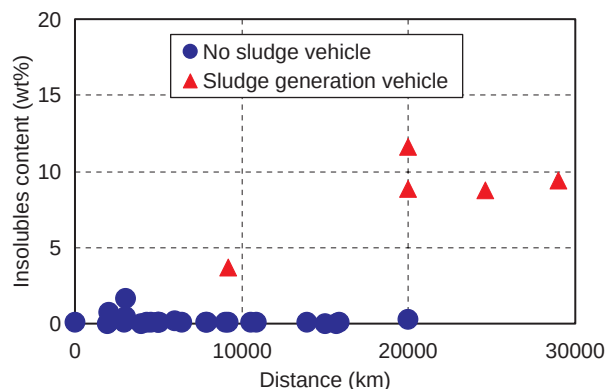


Fig. 4 Market data for recovered oil (nPB method)

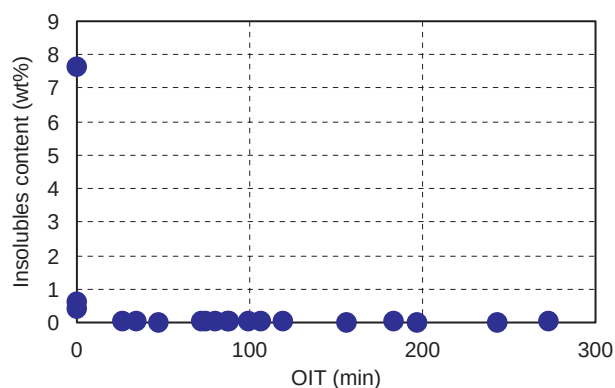


Fig. 5 Relationship between OIT and nPB insolubles

relationship between the production of sludge, insolubles content (determined using the nPB method: JPI-15S-18-80), and driving distance. The production of insolubles preceded the production of sludge in all the engine oils tested. Given that this was the case, even in an oil to which deliberately low amounts of dispersants had been added to promote the production of sludge, it can be predicted that this tendency will hold true for almost all engine oils.

The relationship between insolubles content (nPB method) and remaining OIT is shown in Fig. 5. Insolubles were not produced in any of the engine oils tested if there was remaining OIT. This indicates that OIT would provide a valid criterion for judging deterioration in engine oils.

4. Test Determination of Equation for Rate of OIT Deterioration

4.1. Causes of OIT Deterioration

Oxygen in the air is the first factor that can be indicated as a cause of OIT deterioration. Engine oil is constantly exposed to oxygen, and the base oil and additives react directly with oxygen, causing a deterioration of OIT. NO_x is a second factor in deterioration. NO_x is highly reactive, and may rapidly cause an oxidation reaction when it comes into contact with engine oil, resulting in the deterioration of OIT. Unburnt fuel can be indicated as a third factor. Unburnt fuel, present for example in blow-by gases, is reactive, and may cause an instantaneous reaction when it comes into contact with oil, again causing a deterioration of OIT. In addition, because it has lower oxidation stability than the base oil, the presence of unburnt fuel in the engine oil may cause OIT deterioration even if an instantaneous reaction does not occur. The effect of water can be indicated as a fourth factor. The conversion of water molecules into highly reactive hydroxyl radicals can result in the deterioration of OIT. However, market surveys indicated that the level of water content of engine oils would have almost no effect on OIT, and the effect of water was therefore not considered in the present study.

The effect of the catalyst can be indicated as a fifth factor in causing OIT deterioration. Metals functioning as catalysts also form part of the metallic component of engine oils caused by metal wear. A market survey found no vehicles in which the metallic component of the oil (oils with OIT remaining) was high enough to cause deterioration of the OIT, and the effect of the metallic catalyst was therefore not considered in this study.

Numerous research reports mention the deterioration of engine oil around the pistons and cylinders^{(2), (6)}. However, this research project assumed that the deterioration of the oil in the oil pan was the dominant factor in the deterioration of the engine oil as a whole. The basis for this conjecture is the fact that the volume of oil in the oil pan is far greater than the volume of oil around the pistons and cylinders. For this reason, this research focused exclusively on the deterioration of oil in the oil pan.

4.2. Reaction Mechanisms Causing Deterioration of OIT

As indicated above, the representative reaction mechanisms causing OIT deterioration are the chain termination mechanism and the peroxide decomposition mechanism. Analyzing multiple reaction mechanisms as a single unit and determining a reaction rate would be complex, and would thus represent a challenge. However, if the depletion of additives caused by the chain termination and peroxide decomposition mechanisms could be independently analyzed, the process would be comparatively simple and more accurate. Engine bench tests were therefore conducted, and numerical analysis employed to separate the reaction mechanisms. Because the depletion of the chain terminator is a zero-order reaction and the depletion of the peroxide decomposer is a first-order reaction, the research attempted to determine whether the line of superposition between the reactions corresponded to the actual mode of OIT deterioration. Figure 6 shows the results of superposition, using fitting to determine appropriate constants for Eqs. (1) and (2).

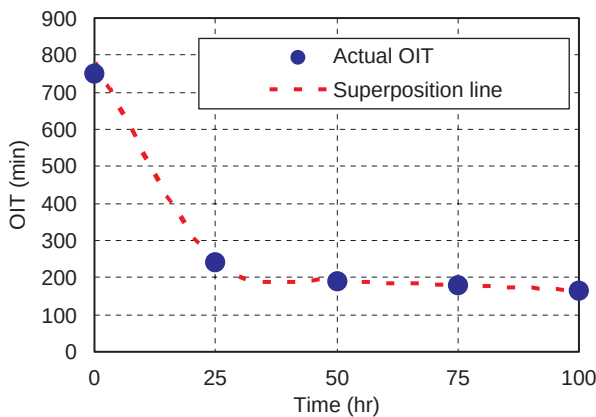


Fig. 6 Comparison of actual OIT with superposition line

The results show a reliable correspondence between the superposition line and the mode of OIT deterioration. This indicates that despite the existence in engine bench tests of a variety of factors causing a deterioration of OIT, the dominant reaction mechanisms in OIT deterioration are zero-order and first-order reactions. Given this, Eqs. (3)-(5) can be proposed as differential equations enabling estimation of the deterioration of OIT.

$$\frac{d[OIT]}{dt} = \frac{d[OIT_{AH}]}{dt} - \frac{d[OIT_{zn}]}{dt} \quad (3)$$

$$\frac{d[OIT_{AH}]}{dt} = [OIT_{AH}]^0 \times \alpha \quad (4)$$

$$\frac{d[OIT_{zn}]}{dt} = [OIT_{zn}]^1 \times \beta \quad (5)$$

[OIT]: Total OIT concentration

[OIT_{AH}]: OIT concentration due to chain terminator

[OIT_{zn}]: OIT concentration due to peroxide decomposer

α : Deterioration caused by chain termination mechanism

β : Deterioration caused by peroxide decomposition mechanism

4.3. Deterioration of OIT due to Air and Heat

Air and heat cannot be eliminated from the environment in which engine oils are used. Air and heat were therefore taken up as factors causing deterioration, and their effect on the depletion of OIT was analyzed. Figure 7 shows Arrhenius plots of the reaction rate constants determined by numerical analysis of the results of an air bubbling test.

As Fig. 7 shows, the results for both the zero-order and first-order reactions display reliable linearity. This indicates that both reaction mechanisms can be expressed as Arrhenius-type reaction rate equations. Expression of the effect of the deterioration due to air and heat in each reaction mechanism as reaction rate equations gives Eqs. (6) and (7).

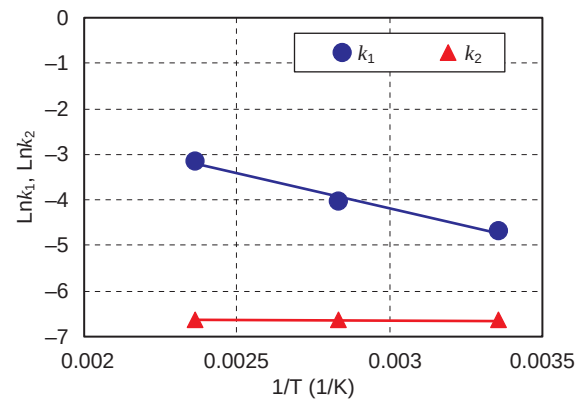


Fig. 7 Influence of air and heat on reaction rate constants k_1 and k_2

$$\frac{d[OIT_{AH}]_{Air, Heat}}{dt} = [OIT_{AH}]^0 \times (k_1) \quad (6)$$

$$\frac{d[OIT_{Zn}]_{Air, Heat}}{dt} = [OIT_{Zn}]^1 \times (k_2) \quad (7)$$

k_1 - k_6 : Reaction rate constants

4.4. Deterioration of OIT due to NOx

The effect of air, heat, and NOx on the mode of OIT deterioration was studied using a NOx bubbling device. Because deterioration occurs even when no NOx is present, it was conjectured that deterioration due to NOx is independent of deterioration due to air and heat. Denominating the term representing the rate of deterioration due to NOx A_{NOx} in the zero-order equation and B_{NOx} in the first-order equation gives Eqs. (8) and (9). The second term in Eqs. (8) and (9) can be obtained in tests by determining the difference in the rate of deterioration when NOx is present and when NOx is not present. Figure 8 shows the results of employing differential calculus to analyze the relationship between NOx concentration and A_{NOx} and B_{NOx} . Figure 8 can be

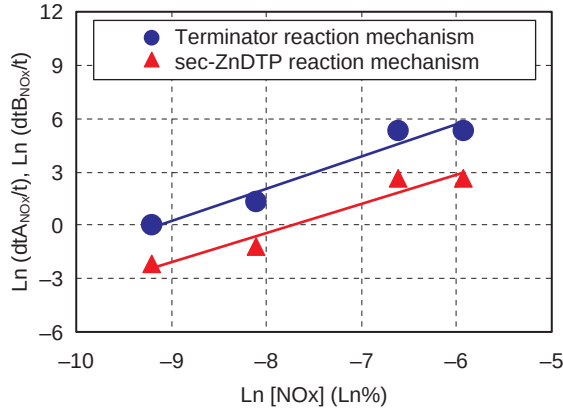


Fig. 8 NOx-dependence of OIT deterioration speed

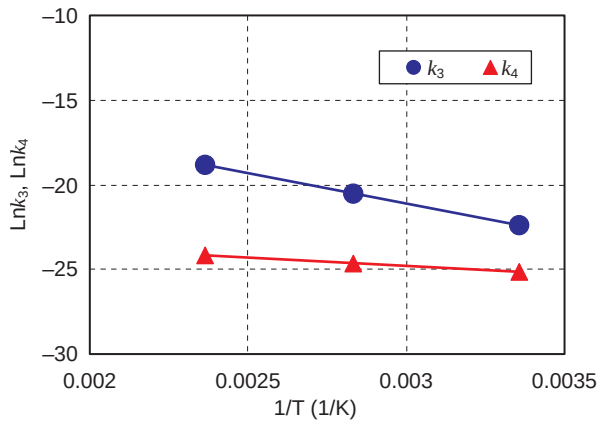


Fig. 9 Influence of NOx on reaction rate constants k_3 and k_4

used to determine the reaction order of NOx deterioration for each reaction mechanism. Expressing these as reaction rate equations gives Eqs. (10) and (11). Figure 9 shows Arrhenius plots of the reaction rate constants k_3 and k_4 . The plots for both reaction mechanisms display reliable linearity.

$$\frac{d[OIT_{AH}]_{Air, Heat, Nox}}{dt} = [OIT_{AH}]^0 \times (k_1 + A_{NOx}) \quad (8)$$

$$\frac{d[OIT_{Zn}]_{Air, Heat, Nox}}{dt} = [OIT_{Zn}]^1 \times (k_2 + B_{NOx}) \quad (9)$$

$$\frac{d[OIT_{AH}]_{Air, Heat, Nox}}{dt} = [OIT_{AH}]^0 \times (k_1 + k_3[NOx]^2) \quad (10)$$

$$\frac{d[OIT_{Zn}]_{Air, Heat, Nox}}{dt} = [OIT_{Zn}]^1 \times (k_2 + k_4[NOx]^2) \quad (11)$$

As in the case of the analysis of the mode of the deterioration of OIT due to NOx, OIT deterioration due to unburnt fuel was considered as an independent term. Denominating OIT deterioration due to unburnt fuel as C_{Fuel} in the zero-order equation and D_{Fuel} in the first-order equation gives Eqs. (12) and (13).

Studying the effect of unburnt fuel using a NOx bubbling device would represent a challenge, and this study therefore employed engine bench tests to analyze the mode of OIT deterioration due to unburnt fuel. In bench tests, the ratio of unburnt fuel that can be present in the oil is largely determined by the temperature of the oil. It is therefore challenging to create conditions in which the concentration of unburnt fuel is varied, while maintaining a constant oil temperature, and to maintain those conditions for an extended period. This makes it challenging to conduct an analysis using differential calculus in which the reaction order is analyzed by plotting the logarithm of OIT on the vertical axis and the logarithm of the concentration of unburnt fuel on the

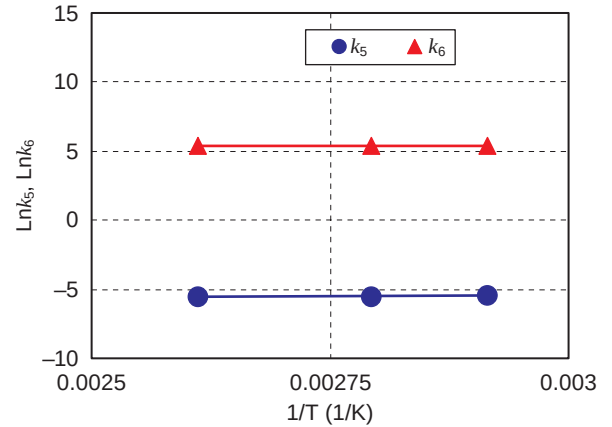


Fig. 10 Influence on dilution reaction rate constants k_5 and k_6

horizontal axis. The present project therefore assumed that the reaction order for unburnt fuel could be approximated using simple integral multiplication. When fitted, both reaction mechanisms could be approximated by 2. Equations (3), (14), and (15) are obtained by reflecting these reaction orders in reaction rate equations.

Figure 10 shows Arrhenius plots of the reaction rate constants for both reaction mechanisms when the reaction order is approximated by 2. As Figure 10 shows, reliable linearity is obtained for both reaction mechanisms.

$$\frac{d[OIT_{AH}]_{Air, Heat, Nox}}{dt} = [OIT_{AH}]^0 \times (k_1 + k_3[NOx]^2 + C_{Fuel}) \quad (12)$$

$$\frac{d[OIT_{Zn}]_{Air, Heat, Nox}}{dt} = [OIT_{Zn}]^1 \times (k_2 + k_4[NOx]^2 + D_{Fuel}) \quad (13)$$

$$\frac{d[OIT_{AH}]_{Air, Heat, Nox}}{dt} = [OIT_{AH}]^0 \times (k_1 + k_3[NOx]^2 + k_5[Fuel]^2) \quad (14)$$

$$\frac{d[OIT_{Zn}]_{Air, Heat, Nox}}{dt} = [OIT_{Zn}]^1 \times (k_2 + k_4[NOx]^2 + k_6[Fuel]^2) \quad (15)$$

5. Verification of OIT Deterioration in Vehicle Tests

5.1. Deterioration Rate Equation for Vehicle Tests

Equations (3), (14), and (15) provide numerical expressions of different causes of OIT deterioration. However, other than the term for unburnt fuel, all the terms in these equations were obtained from tests using a NOx bubbling device. In order to enable these numerical models to be used in verifications in actual vehicle tests, the contact efficiency between the engine oil and each of the factors causing deterioration of OIT inside an engine was denominated η and employed in the air, heat, and NOx terms. The necessary data for vehicle verification was measured or estimated using the following methods:

- (1) Oil temperature
The oil temperature at the oil drain bolt was measured using a thermocouple.
- (2) NOx
The level of NOx in the crankcase was employed as the benchmark figure, and NOx levels were estimated on the basis of driving conditions.
- (3) The level of unburnt fuel in the crankcase was employed as the benchmark figure, and unburnt fuel levels were estimated on the basis of driving conditions⁽¹²⁾.

5.2. Results of Vehicle Verification and Estimation Accuracy

A Honda vehicle and Honda genuine engine oils were employed in vehicle tests. OIT was predicted using Eqs. (3), (16), and (17). Figure 11 shows the correspondence between OIT measurements and calculations in different test modes. There is a reliable correspondence between measured values and simulation results, indicating that the estimation method is sufficiently accurate for practical use.

$$\frac{d[OIT_{AH}]_{Air, Heat, Nox}}{dt} = [OIT_{AH}]^0 \times \{\eta \times (k_1 + k_3[NOx]^2) + k_5[Fuel]^2\} \quad (16)$$

$$\frac{d[OIT_{Zn}]_{Air, Heat, Nox}}{dt} = [OIT_{Zn}]^1 \times \{\eta \times (k_2 + k_4[NOx]^2) + k_6[Fuel]^2\} \quad (17)$$

6. Discussion

The accuracy of the OIT estimation method developed in this research was verified using a number of different types of engine oil. The method was employed for all the oils used in tests, indicating that it possesses an acceptable level of general applicability. This is considered to be because the basic phenomena of causation and mode of OIT deterioration remain unchanged, even when different oils are used. This can be explained in particular by the fact that despite the use of different additives, the mode of OIT deterioration can still be approximated by the superposition of zero- and first-order reactions.

For onboard estimation of the deterioration of OIT, it will be necessary to use sensors or estimation equations to provide accurate data on the temperature of the engine oil, the concentration of NOx, and the concentration of unburnt fuel, which represent the main factors causing deterioration of OIT. In addition, the ability to discriminate between different types of oils employed would be desirable in terms of enabling accurate estimation of OIT. Substitution of the initial OIT level, the threshold value, the deterioration factor, and other parameters for different engine oils would enable more accurate estimation of OIT.

The combination of these techniques and methods of application would enable more accurate estimation of OIT, thus increasing the feasibility of balancing environmental protection with protection of the engine.

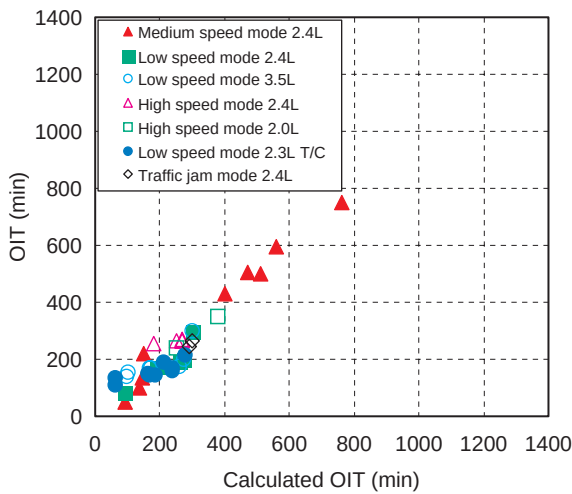


Fig. 11 Correlation between calculation results and OIT measurement values

7. Conclusion

The research discussed in this paper demonstrated the existence of a strong correlation between OIT, an indicator of engine oil deterioration, and the production of sludge. General equations for OIT deterioration were proposed on the basis of unit tests and engine bench tests of engine oil. The equations enabled accurate estimation of OIT deterioration in an actual vehicle. This demonstrates the viability of constructing an onboard system for the estimation of OIT deterioration using these equations.

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