TO: ROBO Surveillance Panel

FROM: Justin Mills – ROBO SP Chair

DATE: June 17, 2019

SUBJECT: Equivalence of concentrated and diluted nitrogen dioxide in ROBO (ASTM D7528)

**Overview:** Nitrogen dioxide, the primary catalyst used in ASTM D7528: Standard Test Method for Bench Oxidation of Engine Oils by ROBO Apparatus, was discontinued by Sigma-Aldrich in 2017 – citing shipping issues related to increased DOT standards. In order to ensure continuity and long term viability of the ROBO test, the ROBO Surveillance Panel investigated the use of 1.13% nitrogen dioxide diluted in air as a suitable alternative to liquid (high purity) nitrogen dioxide. Based on data generated at Labs AM and G, the ROBO Surveillance Panel agrees that this alternative approach offers equivalency.

In the interim, two additional suppliers of liquid (high purity) nitrogen dioxide have been identified: Electronic Fluorocarbons and SpecGas.

**Objective:** Establish dilute nitrogen dioxide (1.13% $NO_2$ in air) as a suitable alternative to concentrated nitrogen dioxide (>99.5% purity) for ASTM D7528: Standard Test Method for Bench Oxidation of Engine Oils by ROBO Apparatus.

**Results and Discussion:** In 2017 Sigma-Aldrich discontinued nitrogen dioxide (purity >99.5%) from its offering, citing difficulty shipping due to increased DOT standards and truck availability. Unknown to the ROBO Surveillance Panel at that time was Sigma-Aldrich was the sole supplier to all labs. To ensure continuity and long-term viability of the ROBO test, the Surveillance Panel agreed to take two actions:

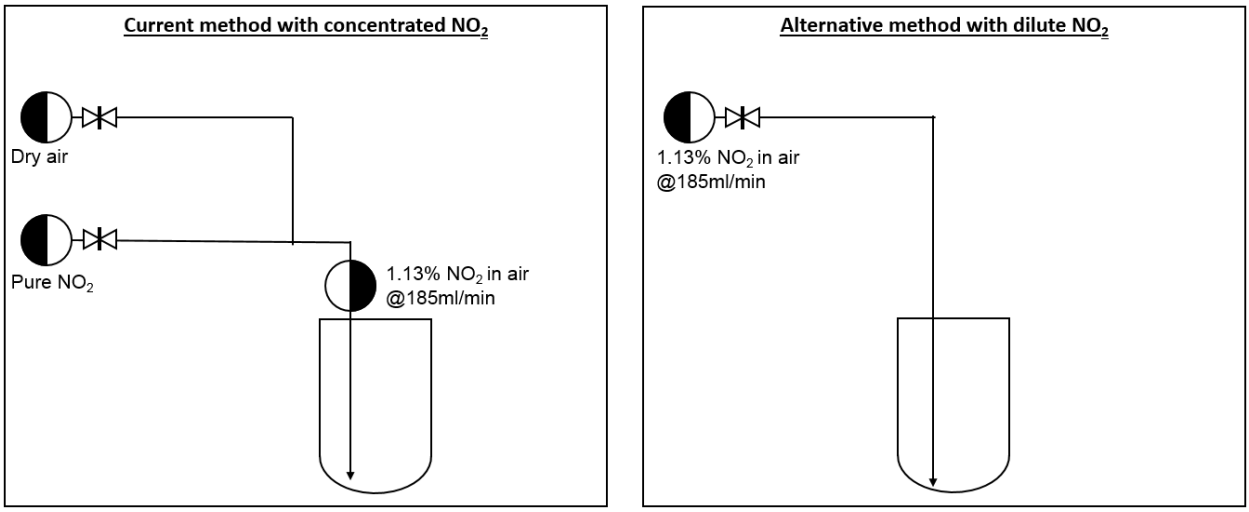
1) Identify alternative suppliers for nitrogen dioxide (>99.5% purity)
2) Evaluate and approve the use of nitrogen dioxide diluted in air as a suitable alternative to liquid (high purity) nitrogen dioxide for ASTM D7528

To satisfy the first action, two additional vendors were identified: Electronic Fluorocarbons and SpecGas. Satisfying the second action would take a much longer, methodical approach. Aside from supply security this approach offered additional benefits including safety (less concentrated), easier to ship, and could potentially provide more consistent results (easier to meter).

The information below details the development and approval of the dilute nitrogen dioxide alternative.

The current ROBO method, ASTMD D7528-17a, requires 2.0 mL ± 0.1 mL of nitrogen dioxide fed into reactor over 12 hours ± 1 hour via subsurface tubing. The flow rate of the nitrogen dioxide is controlled using a precision needle valve. Prior to entering the reaction vessel, the nitrogen dioxide is mixed with dry air flowing at a rate of 185ml/min as their flows intersect in a stainless steel tee before entering the reaction vessel via a subsurface (below the surface of the lubricant) tube.

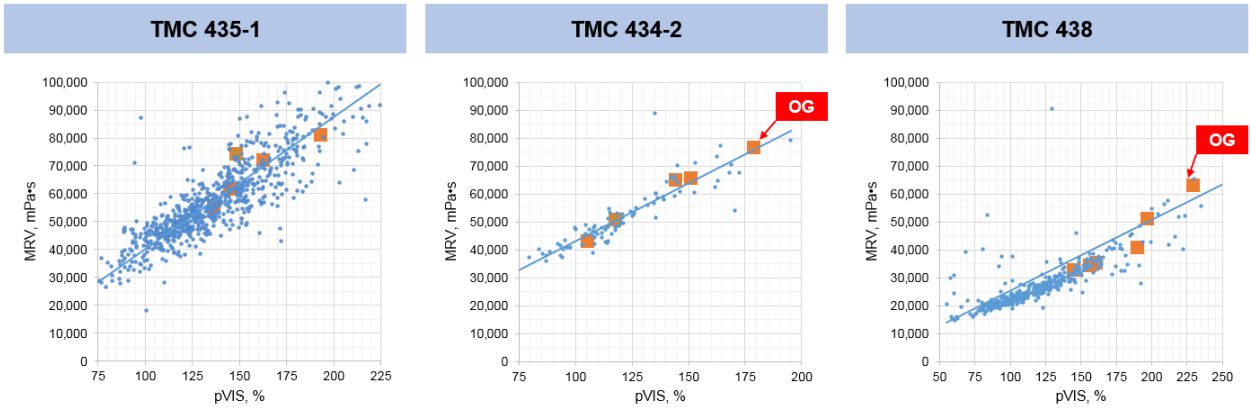
Based on calculations provided in the Appendix 1, it was determined that subsurface feed [dry air + $NO_2$] was equivalent to a concentration of 1.13% nitrogen dioxide in air. In principle, it does not matter whether we use premixed nitrogen dioxide + dry air or we use nitrogen dioxide + dry air mixed in-situ just prior entering the reaction vessel – ultimately the lubricant in the reaction vessel sees the same concentration of nitrogen dioxide in air regardless of how the two components are mixed. This was the basis for all work pertaining to dilute nitrogen dioxide. To further demonstrate this point an illustration is provided below:




A table comparing current ROBO settings to proposed ROBO settings with nitrogen dioxide in dry air is provided below:

| **Ingredient** | **ROBO Setting** | **Proposed dilute NO2 setting** |
|---|---|---|
| Test fluid | 200 grams | 200 grams |
| Iron ferrocene | 15 PPM | 15 PPM |
| Nitrogen dioxide | 2 ml "pure" $NO_2$ fed over first 12 hours | 1.13% $NO_2$ in air fed at 185 ml/min over first 12 hours |
| Dry air | 185 ml / minute (entire test) | 185 ml / minute (12 hours – EOT) |
| Agitation | 200 RPM | 200 RPM |
| Vacuum | 0.61 Bar<br>56.6 L/min | 0.61 Bar<br>56.6 L/min |
| Temperature | 170°C | 170°C |
| Time | 40 Hours | 40 Hours |

The next step was to demonstrate equivalence between the current procedure with liquid nitrogen dioxide and the proposed procedure using the nitrogen dioxide diluted in air. The surveillance panel agreed that an acceptable approach would be test the current reference oils (TMC 434-2, TMC 435-1, TMC 438) using the proposed procedure with nitrogen dioxide diluted in air, then compare those results against the historic values available through TMC's industry reference test data. Labs AM and G each donated 2-3 tests per reference oil. Results are plotted below. Additionally, the dataset is available in Appendix 2.




The results of the study validated our hypothesis: whether we mix the nitrogen dioxide with dry air in-situ prior to entering the reaction vessel or we use a "premix" of 1.13% nitrogen dioxide in air, results will be equivalent. The same trend for MRV vs. pVIS was observed regardless of how nitrogen dioxide was introduced. After all, the lubricant in the reaction sees the same concentration of nitrogen dioxide in air regardless of the mixing process.

On April 11, 2019 the ROBO Surveillance Panel convened and agreed that both means of introducing nitrogen dioxide provided equivalent results.

- End report -

**Appendix 1**

***Concentration of nitrogen dioxide in air calculation.***

**Critical assumptions:**

- Dry air is fed at 185mL per minute
- 2.0mL of nitrogen dioxide is fed over 12 hours

**Typical properties of nitrogen dioxide:**

- Density = 1.448g/ml at 68F (20C)
- Vapor density = 1.58 relative to air = 1.58 * 1.2041*10-$^{3}$ g/ml = 1.903*10$^{-3}$g/ml

**Typical properties of air:**

- Density = 1.2041*10$^{-3}$ g/ml at 68F (20C)

**<u>Concentration by volume:</u>**

Volume of NO2 in vapor phase = mass of NO2 / vapor density of NO2

$$\frac{2.896g\ NO2}{0.001903g/ml} = 1{,}521\ ml\ of\ NO2\ in\ vapor\ phase$$

Concentration by volume = volume of NO2 / (volume of air + volume of NO2)

$$\frac{1{,}521ml\ NO2}{(133{,}200ml\ air + 1{,}521ml\ NO2)} \times 100 = \mathbf{1.129\%\ by\ volume}$$

**Appendix 2**

***Results using nitrogen dioxide diluted in air.***

| IND | TESTKEY | APPARATS | VAL | PVIS | MRVTEMP | MRVYSEOT | MRV | Current limits | Ln MRV | Current limits |
|---|---|---|---|---|---|---|---|---|---|---|
| 435-1 | 116911-ROBO | AM3 | NN | 162.5 | -30 | <35 | 72,200 | | 11.1872 | |
| 435-1 | 140615-ROBO | AM3 | NN | 145 | -30 | <35 | 61,700 | | 11.03 | 10.7048 - 11.4394 |
| 435-1 | 137372-ROBO | AM 3 | NN | 148.3 | -30 | <35 | 74,300 | 44,570 – | 11.2159 | |
| 435-1 | 135714-ROBO | G 8 | AG | 193.3 | -30 | <35 | 81,000 | 92,910 | 11.3022 | (s.d. ln) = 0.20295 |
| 435-1 | 138779-ROBO | G 8 | AG | 136.2 | -30 | <35 | 55,400 | | 10.9223 | |
| ~~435-1~~ | ~~138781-ROBO~~ | ~~G 8~~ | ~~LG~~ | ~~252~~ | ~~-30~~ | ~~<70~~ | ~~223,100~~ | | ~~12.3154~~ | |
| | | | | | | **AVG** | **68,920** | **AVG** | **11.1315** | **AVG** |
| | | | | | | **STDEV** | **10,254** | **STDEV** | **0.1528** | **STDEV** |
| | | | | | | | | | | |
| 438 | 83467-ROBO | AM3 | NN | 197 | -30 | <35 | 51,000 | | 10.8396 | |
| 438 | 119646-ROBO | AM3 | NN | 156.5 | -30 | <35 | 34,500 | | 10.4487 | 9.8683 - 10.6669 |
| 438 | 137387-ROBO | AM 3 | NN | 144.9 | -30 | <35 | 32,900 | 19,308 – | 10.4012 | |
| 438 | 135716-ROBO | G 8 | AG | 189.7 | -30 | <35 | 40,800 | 42,912 | 10.6164 | (s.d. ln) = 0.2037 |
| 438 | 135717-ROBO | G 8 | OG | 229.1 | -30 | <35 | 63,200 | | 11.0541 | |
| 438 | 138795-ROBO | G 8 | AG | 160.7 | -30 | <35 | 35,200 | | 10.4688 | |
| | | | | | | **AVG** | **42,933** | **AVG** | **10.6381** | **AVG** |
| | | | | | | **STDEV** | **11,933** | **STDEV** | **0.2587** | **STDEV** |
| | | | | | | | | | | |
| 434-2 | 119643-ROBO | AM3 | NN | 144.3 | -30 | <35 | 65,100 | | 11.0837 | |
| 434-2 | 113304-ROBO | AM3 | NN | 151 | -30 | <35 | 65,500 | | 11.0898 | 10.6244 - 11.2386 |
| 434-2 | 142329-ROBO | AM 3 | NN | 117.5 | -30 | <35 | 50,900 | 41,126 – | 10.8376 | |
| 434-2 | 138766-ROBO | G 8 | AG | 105.4 | -30 | <35 | 43,100 | 76,008 | 10.6713 | (s.d. ln) = 0.1551 |
| 434-2 | 138767-ROBO | G 8 | OG | 178.7 | -30 | <35 | 76,700 | | 11.2477 | |
| ~~434-2~~ | ~~142038-ROBO~~ | ~~G 8~~ | ~~LG~~ | ~~146.1~~ | ~~-30~~ | ~~<35~~ | ~~69,200~~ | | ~~11.1448~~ | |
| | | | | | | **AVG** | **60,260** | **AVG** | **10.986** | **AVG** |
| | | | | | | **STDEV** | **13,259** | **STDEV** | **0.229** | **STDEV** |