Analysis of a Corrosive Condensate in an Ignition System

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Objective Summary

The purpose of this research project was to identify the chemical composition of a corrosive condensate that formed on metal samples under a test environment simulating a vehicle ignition system. First, a mock engine set up was designed using test equipment that included ignition control boxes, coils, a spark plug and a power supply. After running the model for a few days, representing years of operation and corrosive build up, the corrosive byproduct was produced and contained in a polyethylene bag before being dissolved into a sample solution. The sample solution underwent further dilution in order to be fed to a Total Organic Carbon measuring instrument where the total non-air Nitrogen content of all compounds in the trace sample was plotted and graphically analyzed. From the high concentration of nitrogen and other characteristics of the chemical, the corrosive product and its reaction mechanism were narrowed to nitrous or nitric acid. Finally, a Xanthoproteic test was carried out to observe the reaction of the corrosive condensate with amino acid proteins. The formation of yellow nitrated products revealed nitric acid as the chemical makeup of the condensate, a reasonable finding as significant traces of nitric acid byproducts have been found to form in over a lifetime of use in a number of automotive cylinders.

Background

Corrosion is used to describe a natural process where metals are converted into more stable products through the loss of elections in an oxidation reaction, gradually a refined metal is eroded in chemical reaction with its environment. This type of damage can produce an oxide or a salt of the original metal, typically observed as the formation of a coat around the original metal with a distinctive yellow to orange coloration (Kelly et al., 2006). The corrosion process is harmful as it degrades the useful structure and properties
of a refined metal including its material strength, ductility, shiny and reflective appearance, and even its permeability to liquids and gases (Kelly et al., 2006).

For alloys and metals, the causes of corrosion can differ significantly from material degradation due to mere exposure to the water moisture found in air to corrosion from a reaction with a highly acidic environment. Corrosion spreads through a molecular diffusion-based process, first striking the exposed surface on of the refined metal before affecting the structure of the volume throughout (Kelly et al., 2006). Diffusion through the material and buildup of corrosion is not a uniform process on all surfaces, factors such as the degree of environmental exposure and the presence of pits and cracks can lead a local concentration in corrosion which lead to unevenness in material surface degradation rates.

The most common anti-corrosion treatments consist of painting or plating the surface to apply a layer of anti-corrosive coating that protects the metal (DECC Company, 2015). The anti-corrosive measures, offering resistance as oxidation reactions and other corrosive products become thermodynamically unfavorable (DECC Company, 2015), act as a barrier that inhibits contact between chemical compounds or other corrosive materials with the metal structure. In a vehicle motor interior, the costs of corrosion can include outright material failure, fluid system contamination, and permanent damage to fuel systems.

**Experimental Safety**

Laboratory personal protective equipment provided the minimum safeguards including safety glasses with side shields, closed-toed shoes and lab coats. Other safety measures taken were the use of insulated rubber gloves when setting up and operating the
electrical test equipment. Neoprene gloves, which match favorably against strong corrosive acids like nitric acid, were used when retrieving a spark plug left to corrode inside the polyethylene bag or handling the metal samples coated in the condensate.

Laboratory safety also included establishing emergency shut down procedures and proper waste disposal in response to any safety hazards. The ignition engine test equipment only presented an electrical and possible fire hazard. Shut down procedure included turning off or unplugging the power supply and notifying the lab supervisor and emergency services of any property damage, electrical shock and third-degree burns. Use of the Total Organic Nitrogen instrument for chemical analysis posed a much lesser electrical and fire hazard, shut down procedures consisted of turning off and unplugging the device. Chemical waste disposal material consisted of heavily diluted nitric acid test tubes, a lesser diluted 200 mL sample container, and the corroded metal samples. Nitric acid was properly disposed of in non-halogenated waste containers. As the metal pieces to be tested were rinsed in order to create the 200 mL solution, the pieces were no longer possessed and were disposed as normal solid waste. The Xantoproteic acid protein mixture at the end did not carry any risks that necessitated special PPE and was disposed of as biohazardous waste.

**Procedure**

To recreate the ignition system environment where the corrosive condensate was formed, test equipment was set up in a laboratory environment using MDS Ignition facilities with the aid of engineer Yasha Neparko. Positive, negative, and ground wires were hooked to a regulated DC power supply to provide an electrical power source. The wires were connected to a MSD 6-series digital control box and an MSD digital rpm control tester that set the ignition system at a typical test engine work value of 1100 revolutions per minute.
From the rpm control tester a connector hooked up positive and negative ends from the tester to an MSD Blaster 2 Coil. At the top of this coil extended a spark plug wire hooking up to the spark plug that was to be used with a grounded socket placed on the opposite end of the spark plug. A protective plastic casing with small holes on one side was used to contain the spark plug flame and redirect the heat produced inside. A polyethylene transparent Ziploc bag was prepared with a moist paper towel inside, providing a source of water moisture in the air, along with a metal distributor gear and a metal shaft to be corroded by the condensate. The bag would enclose the plastic casing where the spark plug was contained and provide the environment for the corrosive condensate to form then concentrate by attacking the metal samples inside in localized corrosion.

Figure 1: Polyethylene bag with metal samples, moist paper towel and encased sparkplug.

Figure 2: Set up including cylindrical coil, power supply, control box and control tester.
Use of the mock ignition system followed a simple procedure. For approximately an hour every day, the DC power supply was turned on and adjusted to give an output between 10 to 12 volts and then turned off again. This allowed for the spark plug to create ozone gas inside the polyethylene bag as a byproduct of ignition and necessary for the production of the desired condensate. After several days of this procedure, enough product was produced that polyethylene bag was sealed with the corroded metal samples and the condensate, after this point the test equipment was disconnected, disassembled and stored.

Condensate analysis using the Shimadzu Total Organic Carbon unit followed a technical procedure under the guidance and supervision of laboratory manager Mark Chidester. Distilled water was used to wash out and dissolve as much condensate as possible found inside the polyethylene bag, initially creating a fairly concentrated 200 mL solution. Due to the sensitivity of the instrument, a hundred fold dilution was performed to reduce the detectable chemical quantity of the sample to trace amounts. 5 test tubes were made for analysis by the TOC instrument: a blank run test tube of water followed by two calibration test tubes to define analytical standards, and two condensate sample solution test tubes in order to ensure consistency. The TOC instrument was allowed to run for approximately 3 hours, its settings modified to detect, graph, and then average the concentration of non-air Nitrogen in the sample dilution. After results were retrieved, the TOC instrument was reset and the diluted chemical was properly disposed of as non-halogenated acids.

After narrowing down the results of the TOC to nitrous or nitric acid, a Xanthoproteic test was carried out in order to determine if the corrosive condensate was nitric acid or not. Using a sealed inert glass container, the condensate was mixed in with the protein tyrosine, a simple non-hazardous amino acid carrying aromatic groups. The mixture was then heated for 1 minute in a microwave oven in order to yield Xanthoproteic acid as the result. After the
procedure was carried out to confirm results a second time, the glass container was cleaned and the mixture properly disposed of.

Results

Figure 3: Polyethylene bag and metal samples coated with corrosive condensate.

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Table 1: TOC list of test tubes

Table 2: Total non-air Nitrogen concentration of the sample
The analysis performed by the Total Organic Carbon unit revealed the high concentration of nitrogen compounds found in the corrosive byproduct. By definition, the National Pollution Inventory NEPM states that total nitrogen only refers to the sum of nitrate (NO$_3$), nitrite (NO$_2$), organic nitrogen and ammonia, nitrogen found in air cannot be detected by the TOC (National Pollution Inventory, 2014). Averaging the values and areas under the curve for the 5 different peaks measured in the sample, the mean area and concentration of total nitrogen was 1659 milligrams per Liter and 64.36 millivolts. Accounting for the hundred fold dilution, total nitrogen concentration in the sample can be estimated at a sizable 166 grams per Liter.

A strong acid, relatively high nitrogen concentration, red-orange appearance, and its low pH acidic properties all helped narrow the byproduct from using the TOC to nitric acid. The other possible identity included the byproduct being nitrous acid which also shared a...
similar structure, reddish-orange appearance and only a slightly higher pH than nitric acid. The simple Xanthoproteic test helped to distinguish if the corrosive byproduct was indeed nitric acid or possibly nitrous acid. For this test only a protein with an amino acid structure containing an aromatic group was needed to react with acid. Tyrosine, a common non-essential amino acid found chicken, turkey, fish and milk, was obtained for the test. In a Xanthoproteic test, nitric acid mixed with the protein is heated up for a short period in the microwave to produce yellow-colored nitrated products due to the formation of Xanthoproteic acid. This color change confirmed that nitric acid was the identity of the corrosive condensate as nitrous acid does not react with aromatic amino acids to produce nitrated aromatic rings as indicated by the yellow color in Xanthoproteic acid (Chatterjea, 2004). In general, nitrous acid was a weaker acid that only existed in solution with water and would never have been able to form the condensate and corrode the metal samples inside the polyethylene bag to such a significant extent (Costas et al., 2006).

The reaction pathway that produces nitric acid in the polyethylene bag is likely to follow several steps. In an automotive cylinder, ignition of the spark plug that is fed power is imparted into oxygen molecules, O₂, which advanced them to a configuration of higher reaction energy, ozone molecules or O₃ (Costas et al., 2006). Ozone served as the strong, primary oxidizer inside an automotive cylinder. The lean-burn process, the burning of fuel with excess air in combustion engines, splits nitrogen gas in air which in turn reacts with the ozone to form nitric oxide, NO₃⁻ (Wofsey, 2014). As seen in one of the several reactions that causes acid rain, the nitrate ion reactions with the hydrogen in water vapor to create corrosive nitric acid, HNO₃ the byproduct that comes down as acid rain (Wofsey, 2014). In the mock ignition experimental set up, the spark plug helped produce the ozone, a wet
paper towel partially evaporated to provide water moisture for the air, with the bag providing the moist, contained environment favorable for the sped up reaction.

**Analysis of Error**

As only the chemical composition of the corrosive product was important, any errors in this experiment were not quantifiable and can only be elaborated. In the test equipment set up, the polyethylene bag always had an opening in the corner to both allow room for the spark plug wire and for hot air to escape and not overinflate the bag. It is possible this leak allowed a little of the condensate to escape, corroding the metal samples less and lowering the concentration of the 200 mL solution. The 200 mL solution could have also been a flawed method to retrieve corrosive product from the metal samples, as it may have either failed to obtain enough product from rinsing or simply diluted it too much with excess use of distilled water. Certain statistical noise was present in the Total Organic Carbon detector, factors from how high or how low the concentration of the sample and what kind of standard was used to calibrate its readings all affected how many how peaks were detected in the sample and how high these peaks were.

A discarded part of the experimental procedure included using a pH meter to determine the acidity of the 200 mL solution. As it was suspected too much distilled water diluted the true acidity of the collected sample, no conclusions could be drawn from the moderately acidic pH reading. Furthermore, nitric acid and nitrous acid possess a relatively close pH range, meaning the sample and the reading would have to be quite accurate in order for pH to help determine the likeliness of one acid over the other. The accuracy of this analysis then became based on the tools available to work with, giving way to the chosen non-quantitative Xanthoproteic test as a sure means of confirmation.
Conclusion

By constructing a mock ignition system to simulate decades of corrosion and degradation, the damage to materials can be scaled, the chemical culprits identified, and the reaction pathways better understood in order to design a better engine. Starting with an informed hunch based on the chemical components available inside the contained environment, a total organic nitrogen analysis using a TOC unit followed by a Xandoproteic test identified the corrosive condensate as nitric acid in this experiment. Models are useful in research and engineering design to help identify problems before they happen years later in the real world process, but as models capture some aspects of reality, they lose others and it is imperative they are based on educated guesses and assumptions derived from fundamental knowledge and acquired engineering experience.
References


