

Investigation of Mechanism for Formation of EGR Deposit by in situ ATR-FTIR Spectrometer and SEM

Kotaro Tanaka, Kazuki Hiroki, Tomoki Kikuchi, and Mitsuru Konno
Ibaraki University

Mitsuharu Oguma
National Institute of AIST

ABSTRACT

Exhaust gas recirculation (EGR) is widely used in diesel engines to reduce nitrogen oxide (NO_x) emissions. However, a lacquer is formed on the EGR valve or EGR cooler due to particulate matter and other components present in diesel exhaust, causing serious problems. In this study, the mechanism of lacquer deposition is investigated using attenuated total reflection Fourier transform infrared spectrometry (ATR-FTIR) and scanning electron microscopy (SEM). Deposition of temperature-dependent lacquers was evaluated by varying the temperature of a diamond prism between 80 and 120 °C in an ATR-FTIR spectrometer integrated into a custom-built sample line, which branched off from the exhaust pipe of a diesel engine. Lacquers were deposited on the diamond prism at 100 °C or less, while no lacquer was deposited at 120 °C. Time-dependent ATR-FTIR spectra were obtained for approximately 2 h from the beginning of the experiment. When the engine was started, water was detected during the initial period for all temperatures used. After the evaporation of water, spectra of aromatic hydrocarbons were observed at lower temperatures, while C=O absorption peaks were observed in the case of higher temperatures. Images of the lacquer obtained by SEM showed the presence of soot in the lacquer. These experimental results formed the basis for the elucidation of the lacquer formation mechanism.

CITATION: Tanaka, K., Hiroki, K., Kikuchi, T., Konno, M. et al., "Investigation of Mechanism for Formation of EGR Deposit by in situ ATR-FTIR Spectrometer and SEM," *SAE Int. J. Engines* 9(4):2016, doi:10.4271/2016-01-2351.

INTRODUCTION

Nitrogen oxides (NO_x) and particulate matter (PM) emitted from diesel engines are hazardous pollutants. To reduce these emissions, strict emission standards requiring increased application of exhaust gas recirculation (EGR) are enforced. EGR systems are very useful in reducing NO_x in diesel exhaust. Due to the decreased oxygen concentration in the cylinder and the increased thermal mass of the intake charge (owing to the presence of CO_2 and H_2O in the EGR gas that have higher specific heat capacities than air), NO_x can be reduced. Cooling the EGR gas provides a more effective way of NO_x reduction. However, since EGR gas contains PM and hydrocarbons, lacquers are deposited on EGR valves or EGR coolers [1, 2, 3, 4, 5, 6]. During engine operation, fouling of the EGR cooler and sticking of the EGR valve are observed, and the amount of deposited lacquers increases until a plateau is reached. These lacquers disturb the precise control of EGR systems.

Some studies have investigated the formation mechanism of lacquers, and have suggested models of the lacquer formation. [4, 5, 6, 7, 8, 9, 10]. From these studies, *diffusion*, *diffusiophoresis*, *impaction*, and *thermophoresis* were put forward as important mechanisms for lacquer formation on EGR coolers and valves, summarized by Hornig et al. [10]. *Diffusion* assumes that small particles are transported to the wall surface due to Brownian motion, with particle size and flow

velocity being important. *Diffusiophoresis* assumes that the condensation of gaseous hydrocarbons creates a vapor concentration gradient, which provides direct transportation of particles to the wall surface. *Impaction* states that inertia causes particles larger than a critical size to be deposited. *Thermophoresis* implies that a temperature gradient facilitates the transportation of particles from the hot gas to the cool wall. Based on the above-mentioned mechanism, a one-dimensional model was also constructed.

Although the physical mechanisms of lacquer formation involving particles and hydrocarbons in the exhaust were investigated, few studies have investigated the chemical mechanism [11]. Furukawa et al. evaluated the formation of lacquers based on the chemistry and kinds of hydrocarbons present in the exhaust, with their dew points suggested to be important [11]. Synthesis tests were also performed using batch reactors, and lacquers were formed, for instance, by phenol, formaldehyde, and nitric acid [11]. Although a chemical mechanism for the lacquer formation by using hydrocarbons and strong acids has been suggested, the complete mechanism of lacquer formation has not been well investigated.

In this study, in situ measurements using attenuated total reflection Fourier transform infrared spectrometry (ATR-FTIR) were performed to evaluate the chemical mechanism of lacquer formation. To the best

of our knowledge, this is the first study on real-time measurements of lacquer formation. Scanning electron microscopy (SEM) was also used to observe lacquers and suggest a mechanism of their formation.

EXPERIMENTAL

Experimental Setup

A schematic diagram of the experimental setup is shown in Fig. 1. The lacquers were formed in a custom-built sample line branching off from the exhaust pipe of a diesel engine. The branching point was 0.5 m downstream from the engine exhaust port. No diesel oxidation catalyst (DOC) and diesel particulate filter (DPF) were used in the exhaust pipe. The sample line was a stainless steel tube with 1/2 inch diameter and a total length of 10 m, and experienced a temperature gradient generated by the diesel exhaust. The gas temperature at the branching point under the conditions of lacquer formation was approximately 520 °C, and the endpoint temperature of the sampling pump was set to 70 °C under identical conditions, with the gas flow set to 70 L min⁻¹. To avoid the condensation of water, the part of the sample line where the gas temperature was below 115 °C could be heated to 60–80 °C. The ATR-FTIR system was installed 5 m downstream from the branching point, where the gas temperature was approximately 100–110 °C, to observe in situ lacquer formation on the wall of the sample tube. As in the preliminary experiment, lacquers were formed under conditions where the gas temperature was between 70 and 158 °C, shown in the ‘Results and discussion’ section, and the ATR-FTIR system was set at those temperature points.

ATR measurements were performed using a SHIMADZU IRTracer-100 FTIR spectrometer equipped with an electrically cooled MCT detector. A custom-made ATR unit constructed by SHIMADZU was integrated in the sample line, as shown in Fig. 2. A diamond prism was built into the sample line, and time-dependent FTIR spectra of the lacquers formed on the diamond prism were measured, and data were stored on a laptop PC. The infrared beam passing through the diamond prism was estimated to penetrate the lacquers up to 5 µm deep, based on the used wavelength, the refraction index of air, and the refraction index of the lacquers, which is assumed to be equal to that of soot. Heaters were placed around the diamond prism, and the temperature was controlled between room temperature and 160 °C.

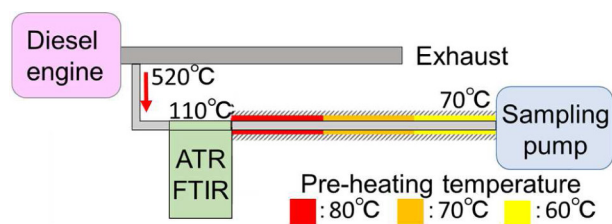


Figure 1. Experimental setup for forming temperature-dependent lacquers using a diesel engine exhaust.

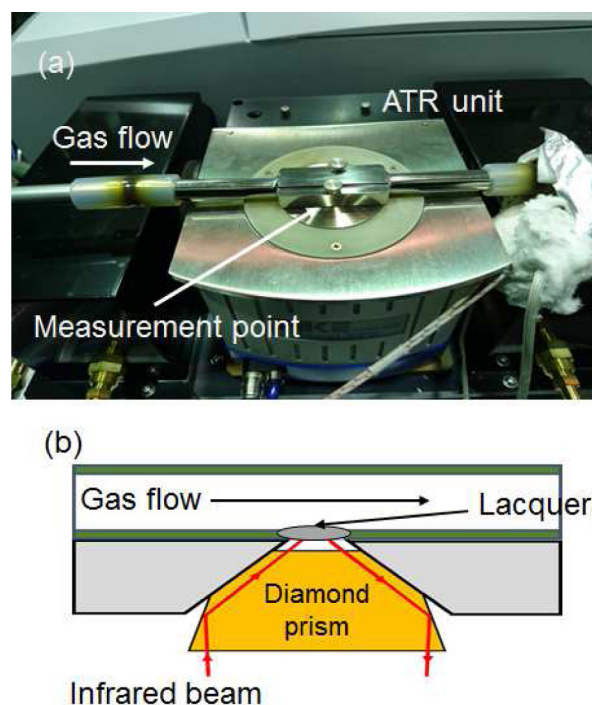


Figure 2. ATR unit set in the sample line for lacquer formation. (a) Picture of the ATR unit, (b) Schematic diagram of the ATR unit.

A picture of the overall experimental setup is shown in Fig. 3. The ATR-FTIR system was placed next to the diesel engine and the ATR unit was set up in the sample line where the lacquers were formed. To avoid the oscillation caused by the diesel engine, a small optical bench was placed under the ATR-FTIR system. The specifications of the diesel engine are summarized in Table 1. A 1.6 L four-cylinder diesel engine was used. The compression ratio was 16.0, and the EGR system contained a high- and low-pressure loop. Fuel used in this study was JIS 2 grade Japanese diesel fuel. Lacquers formed in the sample line were also characterized using SEM to observe their microscopic structures. A Hitachi S-4300 and JEOL JSM-7400F instruments were used for SEM imaging.

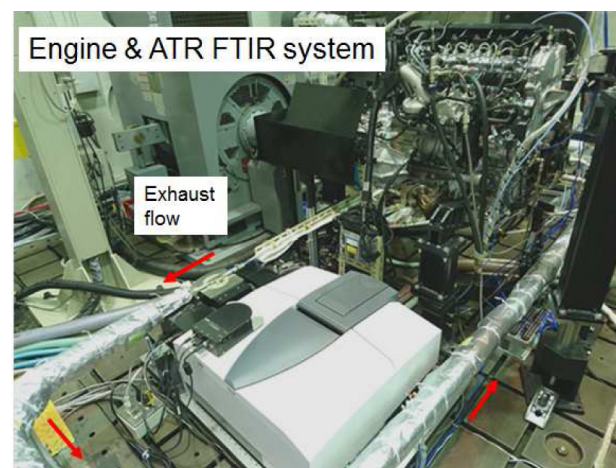


Figure 3. Picture of the experimental setup with the diesel engine and the ATR-FTIR system in the custom-made line for lacquer formation.

Table 1. Specifications of the diesel engine used in this study.

Type	Inline 4 DI
Displaced volume	1597 cc
Bore × Stroke	76 × 88 mm
Compression ratio	16.0
EGR system	HPL and/or LPL system
EGR valve type	Butterfly

Experimental Procedures

Lacquers were formed using the diesel engine exhaust in the custom-made sample line. The engine was operated under fuel-rich conditions, where overall equivalence ratio was 0.94 and filter smoke number was 1.8 - 2.0. A post injection was assisting fulfillment of the fuel-rich condition. Concentrations of hydrocarbons, carbon dioxide, and nitrogen oxide were approximately 6000 - 7000 ppmC, 5000 ppm, and 300 ppm, respectively. To form the lacquers, the engine was operated continuously for 12 hours. The diamond prism in the ATR-FTIR module was heated to 80-120 °C before the exhaust was introduced into the sample line. The sample line between the ATR unit and the sampling pump was heated in three stages: the temperature was set to 80, 70, and 60 °C 0-2, 2-4, and 4-6 m downstream from the ATR unit, respectively (Fig. 4). After the exhaust was introduced into the sample line and the temperature of the heated area exceeded the pre-heating temperature, the heaters were turned off. ATR spectra acquisition was started directly after introducing the exhaust into the sample line. The spectra were recorded every minute for 120 min with averaging over 60 signals.

RESULTS AND DISCUSSION

Lacquer Formation

Prior to ATR-FTIR measurements, we confirmed that lacquers were formed in the sample line without the ATR unit under the same experimental conditions as those used for ATR-FTIR measurements [12], with results shown in Fig. 4. The horizontal axis represents the distance from the branching point, which was 0.5 m downstream from the engine exhaust port. The exhaust was not passed through DOC and DPF. The deposit started to be formed 1 m downstream from the branching point, where the gas temperature was ca. 230 °C, and the onset of lacquer formation was located approximately 2 m downstream from the branching point, where the gas temperature was ca. 180 °C. A powdery deposit also formed on the lacquers (definitions of 'lacquer' and 'powdery deposit' is shown in the section of 'SEM characterization of the lacquers' and summarized in the section of 'Definitions/Abbreviations'). The total deposit amounts were largest between the 2 m and 4 m points of the sample line, in the gas temperature range of 113-178 °C. When the gas temperature was less than 113 °C, less total deposit was formed than 2-4 m downstream from the branching point. In the area where the gas temperature was less than 113 °C, the sample line was pre-heated, which may affect the formation of the deposit. The mechanism of

lacquer formation is discussed in the section below. While the total deposit amount decreased with decreasing gas temperature, the amount of lacquer gradually increased. The lacquers formed at gas temperatures below 79 °C exhibited thermoplasticity. Lacquers not exhibiting thermoplasticity are called high temperature (HT) lacquers, and the ones having thermoplasticity are called low temperature (LT) lacquers in this paper. Based on these results, to measure the in situ FTIR spectra of the formed lacquer, the ATR unit was positioned 4 m downstream from the branching point, at a point where the lacquer formation in the sample line was maximal.

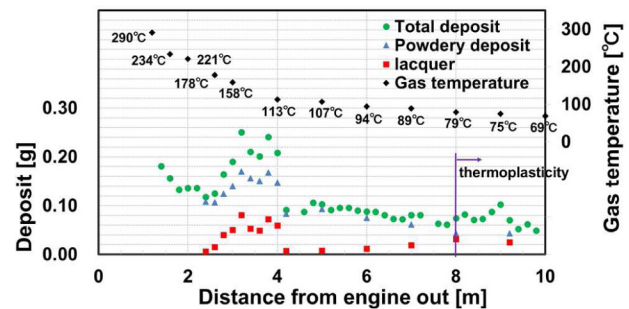


Figure 4. Amount of deposit formed on the inner wall of the sample line at different gas temperatures versus the distance from the branching point [12].

SEM Characterization of the Lacquers

The microscopic structure of the deposit formed on the inner wall of the sample line was characterized by SEM. The sample line was cut as shown in Fig. 5, and the deposit was observed from the side of the sample line, indicated by the yellow arrow in Fig. 5. The sampling position was 3.4 m downstream from the branching point.

SEM images of the sample line wall are shown in Fig. 6. Image (a) in Fig. 6 shows the surface of the sample line. The existing deposit was found to have two types of constituents: one is powdery and the other one is firm. We call the former 'powdery deposit' and the latter 'lacquer' in this paper. As these lacquers exhibited no thermoplasticity, they were called HT lacquers. These lacquers were formed on the sample tube wall, and the powdery deposits were formed on the HT lacquers. Image (b) shows the expanded yellow square area of image (a), and image (c) also shows the expanded yellow square area of image (b). While the powdery deposit exhibited porosity, the HT lacquers had a dense structure. The most expanded image of the three showed that small particles are present in the HT lacquers.

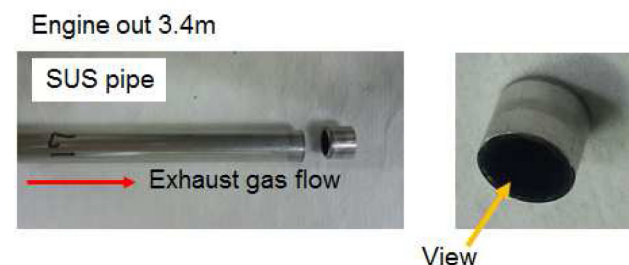


Figure 5. Sample line characterized by SEM.