Analysis of Mechanism Intermixing Combustion Products in Engine Oil*

Yasuhiro MURAKAMI**, Hisamoto AIHARA**
and Jyōji KUNIYA**

It is widely known that NO_x emission from an engine plays an important role in the formation of varnish and sludge in engine oil. Therefore, the authors measured the concentrations of nitric and nitrous acid ions in lubricating oil and analyzed the process through which NO_x mixes into the lubricating oil. The latter was found to occur through oil film on the cylinder wall and through crankcase gas, the amount being proportional to the NO_x concentration in the exhaust and crankcase gas. It was also found that a rapid increase in the concentration of nitrous acid ions when the engine temperature drops results in the condensation of water vapor contained in crankcase gas.

Key Words: Lubrication, Internal Combustion Engine, Engine Oil, Varnish, Sludge

1. Introduction

When dealing with reciprocating engines, one is faced with a problem which originates in the combustion process: that problem is oil deterioration which is caused by the mixing of combustion products into the lubricating oil. Of these combustion products, water and NO_x in particular react to form nitric and nitrous acids which mix into the lubricating oil to cause corrosive wear. It is further known that NO_x reacts with unburned fuel to form sludge binder precursors (liquid oxygen products) which are considered to be the source of varnish and sludge.⁽¹⁾⁻⁽³⁾ However, it has not yet been elucidated in what part of the engine, through which routes, and in what amount NO_x in the combustion gases mixes into the engine oil.

In this study, the route through which NO_x in combustion gases mixes into the lubricating oil and

the amount involved is investigated by analyzing the nitric and nitrous acid ion concentrations in the oil. The effect of engine temperatures during operation, namely, the lubricating oil and cylinder wall temperatures, on the amount of NO_x mixing into lubricating oil is also clarified.

2. Experimental Apparatus and Procedures

2.1 Experimental apparatus

The specifications of the engine used in the experiments are shown in Table 1, and the experimental apparatus is shown in Fig. 1.

Concentrations of CO , CO_2 , HC , and NO_x in the exhaust gas and concentrations including O_2 in the crankcase gas were measured with a non-dispersive

Table 1 Test engine specifications

TYPE...	FOUR CYCLE, 4-CYLINDER, WATER-COOLING GASOLINE ENGINE
DISPLACEMENT.....	1809cc
BORE.....	83mm
STROKE.....	83.6mm
COMPRESSION RATIO.....	8.8
FUEL SUPPLY SYSTEM.....	CARBURETOR

* Received 14th November, 1987. Paper No. 87-0138A

** Central Engineering Laboratories, Nissan Motor Co., Ltd., 1 Natsushima-cho, Yokosuka, 237, Japan

Fig. 1 Experimental apparatus

infrared analyzer (NDIR), a flame ionization detector (FID), a chemiluminescence analyzer (CLA), and a magnetic oxygen analyzer (MOA).

The compositions of the gases in the crankcase and cylinder head cover were analyzed and compared with each other. No differences were found between the compositions of these two gases; therefore, only the concentrations of the crankcase gas components were measured. Since the flow rate of blowby gas was small, the crankcase gas was collected in a sampling bag and then analyzed.

The test engine was operated at an inlet air temperature of 20°C and humidity of 60%.

SAE 10W-30 SF grade engine oil was used in a filling volume fixed at 3 liters. After each test, the oil gallery was flushed twice with new oil, and the oil and oil filter were changed.

2.2 Experimental procedures

2.2.1 Route through which NO_x mixes into lubricating oil It is considered that NO_x mixes into the lubricating oil through two routes in which combustion gases come into direct contact with the oil, as shown in Fig. 2.

Route ①: through the oil film on the cylinder wall and oil in the piston ring grooves;

Route ②: through the gases in the crankcase and cylinder head cover.

In route ①, NO_x in the combustion gases comes into contact with the oil film on the cylinder wall during the expansion and exhaust strokes, and it also makes contact with the oil in the piston ring grooves when the combustion gases blow from the combustion chamber into the crankcase.

In route ②, NO_x in the gases blown into the crankcase and the cylinder head cover comes into contact with the oil in the crankcase, oil pan and cylinder head cover.

Fig. 2 Route of NO_x mixing into oil

2.2.2 Measurement of amount of NO_x mixing into the lubricating oil It is known that the NO_x in the combustion gases reacts with unsaturated fuel components such as olefins to form esters and other compounds.⁽⁴⁾ However, after about 10 hours of operation, the presence of organic nitrogen oxides such as esters in the oil were not detected using a Fourier transform infrared spectroscopy apparatus.

In this study, the nitric and nitrous acids in the oil were extracted by water, and the nitric acid ions (NO_3^-) and nitrous acid ions (NO_2^-) were analyzed using an ion chromatograph.

The amount of NO_x which mixes into the oil through each route mentioned above was investigated as follows. Route ① was designated as that in which the combustion gases come into direct contact with the oil. Route ② was designated as that in which the crankcase gas comes into contact with the oil. Therefore, the NO_x concentrations in the exhaust gas and the crankcase gas were varied independently to investigate the amount of NO_x mixing into the oil through each route. When NO_x concentration in the exhaust gas is varied, the crankcase gas NO_x concentration changes with that in the exhaust gas.

The NO_x concentration in the crankcase gas was varied while the exhaust gas NO_x concentration was

kept constant. Changes in nitric and nitrous acid ion concentrations in oil taken from the oil pan were investigated after a fixed number of operation hours.

The NO_x concentrations in the exhaust gas were varied by changing air-fuel ratio and load.

The NO_x concentrations contained in the gases in the crankcase and cylinder head cover were varied by introducing some of the exhaust gas into the crankcase. By comparing the exhaust gas introduced into the crankcase with that diluted by air, the effect of changes in the gas flow rate in the crankcase on the nitric and nitrous acid ion concentrations in the oil

was examined.

The effect of engine oil and cylinder wall temperatures on the amount of NO_x mixing into the oil was also investigated. The engine oil and cylinder wall temperatures were adjusted by the engine coolant temperature using an on-board water-cooled compact oil cooler. The cylinder wall temperature was measured at the No. 1 cylinder. The representative temperature used is the wall temperature at the compression ring when the piston is midway between the top and bottom dead center.

3. Experimental Results and Considerations

3.1 Route and amount of NO_x mixing into oil

3.1.1 Effect of exhaust gas NO_x concentrations

The relationship between exhaust gas NO_x concentrations and nitric acid and nitrous acid ion concentrations when varying the air-fuel ratio and load is shown in Figs. 3 and 4. The NO_x concentration in the exhaust gas is highest when the air-fuel ratio is near 16. Likewise, the nitric acid and nitrous acid ion concentrations in the oil also are highest when the air-fuel ratio is near 16.

On the other hand, when the load is changed, the exhaust gas NO_x concentrations increase as the load increases. The nitric acid and nitrous acid ion concentrations in the oil also increase with load.

The results shown in Figs. 3 and 4 are consolidated for exhaust gas NO_x concentrations in Fig. 5. Both the nitric and nitrous acid ions in the oil increase linearly as exhaust gas NO_x concentrations increase. However, the nitrous acid ion concentration is lower than that of nitric acid ion.

3.1.2 Effect of crankcase gas NO_x concentrations

Relationship between crankcase gas NO_x concentrations and nitric acid and nitrous acid ion

Fig. 3 Effect of air-fuel ratio on nitric and nitrous acid ion concentrations in oil

Fig. 4 Effect of load on nitric and nitrous acid ion concentrations in oil

Fig. 5 Effect of exhaust NO_x concentrations on nitric and nitrous acid ion concentrations in oil

concentrations when some of the exhaust gases are introduced into the crankcase is shown in Fig. 6.

The nitric and nitrous acid ion concentrations both increase linearly as NO_x concentrations in the crankcase gas increase. The gas flow to the crankcase is greater when it is diluted with air for the same concentrations of NO_x . Here, the nitric acid and nitrous acid ion concentrations in the oil exhibit the same values against the NO_x concentrations. The difference relative to the presence of air in the flow is small. Thus, the rate of absorption of NO_x containing NO and NO_2 by the water depends solely upon the NO_x concentrations, not upon the flow rate of the gases containing NO_x . This corresponds with the results reported by Garcia.⁽⁵⁾

3.1.3 Route and amount of exhaust gas NO_x mixing into oil It became clear that both nitric and nitrous acid ion concentrations in the oil increase linearly as exhaust and crankcase NO_x concentrations increase. Based on this finding, the amounts of nitric and nitrous acid ions intermixed in oil from the routes shown in Fig. 2 were examined.

When the crankcase NO_x concentration is 0 ppm, the extrapolated concentration of nitrous acid ions is found to be nearly 0 ppm from Fig. 6. Thus, the NO_x which transforms into nitrous acid ions in the oil is considered to intermix through route ② described in 2.

Fig. 6 Effect of crankcase NO_x concentrations on nitric and nitrous acid ions in oil

2.1 above. In Fig. 5, the concentration of nitrous acid ions increases as exhaust gas NO_x concentrations increase. However, this is also due to the fact that NO_x concentrations in the crankcase and cylinder head cover increase because NO_x concentrations increase due to combustion.

However, even if the crankcase NO_x concentration is 0 ppm, the nitric acid ion concentration in the oil is about 14 ppm, not 0 ppm, as shown in Fig. 6. Therefore the NO_x which transforms into nitric acid ions also mixes into the oil through route ① described in 2.2.1 above. The amount, as shown in Fig. 6, is 14 ppm at engine operating conditions of 1500 rpm and 49 N·m. Increasing crankcase NO_x concentration also increases the nitric acid ion concentration in the oil at the same rate as the nitrous acid ion concentration is increased. The NO_x which forms nitric acid ions in the oil is also believed to mix through route ②.

The amount of NO_x which mixes into oil through routes ① and ② to form nitric acid ions is considered as follows.

The NO_x concentration in the crankcase is approximately 110 ppm at 1500 rpm and 49 N·m. Under these engine operating conditions, the amount of nitric acid ions in the oil is 21 ppm (symbol ● in Fig. 6). Because 14 ppm mixes into the oil through route ①, the amount of mixing through route ② is 7 ppm, i.e., 21 - 14 ppm. Therefore, it is considered that route ① described in 2.2.1 is the main route through which NO_x mixes to form the nitric acid ion in the oil.

3.2 Effects of engine temperature during operation on amount of NO_x which mixes into oil

3.2.1 Effects of oil and cylinder wall temperatures Figure 7 shows the effect of a simultaneous change in engine oil and cylinder wall temperatures on nitric acid and nitrous acid ion concentrations in the oil. The effect of this change on gasoline and water concentrations is shown in Fig. 8. The concentration of nitric acid ions is nearly constant relative to changes in engine oil and cylinder wall temperatures. However, the nitrous acid ion concentration increases rapidly at about 40°C when the temperatures are decreased. The gasoline and water concentrations in the oil also increase when the temperatures are decreased. Water concentration, in particular, increases rapidly from about 40°C, as in case of the nitrous acid ion concentrations. The reason for this is considered to be that water vapor in the crankcase condenses when overall engine temperature (i.e., oil and cylinder wall temperatures) decreases, absorbing NO_x which mixes into the oil with water.

The temperature of the inner surface of the cylinder head cover was measured, and the dew point of the water vapor was calculated from components of

the crankcase gas.⁽⁶⁾ When the oil and cylinder wall temperatures are 40°C, the surface temperature inside the cylinder head cover is 29°C and the dew point of the water vapor in the crankcase is 31.5°C. Therefore, the oil film on the inner surface of the cylinder head cover becomes milky, having a mayonnaise-like consistency. Thus, it is believed that condensation of the water vapor in the crankcase is the main cause of the

Fig. 7 Effect of engine temperature on nitric and nitrous acid ion concentrations

Fig. 8 Effect of engine temperature on gasoline and water concentrations

sharp increase in the nitrous acid ion concentration when the oil and cylinder wall temperatures are decreased, as indicated in Fig. 7.

3.2.2. Effect of water vapor condensation

Figure 9 shows the nitrous acid ion concentration in the oil when water vapor is introduced into the crankcase at engine temperatures at which it does not condense on the inner surface of the cylinder head cover (oil and cylinder wall temperatures of 60°C). The horizontal axis represents the rate of water converted to steam and introduced into the crankcase. It was measured before vaporization using the graduated cylinder shown in Fig. 1. The oil film on the inner surface of the cylinder head cover became milky when the water vapor was introduced.

The concentration of nitrous acid ion increases by a step immediately upon water vapor being introduced into the crankcase. This is because water vapor condenses when it is introduced, even at oil and cylinder wall temperatures of 60°C. Since NO_x is absorbed by the water and mixes into the oil, the nitrous acid ion concentration in the oil increases. However, the crankcase NO_x concentration does not change even when the rate of water vapor increases. The amount of NO_x which can be absorbed by the water is, then, the factor which determines the concentrations of nitrous acid ions in the oil. Therefore, the nitrous acid ion concentration in the oil will only increase to a certain level, where it remains constant.

3.2.3. Effect of crankcase gas temperature

When engine oil and cylinder wall temperatures were 60°C and the introduced water vapor was allowed to

Fig. 9 Influence of water vapor infused into the crankcase on nitrous acid ion concentration in oil

condense on the inside of the cylinder head cover, the nitrous acid ion concentration became 26 ppm after 3 hours of operation (see Fig. 9).

When the water vapor in the crankcase condensed, the nitrous acid ion concentration was 50 ppm at 40°C after the same length of operation. Little difference in crankcase NO_x concentration was observed during these tests, with values of 200 ppm and 230 ppm respectively. Despite this, there is an approximately twofold increase in the nitrous acid ion concentration. This indicates that factors other than water vapor condensation may be involved. This aspect is currently being investigated.

4. Conclusions

The routes and amounts of the NO_x in the combustion gas mixing into the lubricating oil have been investigated as major factors in sludge formation. The following information has been derived.

(1) Route of Mixture

The following routes of combustion gas NO_x mixing into oil are indicated. The NO_x which transforms into nitric acid ions in the oil mixes primarily through the oil film on the cylinder wall and through oil in the piston ring grooves. The NO_x which transforms into nitrous acid ions in the oil mixes through the gas in the crankcase and cylinder head cover.

(2) Amount of mixture

The amount of NO_x mixing into the oil increases in proportion to the NO_x concentrations in the exhaust and crankcase gases.

(3) Engine temperature conditions

Nitrous acid ions in the oil increase rapidly when engine temperature is decreased. At this time, the inner surface temperature of the cylinder head cover is nearly the same as the dew point of the water vapor in the crankcase gases. Condensation of the water vapor in the crankcase gases is a governing factor in the rapid increase of nitrous acid ion concentrations in oil at low temperatures.

References

- (1) Vineyard, B. D. and Coran, A. Y., Gasoline Engine Deposition, Am. Chem. Soc. Prepr., Div. Petrol. Chem., (1969), p A25.
- (2) Anderson, D. J., Mechanisms of Engine Deposit and Wear: a Progress Report, Prepr. of Jpn. Petrol. Instit. Meet. Tokyo, (1968-10).
- (3) Dimitroff, E., Moffitt, J. V. and Quillian, R. D. Jr., Why, What, and How: Engine Varnish, Trans. ASME, J. Lubr. Technol., Vol. 91, No. 3 (1969), p. 406.
- (4) The Chemical Society of Japan, Shin-kagakujikenkouza 14; Synthesis and Reaction of Organic Compound III (in Japanese), Tokyo, (1976), p. 1286, Maruzen Press.
- (5) Garcia, L., H., Proc. of 2nd Int. Lime/Limestone Wet-Scrubbing Symp., Vol. I, (1972), p. 233, EPA, USA.
- (6) Furuhashi, S. and Kato, S., Components of Crankcase Gas of an Automobile Gasoline Engine (in Japanese), J. Soc. Auto. Eng. Jpn., Vol. 24, No. 4 (1970), p. 347.