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May 21-25, 2017

BASE OIL AND ANTIOXIDANT SELECTION – THE ROLE OF SECONDARY ANTIOXIDANTS AND BASE OIL SULFUR CONTENT

Lubrication Fundamentals I, Additives & Additives Degradation

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INTRODUCTION

With the Group I base oil production capacity rapidly declining, industrial lubricants are facing new challenges with compatibility, solubility and extensive re-formulations. Nynas has developed a new range of Group I replacement base oils which has proven to fulfil the viscosity and solvency needs for industrial lubricants [1]. However, due to the low sulfur content in the new range oils, higher demands are put on the appropriate antioxidant selection compared to a Group I base oil with its inherent high sulfur content. Thus, we have investigated the antioxidant response of the new range oils in relation to sulfur content and can here recommend suitable antioxidant packages for the series to perform better than Group I oils in standard oxidation tests.

RESULTS AND DISCUSSION

Base Oil Sulfur Content and Response to Primary Antioxidants

Due to different refining conditions, the new range series has a lower sulfur content than normal Group I oils. It is clear that high intrinsic sulfur of solvent refined oils is beneficial from an antioxidant perspective [2]. Here, the effect of the sulfur content in base oils is investigated using High Pressure Differential Scanning Calorimetry (HPDSC) [3]. The oxidation induction time (OIT) of HPDSC is determined at 35 bar O_2, 200 °C and with 3.0-3.3 mg sample size. Clearly, sulfur content impacts OIT as base oil SN 150 A has a higher sulfur content compared to the new range 150 (NR 150) and withstand severe oxidation longer (Figure 1). Doping NR 150 with a model sulfide compound to 700 ppm S and further to 0.3 wt% S increases the OIT significantly, resulting in excellent oxidation stability. However, doping NR 150 with a model thiophene compound did not have the same effect on the oxidation stability, indicating that the actual chemical composition of sulfur is important from an antioxidant perspective. Thus, care must be taken to choose the most active form of sulfur-containing secondary antioxidant for the specific base oil [2].

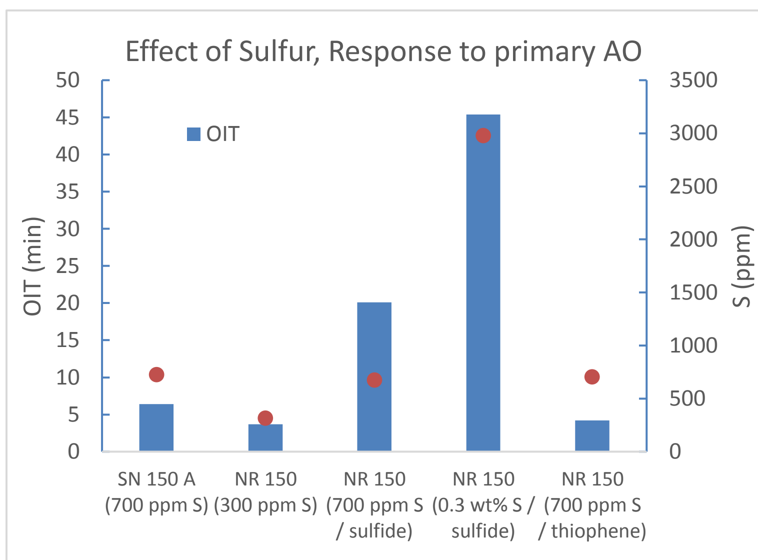


Figure 1. Response to primary AO measured by HPDSC [2]. Effect of different sulfur content/compounds in the new range 150 compared to SN 150 A.

Optimizing New Range Antioxidant Behavior with Secondary Antioxidants

The oxidative response of base oils with different sulfur content indicates that the oxidation stability of the new range oils can be improved with the addition of a secondary antioxidant. A range of secondary antioxidants was thus investigated [4] [5], and the oxidizing behavior of the different base oil formulations were investigated using HPDSC. Not surprisingly, NR 150 responded very well to sulfur-containing antioxidants (Figure 2), a synergism previously noted for such formulations [6]. Dithiocarbamate (S2N) and inactive sulfur carrier (InAcS) would be excellent choices for antioxidant formulation. Phosphorus-containing antioxidants (Pho) were however not effective at all in these systems.

It is evident that NR 150 respond better to S2N than corresponding solvent neutral Group I oil given the same oxidative conditions (Figure 3).

The oxidation stability of a range of base oils were also investigated using RPVOT [7]. The S2N-formulated NR 150 (390 min) performs better than benchmark SN 150 B (310 min). Both oils adhere to the pass level set to >300 minutes for hydraulic oils in the Swedish Standard [8]. Group II oil are designed to respond very well to secondary antioxidants, which reflects the superior result of Paraffinic GII in this evaluation (Figure 4). That sulfur content of base oils plays an important role in oxidation behavior could again be verified in the RPVOT results as sulfide-doped NR 150 performed better that the low-sulfur base oil. The properties of SN 150 A (e.g. relatively low sulfur content) suggest that the oil is refined to an intermediate Group I/II oil.

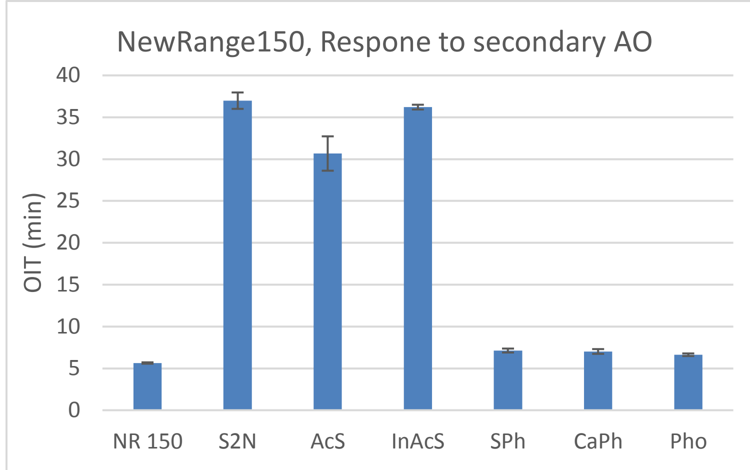


Figure 2. Response of New Range (NR) 150 to 6 different secondary AOs, measured by OIT/HPDSC.

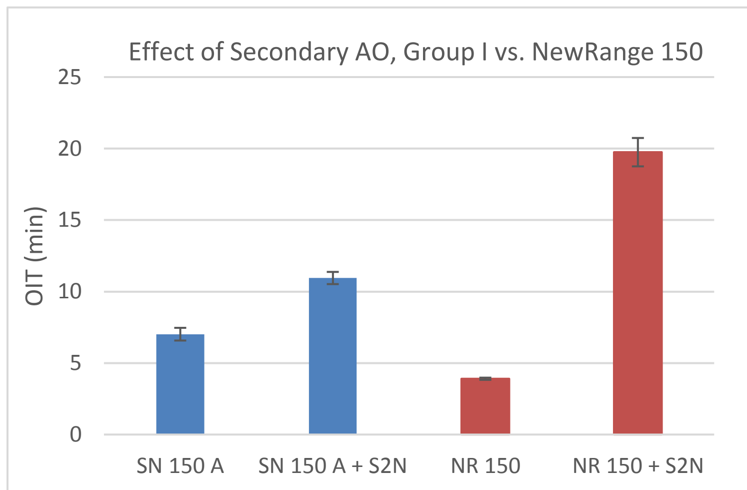


Figure 3. Effect of dithiocarbamate (S2N) in SN 150 compared to NR 150, measured by OIT/HPDSC

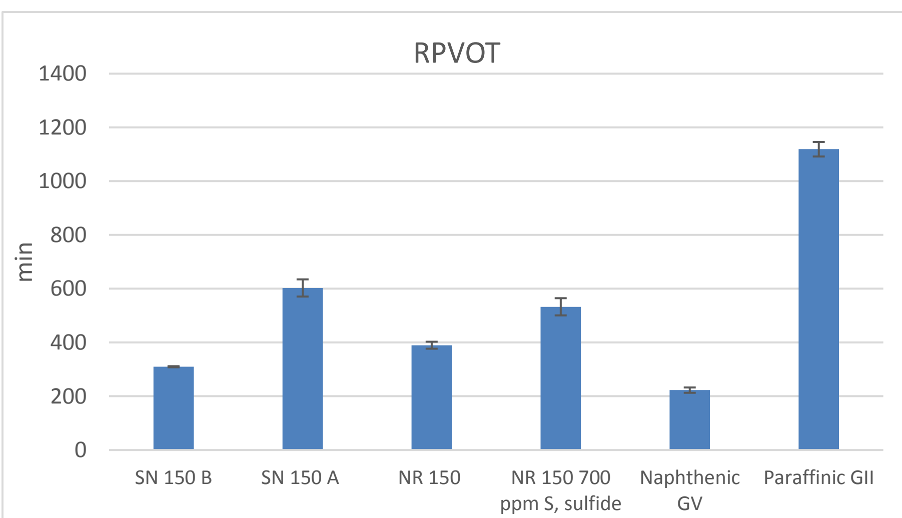


Figure 4. RPVOT results. Base oils formulated with primary antioxidant (0.2 wt%, BHT + phenyl amine) and secondary antioxidant S2N (0.1 wt%).

The HPDSC and RPVOT results in this study clearly demonstrate how antioxidant response and ranking can change based on the oxidation test employed, as also demonstrated in previous studies [6] [9]. In fact, it proved impossible to evaluate high sulfur content Group I oils (~0.3 wt % S) using isothermal HPDSC conditions as no appreciable exotherm could be noted. Oils with high sulfur content have previously been found incompatible with isothermal HPDSC evaluation [9]. However, dynamic HPDSC measurements which record the Onset Oxidation Temperature (OOT) works well for all base oils. Again, it is suspected that the natural sulfur inhibitors act in favor of the SN 150 B oil having both the far highest sulfur content and OOT (Table 1).

	RPVOT (min)	HPDSC/OIT (min)	HPDSC/OOT (° C)
SN 150 A (700 ppm S)	603	10.95	199.5
SN 150 B (0.3 wt% S)	310		222.2
New Range 150 (300 ppm S)	390	19.75	197.9
New Range 150 (700 ppm S, sulfide doped)	533	31.45	229.3
Naphthenic oil GV (400 ppm S)	223	10.57	188.4
Paraffinic oil GII (<15 ppm S)	1119	11.93	198.1

Table 1. Results of investigation of oxidative stability. Base oils formulated with primary antioxidants (0.2 wt%, BHT + diphenylamine) and secondary antioxidants (0.1 wt%, S2N) for RPVOT and HPDSC/OIT. Pure base oils for HPDSC/OOT.

Conclusions

The new range 150 seem to have lower response to primary antioxidants than solvent neutral Group I oils. However, with the addition of sulfur-containing secondary antioxidants, NR 150 perform better than Group I oils in RPVOT and HPDSC oxidation tests. A combination of BHT + phenylamine and secondary antioxidant, either dithiocarbamate (S2N) or inactive sulfur carrier (InAcS), would provide an excellent oxidation stability of the base oil. The results support the theory that the low intrinsic sulfur in the new range series is at least partly responsible for the poor response to primary antioxidants. The inconsistent results of the oils in the various oxidation tests indicates different oxidation mechanisms at the various conditions employed during the tests.

ACKNOWLEDGMENTS

Antioxidant samples kindly provided by Lanxess Rhein Chemie and the Lubrizol Corp.

REFERENCES

[1] Norrby, T., Salomonsson, P., and Malm, L., 2016, “Group I Replacement Fluids – a Hydraulic Fluid Formulation and Compatibility Study”, 20th International Colloquium Tribology Industrial and Automotive Lubrication, Technische Akademie Esslingen e.V, Germany.

[2] Bala, V., Hartley, R. J., Hughes, L. J., 1996, “The Influence of Chemical Structure on the Oxidative Stability of Organic Sulfides”, *Lubr. Eng.*, **52**(12), pp. 868-873

[3] ASTM D 6186-08, “Standard Test Method for Oxidation Induction Time of Lubricants by Pressure Differential Scanning Calorimetry (PDSC)”

[4] Dithiocarbamate (S2N), active sulfur carrier (AcS), inactive sulfur carrier (InAcS), sulfur containing phenolic antioxidant (SPh)

[5] Calcium phenate detergent (CaPh), phosphite antioxidant (Pho)

[6] Gatto, V. J., Grina, M. A., “Effects of Base Oil Type, oxidation test Conditions and Phenolic Antioxidant Structure on the Detection and Magnitude of Hindered Phenol/Diphenylamine Synergism©”, *Lubr. Eng.*, **55**(1), pp. 11-20

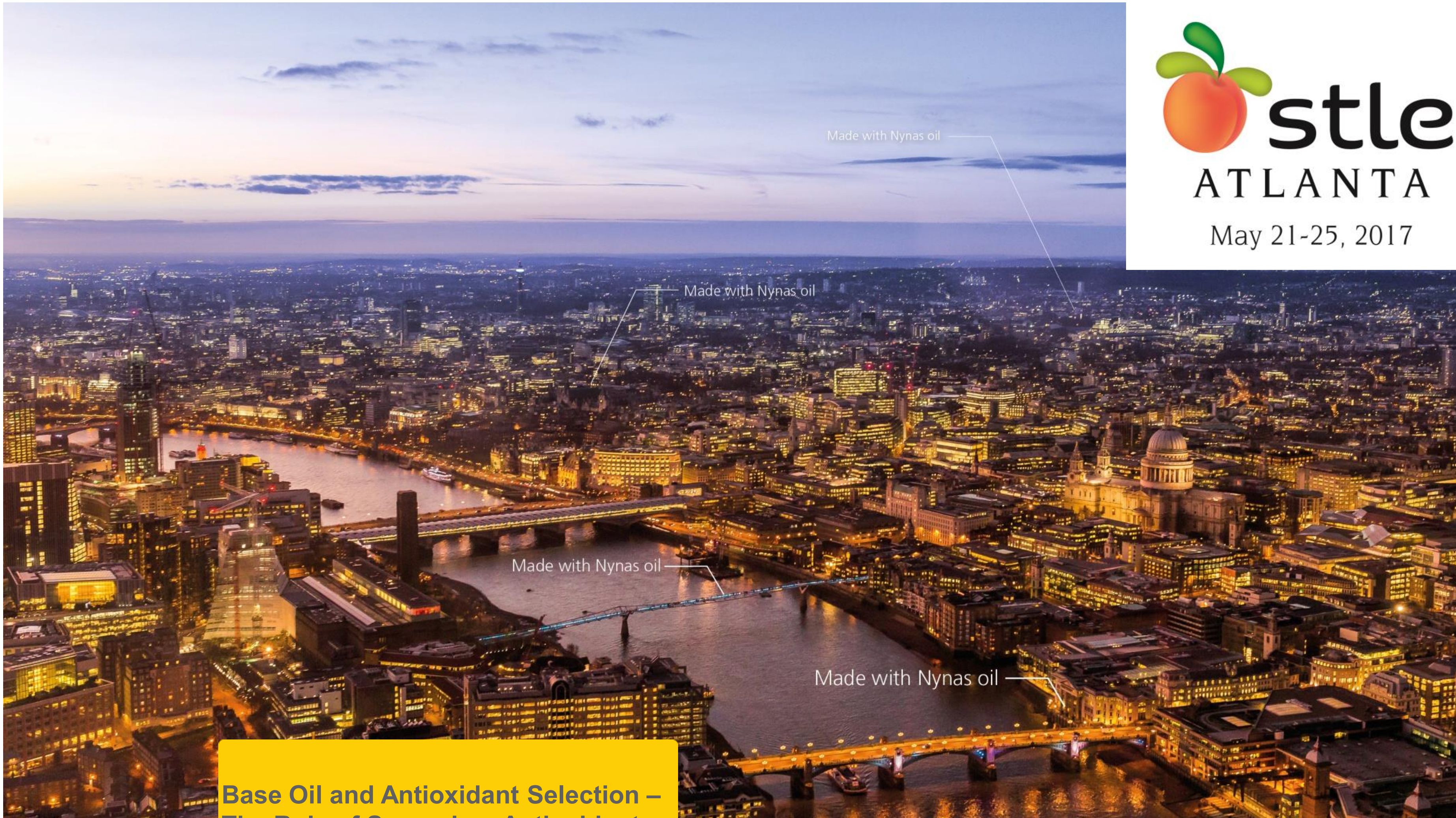
[7] ASTM D 2272-14a “Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel

[8] Swedish Standard 155434:2015 ”Hydraulic fluids- Technical requirements, environmental properties and test methods”

[9] Qiu, C., Han, S., Cheng, X., Ren, T., 2006, “Determining the antioxidant activities of organic sulfide by rotary bomb oxidation test and pressurized differential scanning calorimetry,” *Termochim. Acta,* **447**, pp. 36-40

KEYWORDS

Antioxidants, Secondary Antioxidants, base oil Sulfur, OIT, HPDSC, RPVOT



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Base Oil and Antioxidant Selection – The Role of Secondary Antioxidants and Base Oil Sulfur Content

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NYNAS

Nynas was founded in Sweden 1928

- Nynas AB is the largest specialty oil producer in Europe
- Offices in more than 30 countries around the globe
- Net Sales: 1.4 Billion USD (2016)
- Average number of employees: 1000
- Refineries in Nynäshamn (SE), Harburg (DE), Isla JV (Curacao), Eastham JV (UK), Gothenburg (SE)

Nynashamn

Harburg

What we can do for you

PROCESS OILS

- Adhesives and sealants
- Printing inks
- Battery separators
- Rubbers and plastics
- Insoluble sulfur
- Antifoams

TYRE OILS

- Used as extender oil in a tyre rubber formulation
- Oil extended polymers

TRANSFORMER OILS

- Insulating oils for industrial transformers
- Finished products
- Best for:
  HVDC power trans-formers, instrument transformers, distribution transformers

BASE OILS

- Lubricating Greases
- Metalworking Fluids
- Hydraulic Fluids
- Gear Oils
- Additive carriers
- Other industrial lubricants

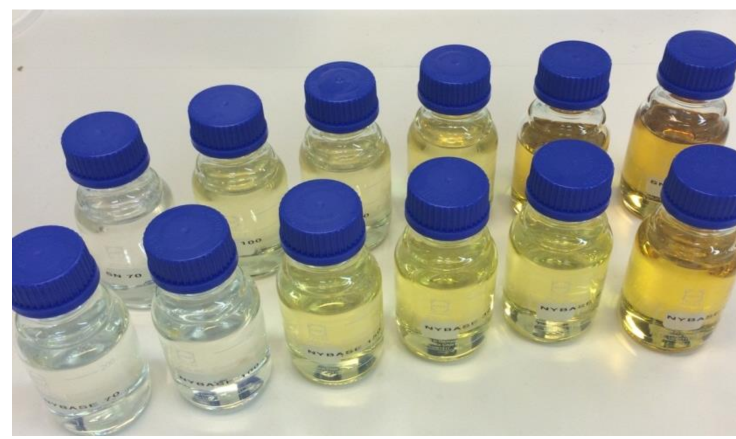
A few words on the Nynas new range base oils…

A new specialty base oil product range

- Can be widely applied in industrial lubricant formulations
- Naphthenic + Paraffinic blends

- Main advantages of the “New Range” (NR)
  - Most similar base oil compared to Group I oils
  - High degree of flexibility in blending
  - Will be available over time
  - Superior low temperature performance

- Main challenges vs Group I base oils
  - Lower Sulphur content
  - Slightly higher volatility
  - Lower flash point
  - Slightly lower VI



Basic requirements of the New Range

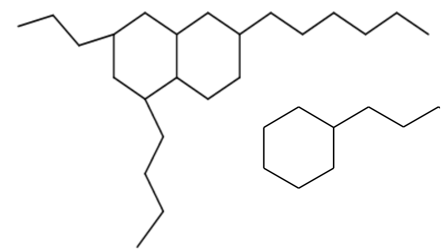
- The New Range range should:
  - Closely match the Kinematic Viscosity (@ 40 °C) and Aniline Point of a representative reference base oil range of Solvent Neutral (SN) Group I paraffinic base oils
    - Allow industrial lubricant manufacturers to maintain key properties of their products by offering retained viscosity and solvency
  - Allow direct replacement
  - Or with as little re-formulation and re-working of labels, PDS and other marketing material as possible (drop-in replacement)

Chemical composition of mineral base oils

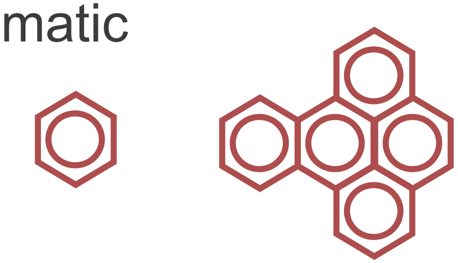
- Mineral base oils consist mainly of naphthenic, paraffinic and aromatic molecules
- The relative amount of these molecules in the oil determines whether the oil is considered naphthenic or paraffinic
  - C_P (IR) 42-50% Naphthenic
  - C_P (IR) 56-67% Paraffinic
- Aromatic molecules confer high solvency to the oil, but some polyaromatic compounds are harmful to human health, and to the environment, so they are removed or converted during the refining process.

Paraffinic

Naphthenic



Aromatic

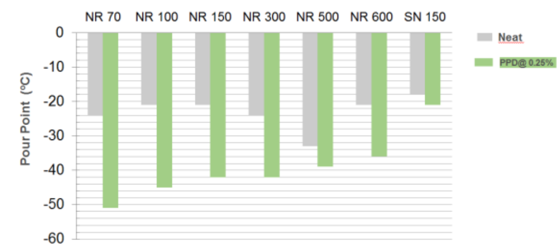


The New Range vs. SN reference base oils

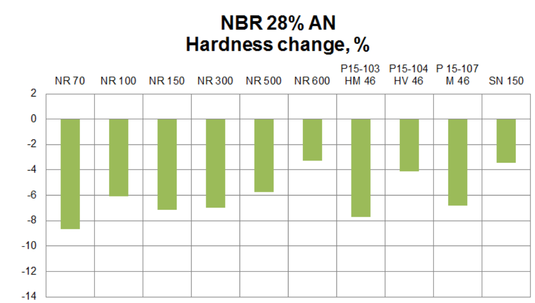
	NR 70	SN 70	NR 100	SN 100	NR 150	SN 150	NR 300	SN 300	NR 500	SN 500	NR 600	SN 600
Density (kg/m3)	0,873	0,849	0,867	0,859	0,871	0,868	0,886	0,876	0,889	0,879	0,876	0,880
FP COC (°C)	168	190	196	206	222	224	220	258	242	262	268	278
PP (°C)	-27	-12	-24	-18	-24	-18	-21	-18	-21	-9	-15	-9
Viscosity @40 °C (cSt)	**14**	**12**	**22**	**17**	**30**	**30**	**60**	**58**	**100**	**94**	**120**	**115**
Viscosity @100°C (cSt)	3,1	2,9	4,2	3,7	5,0	5,2	7,3	7,8	10,2	10,7	12,6	12,2
VI	67	92	88	104	89	103	75	98	79	97	98	96
Aniline Pt. (°C)	**90**	**90**	**100**	**98**	**101**	**102**	**103**	**109**	**111**	**115**	**123**	**117**
Sulfur (m-%)	0,02	0,2	0,01	0,2	0,04	0,2	0,02	0,2	0,03	0,3	0,02	0,3
CA	3	7	2	3	3	3	4	3	3	2	2	3
CN	42	27	36	32	35	33	36	32	36	31	30	29
CP	55	66	62	65	62	64	60	65	61	67	69	68
Refractive index	1,477	1,468	1,475	1,472	1,479	1,477	1,485	1,481	1,487	1,483	1,481	1,483

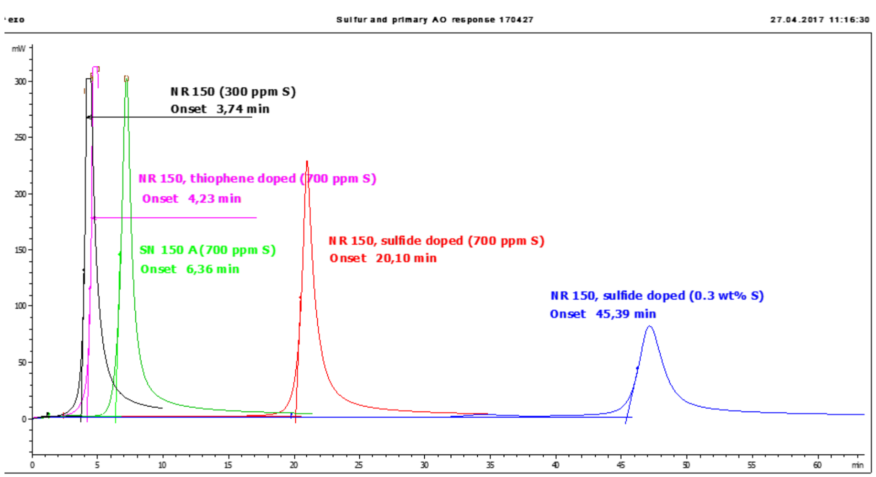
Properties of the New Range base oils have been investigated for several years by now

- Low temperature
  - Pour Point
- Elastomer Compatibility
  - Seals and gaskets in machinery
- Formulation of model hydraulic fluids (STLE 2016)
  - Determination of properties
  - Benchmarking vs commercial hydraulic fluids
- **Antioxidant Response: STLE 2017**



NBR 28% AN, Sulfur cured





Physical Properties HM

Test	Unit	HM 46	ISO 11158, HM	Method
Filterability I/II*		97/94	80/60	ISO 13357-2
Foam I @ 24 °C	ml/ml	10/0	150/0	ISO 6247:1998
Foam II @ 93 °C	ml/ml	30/0	80/0	ISO 6247:1998
Foam III @ 24 °C	ml/ml	10/0	150/0	ISO 6247:1998
Air Release	min	2,0	10	ISO 9120
Demulsibility	min	10	30	ISO 6614
Oil/water/emuls.	ml	40/40/0	40/37/3	ISO 6614
TOST (1000 h)	mg KOH/g	-[a]	≤2	ISO 4263-1
RPVOT	min	374	300[a]	ASTM D 2272-11 method A

*= Dry (no added water), Applied Pressure 100 kPa
a = SS 15 54 34:2015, Swedish Standard for Hydraulic Fluids, Level A, equal to 1000 h TOST

Antioxidant response study

Base oil properties – sulfur content

- The New Range series has been designed as a Group I replacement range
- It is based in blends of Naphthenic oils and Group II base oils
  - Both kinds are highly refined and hydrotreated
- Due to the refining conditions of the component base oils, the New Range series has a lower sulfur content than normal Group I oils
- It is clear that high intrinsic sulfur of solvent refined oils is beneficial from an antioxidant perspective [1]
- Thus, we have investigated the antioxidant response of Nybase oil in relation to sulfur content
- We are searching for formulation guidelines for an optimal AO response

[1] Bala, V., Hartley, R. J., Hughes, L. J., 1996, "The Influence of Chemical Structure on the Oxidative Stability of Organic Sulfides", *Lubr. Eng.*, **52**(12), pp. 868-873

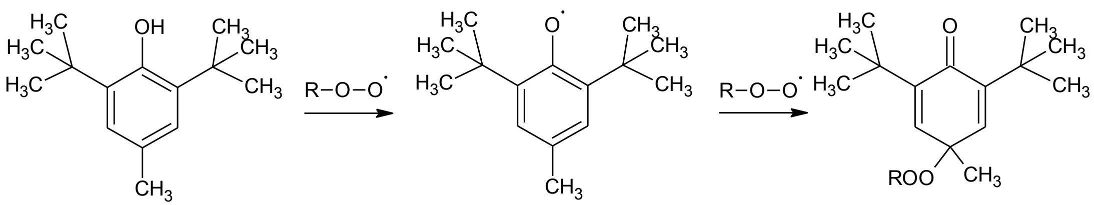
Focus of the present study

- Here, the effect of the sulfur content in base oils is investigated using High Pressure Differential Scanning Calorimetry (HPDSC) [2]
- The oxidation induction time (OIT) of HPDSC is determined at 35 bar O_2, 200 °C and with 3.0-3.3 mg sample size
- We will look for any correlation between
  - "Base oil" sulfur
  - Added sulfur-containing Secondary Antioxidants
  - Primary Antioxidant type and concentration

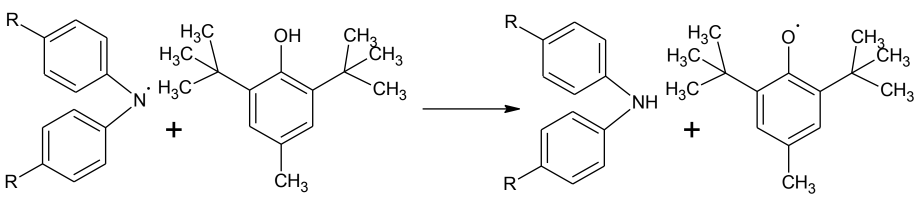
[2] ASTM D 6186-08, "Standard Test Method for Oxidation Induction Time of Lubricants by Pressure Differential Scanning Calorimetry (PDSC)"

Antioxidants in this study

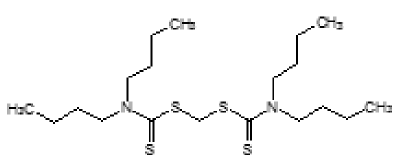
- Primary AO
  - Radical scavengers (propagation step)
  - Hindered phenols, aromatic amines

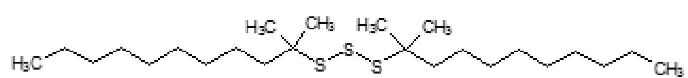


  - Synergistic effect



- Secondary AO
  - Hydroperoxide decomposers (branching step)
  - Sulfur/phosphorus-containing





Nybase Antioxidant Response

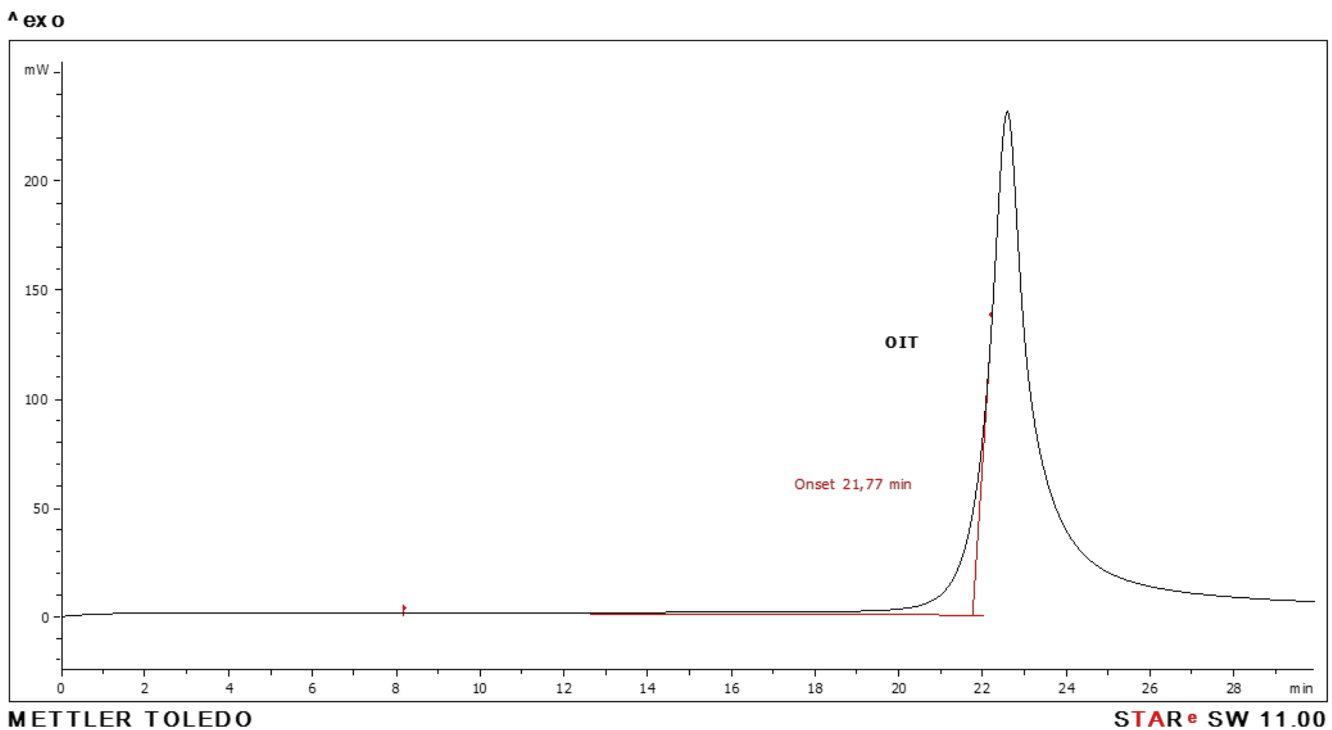
1. Oxidation behaviour of Group I oils vs. Group II/New Range oils

2. Antioxidant response of New Range oils to secondary antioxidants

Group I base oils

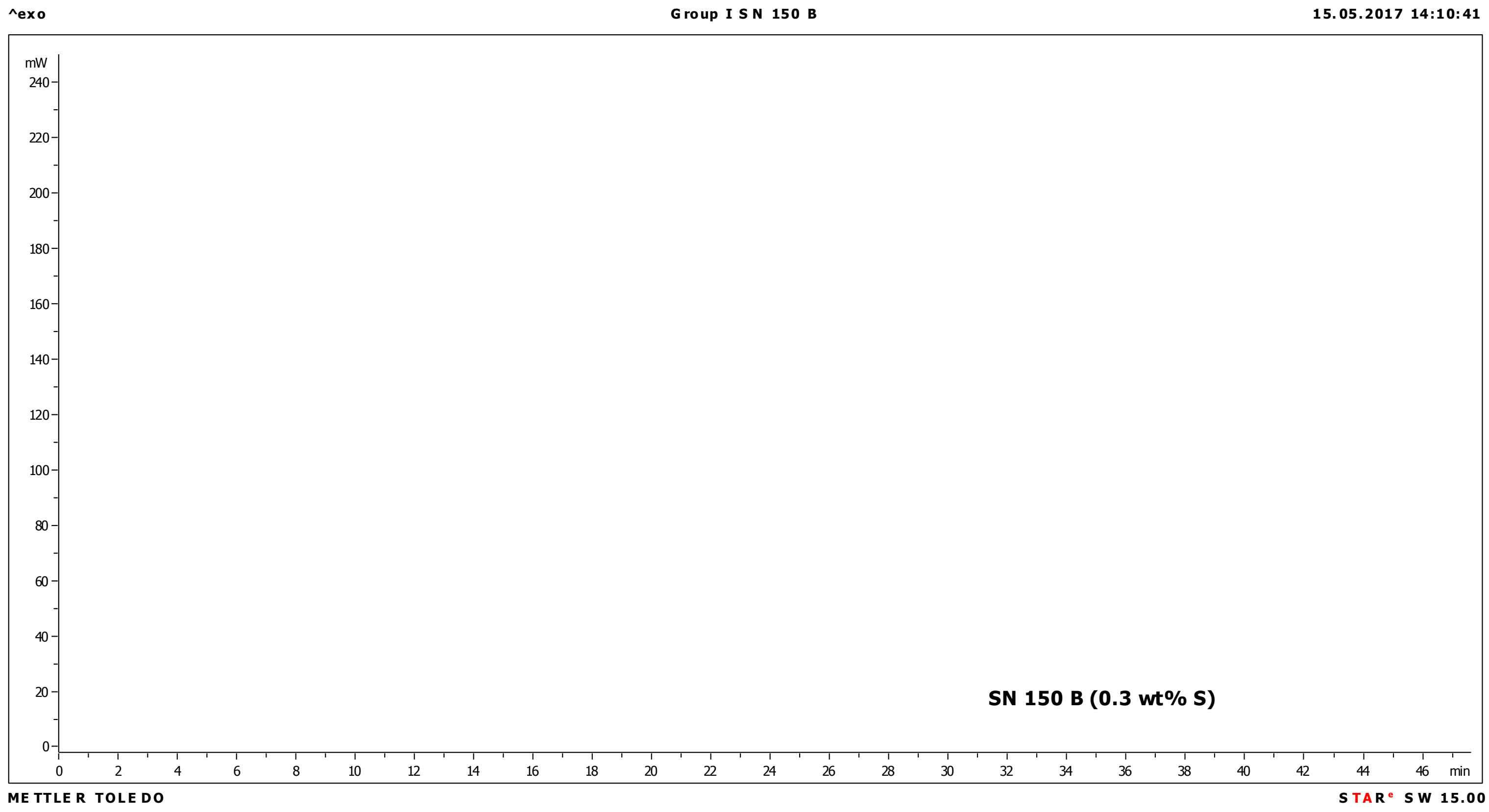
Oxidation behaviour of Group I oils – HPDSC/OIT

- HPDSC, High Pressure Differential Scanning Calorimetry
- OIT, Oxidation Induction Time for inhibited oils
- OIT measures of how long time the oil can withstand severe oxidation at the chosen elevated temperature and oxygen pressure. When the inhibitor is depleted, the oil is subjected to rapid oxidation and a strong exothermic reaction is noted.



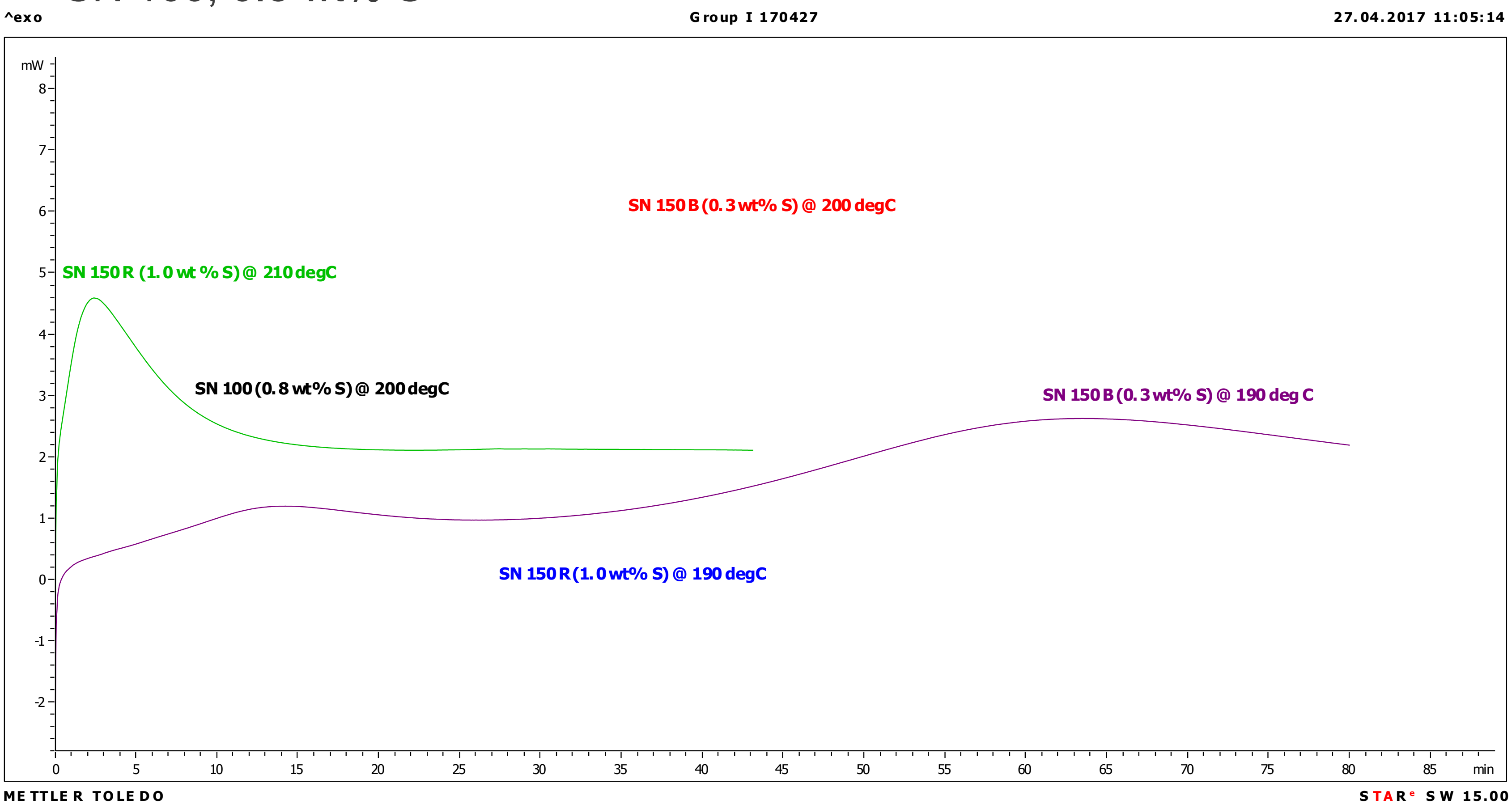
Oxidation behaviour of Group I oils – HPDSC/OIT

- No exotherm, Oxidation Induction Time (OIT) for Group I oils
  - @ 200 °C, 35 bar O_2
- Oxidation is ongoing from start at a very slow and steady pace? - high intrinsic sulfur → natural inhibitors in the oxidation process



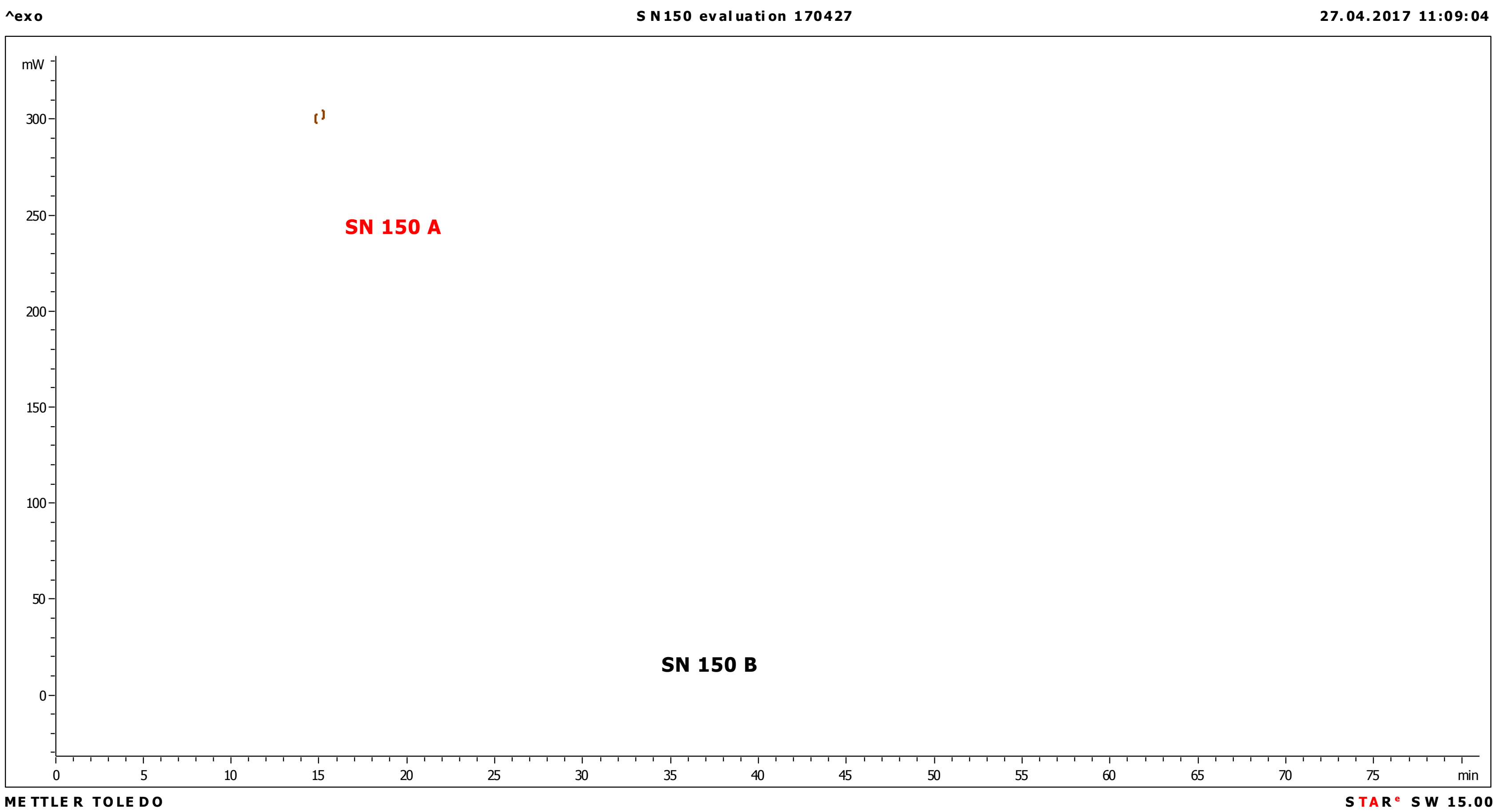
Oxidation behaviour of Group I oils – HPDSC/OIT

- Similar behaviour for several high-sulfur Group I oils
  - SN 150 B, 0.3 wt% S
  - SN 150 R,1.0 wt% S
  - SN 100, 0.8 wt% S



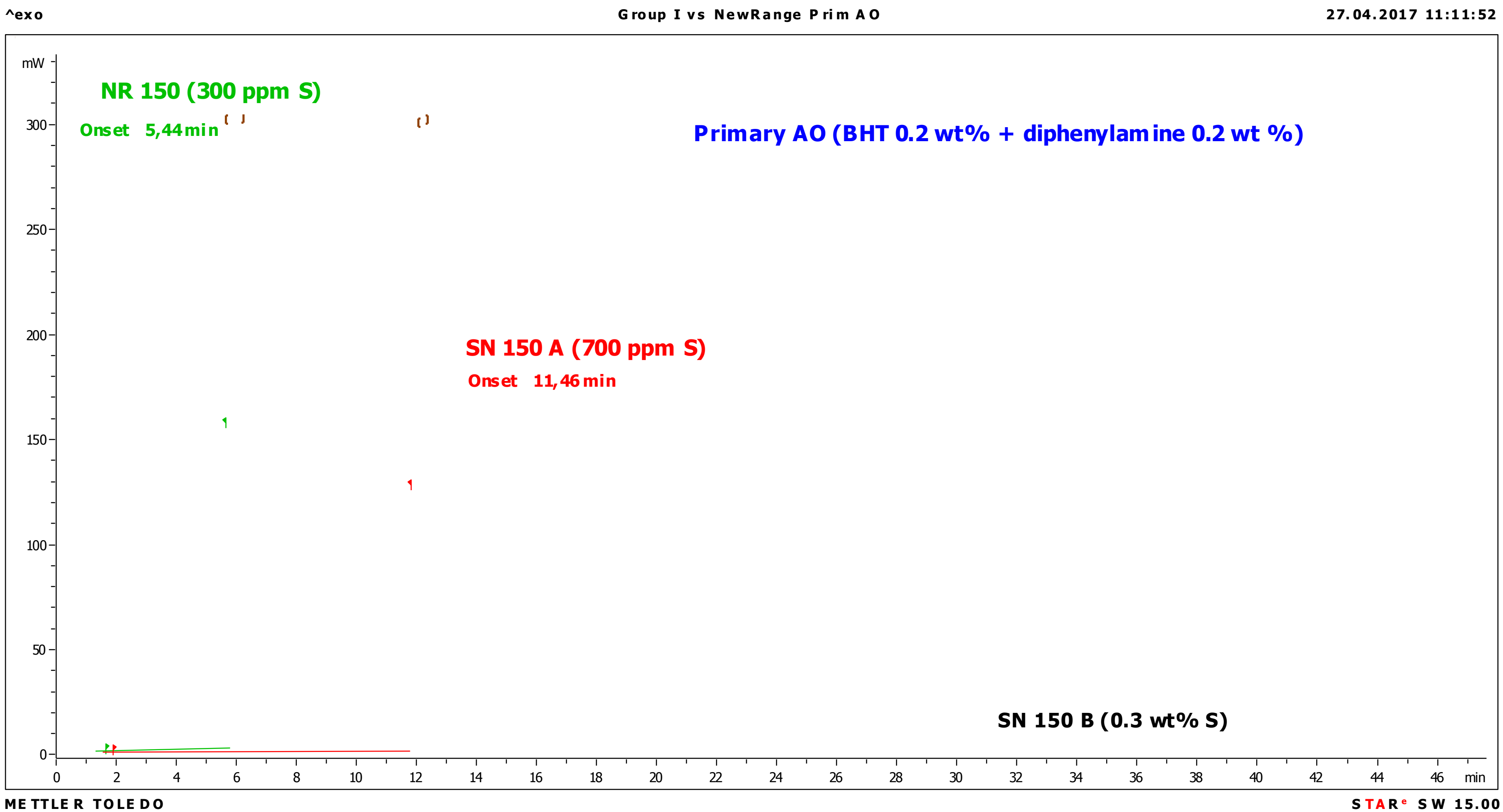
Oxidation behaviour of Group I oils – HPDSC/OIT

- SN 150 A - intermediate “Group I/II”
  - Low sulfur content, 700 ppm S (Group I 0.3-1.0 wt% S)



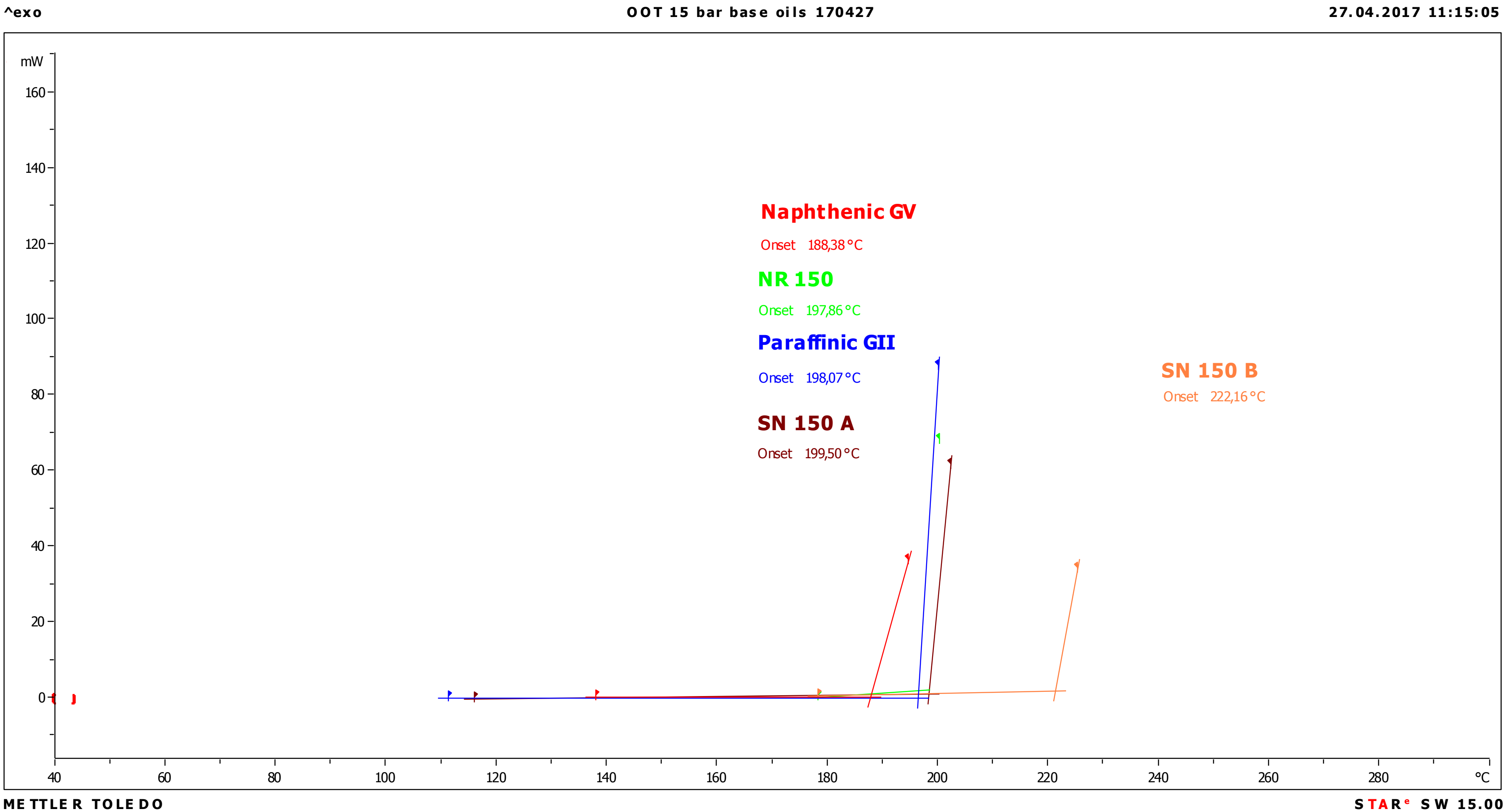
New Range Group I replacement base oils

Oxidation behaviour of Group I oils vs. New Range oil – HPDSC/OIT



Oxidation behaviour of base oils – HPDSC/OOT

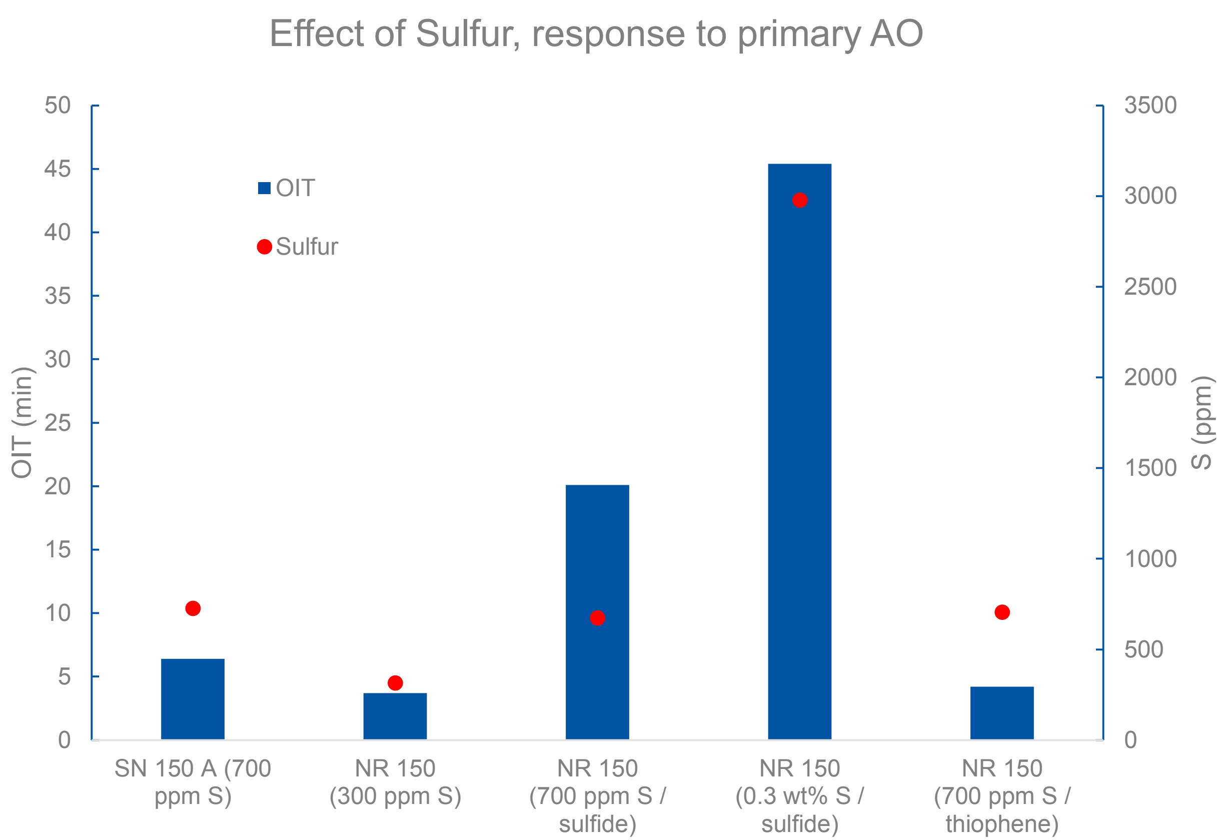
- OOT - Group I, high Oxidation Onset Temperature (OOT)
  - Different oxidation mechanisms OOT/OIT



The effect of Base Oil Sulfur

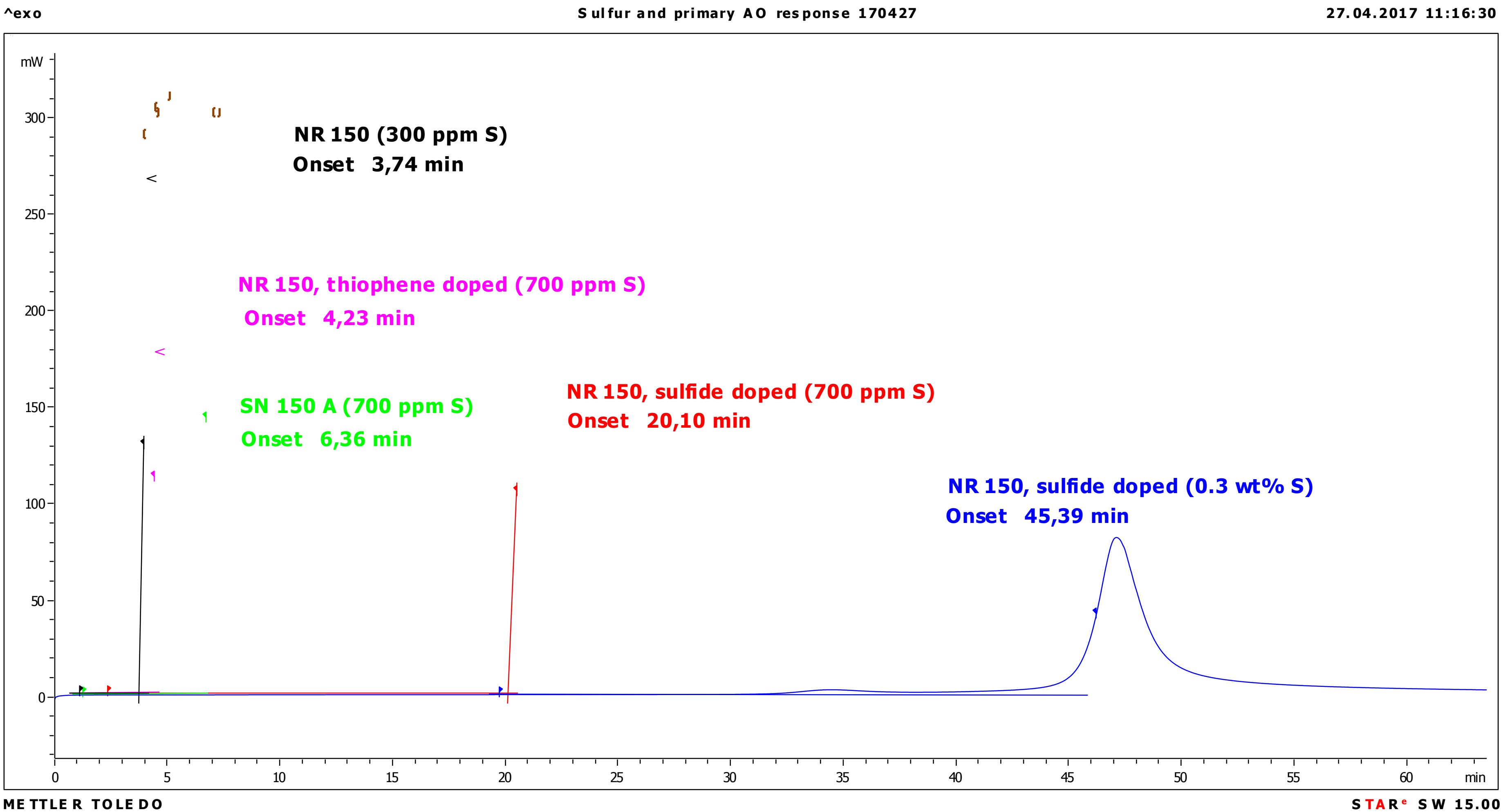
Antioxidant response of New Range oils – the effect of Sulfur

- Increasing amount of sulfur (doping with S-model compounds) in New Range150 (NR 150) gives better response to primary antioxidants (OIT)
  - Sulfides more effective than thiophenes



Antioxidant response of New Range oils – the effect of Sulfur (II)

- OIT, Oxidation Induction Time

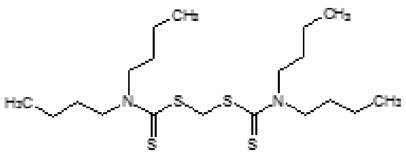


The effect of Secondary Antioxidants

Secondary Antioxidant Optimization

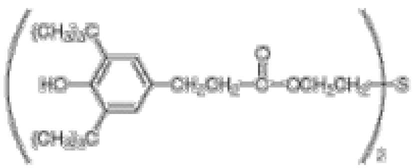
Antioxidant response of New Range series to Secondary Antioxidants

1. S2N: dithiocarbamate (methylene-bis-dibutylthiocarbamate)



2. AcS: light coloured, active sulfur carrier (dialkylpentasulfide)

3. InAcS: light coloured, inactive sulfur carrier (di-tert-dodecyl trisulfide)



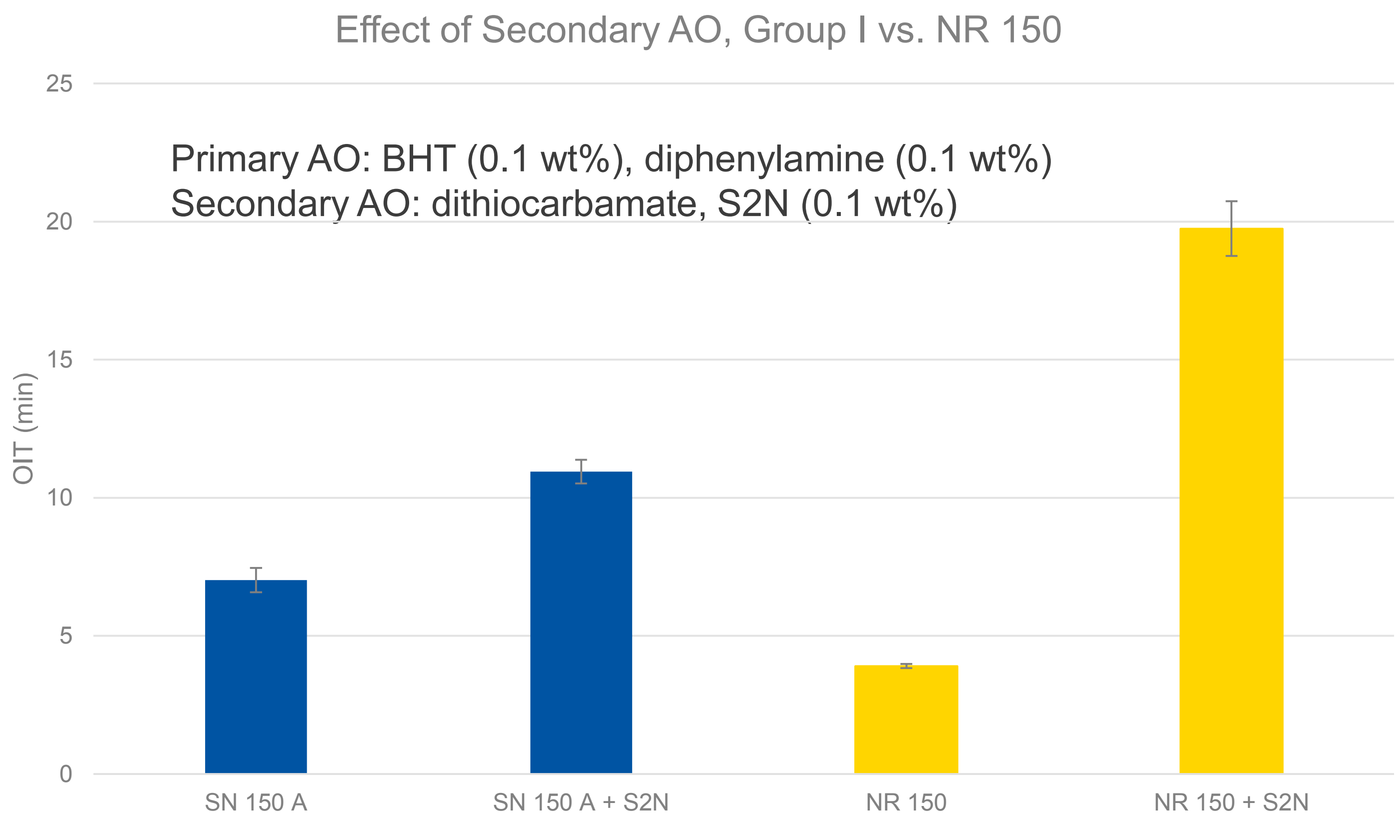
4. SPh: sulfur containing phenolic antioxidant

5. CaPh: calcium phenate detergent

6. PhO: phosphite containing antioxidant

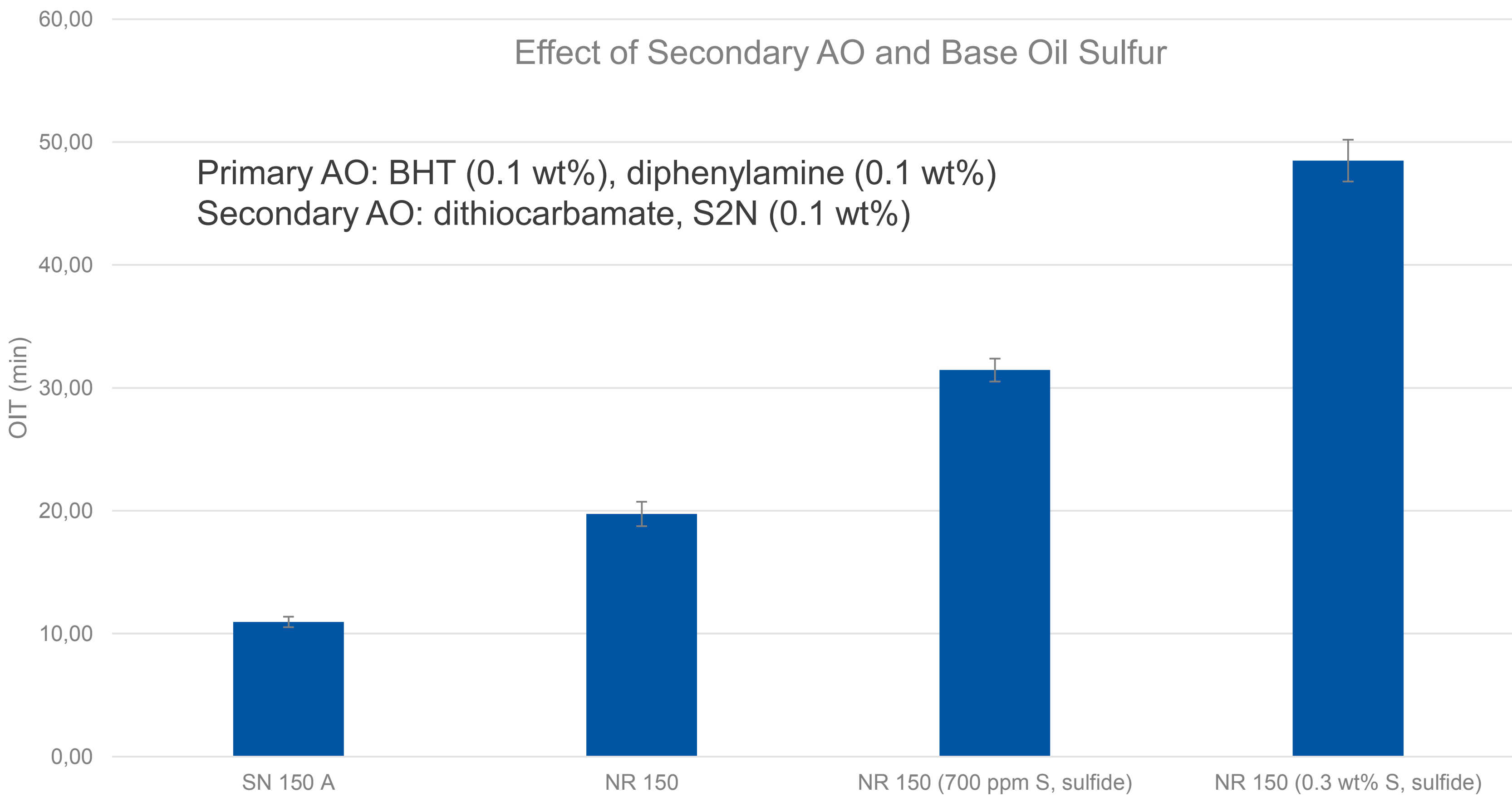
Antioxidant response of New Range oil to secondary antioxidants (OIT)

- NR 150 have a **better** response to Secondary Antioxidants compared to SN 150



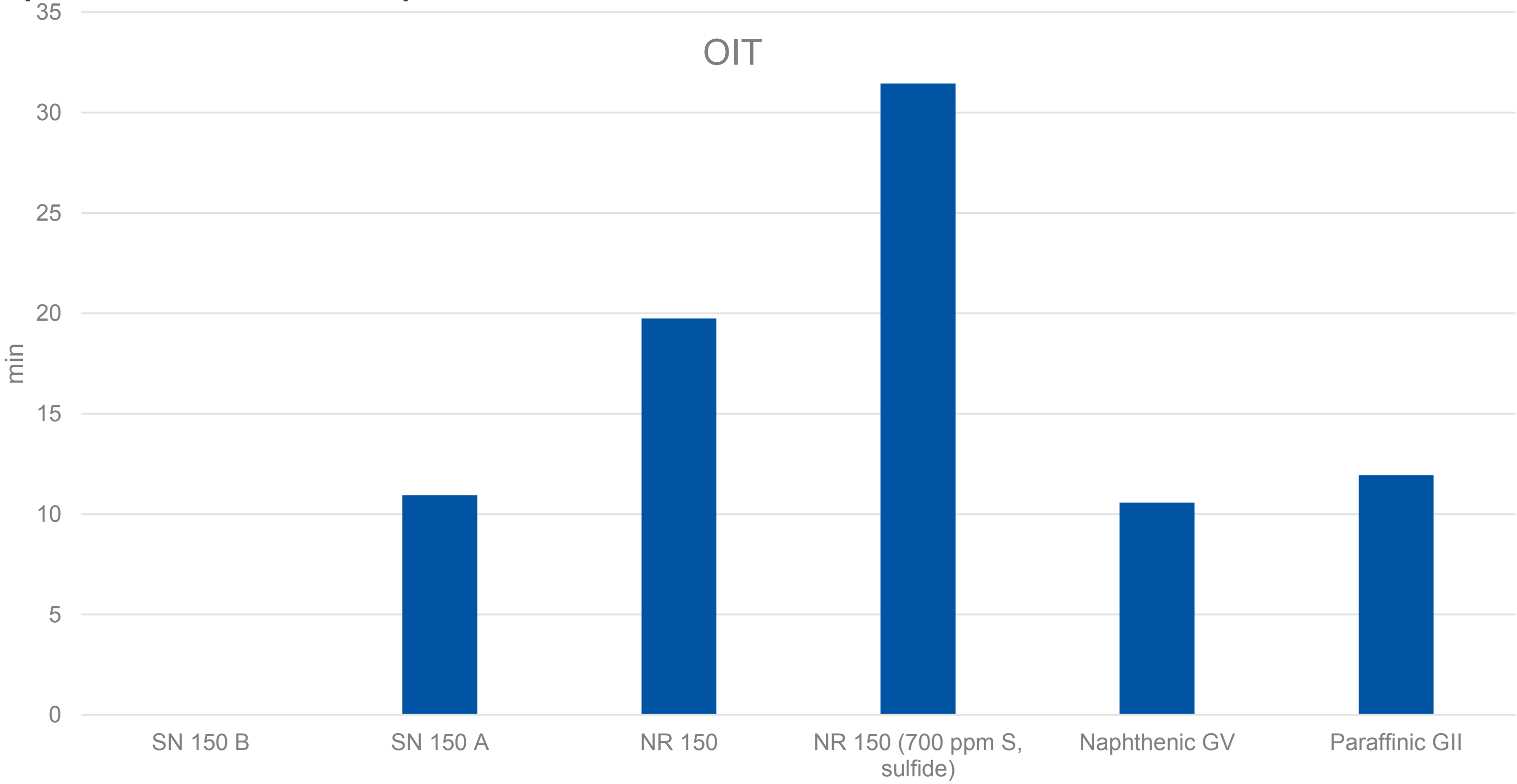
Antioxidant response of New Range oils to secondary antioxidants (OIT)

The additional effect of added “base oil” Sulfur (Sulfide type)



Antioxidant response of New Range oils to Sec. AO, (OIT)

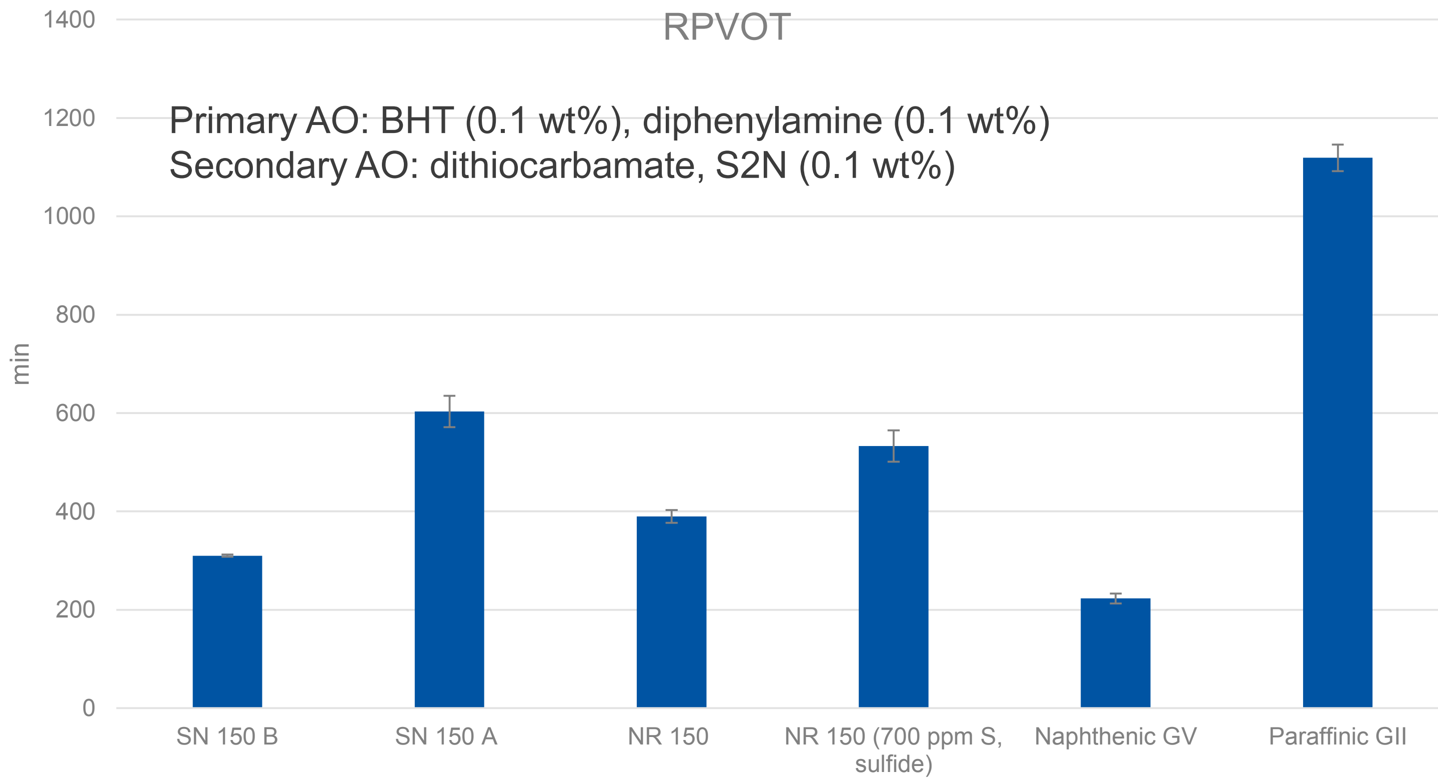
The additional effect of added “base oil” Sulfur (Sulfide type) – vs. Naphthenic and Group II base oils



Primary AO: BHT (0.1 wt%), diphenylamine (0.1 wt%)
Secondary AO: dithiocarbamate, S2N (0.1 wt%)

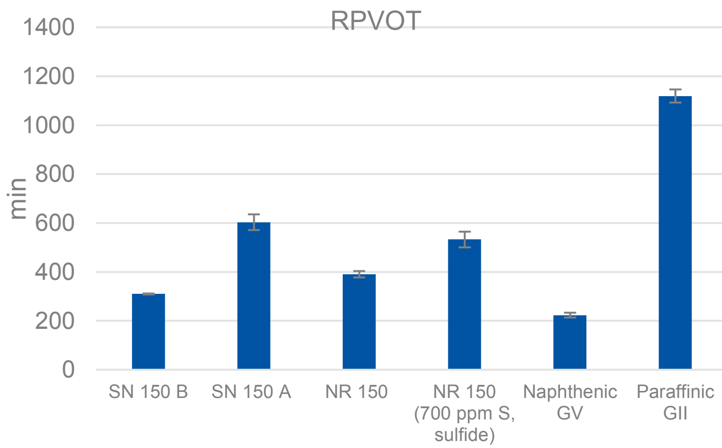
Antioxidant response of New Range oils to Sec. AO by RPVOT (ASTM D 2272)

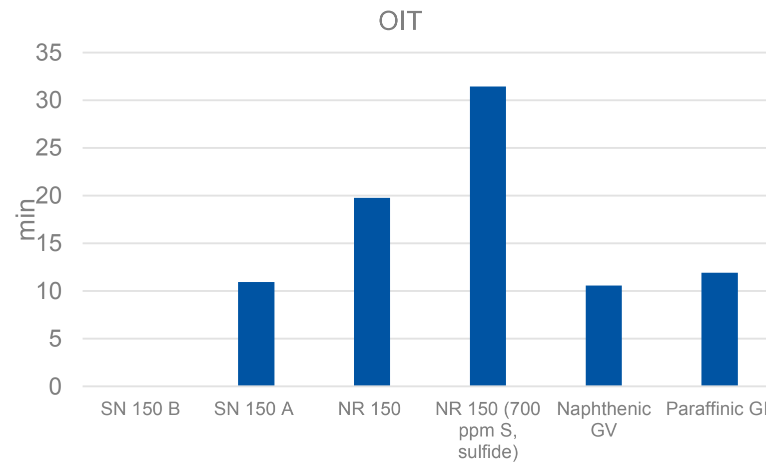
- Rotating Pressure Vessel Oxidation Test
  - SN, NR, Naphtheic and Group II base oils

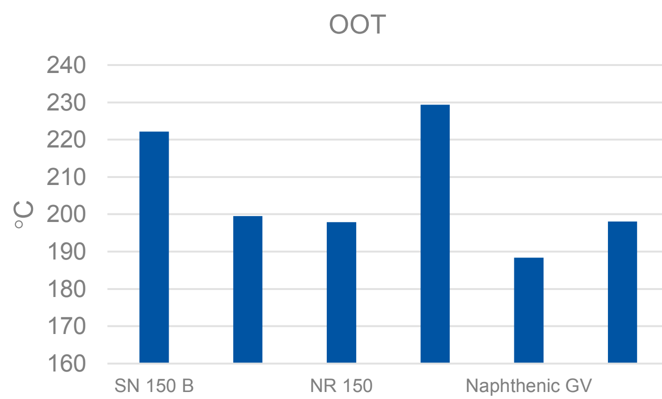


HPDSC vs. RPVOT – a method comparison

- The results are not perfectly aligned
- Fair to poor agreement between methods (different test conditions giving different oxidation mechanisms?)

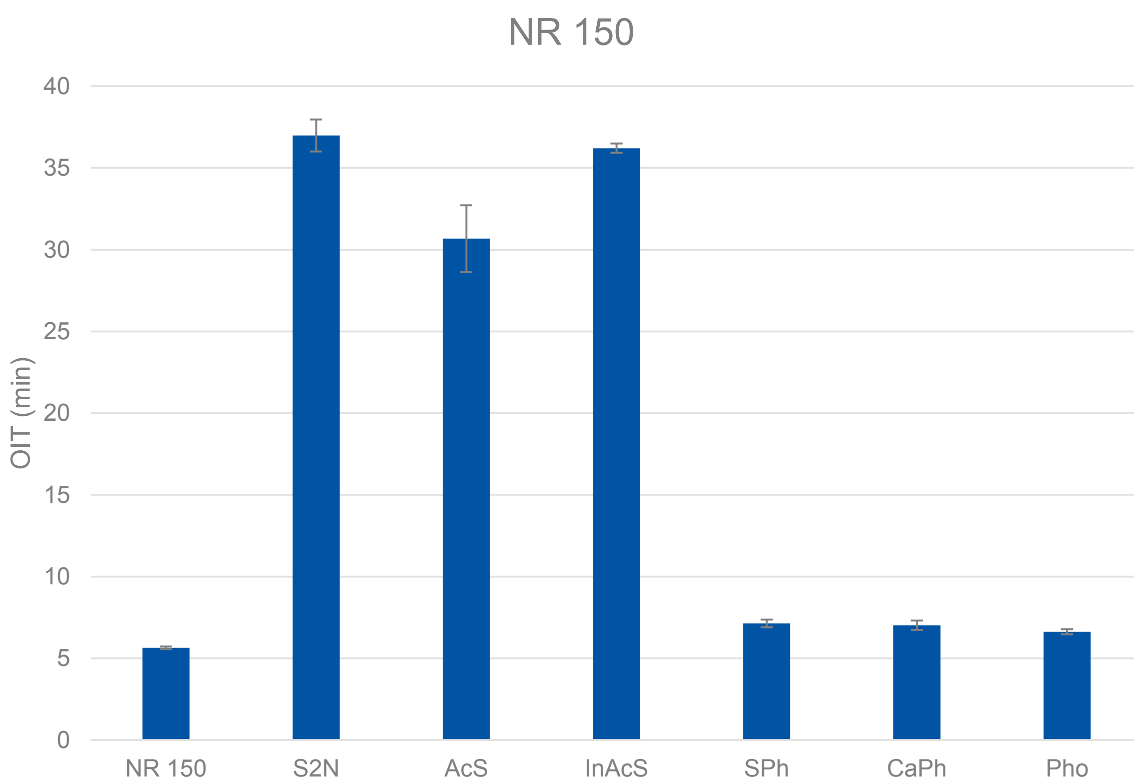






Antioxidant response of New Range 150 to Sec. A (OIT)

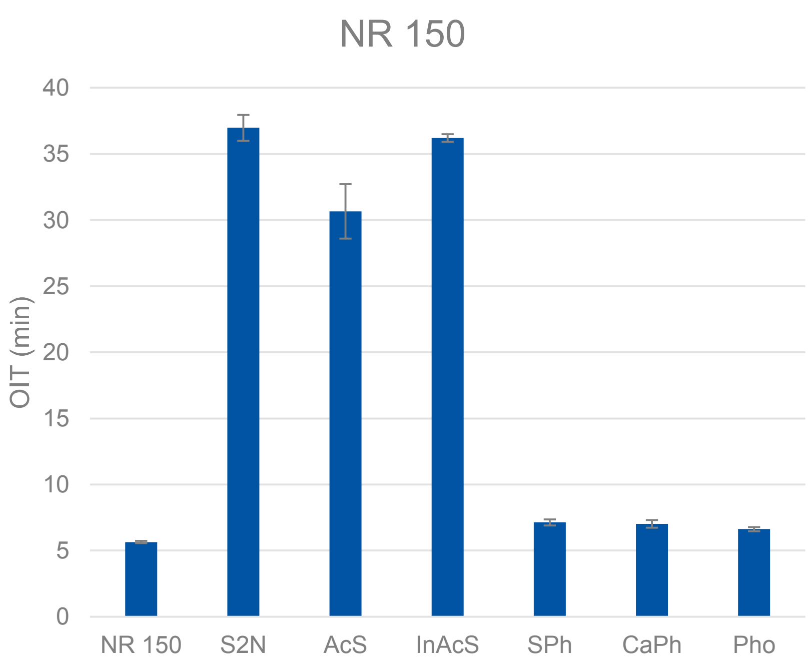
- Dithiocarbamate (S2N), active sulfur carrier (AcS), inactive sulfur carrier (InAcS) → good response
- S-containing phenolic (SPh), calcium phenate (CaPh), phosphite (Pho) → poor response

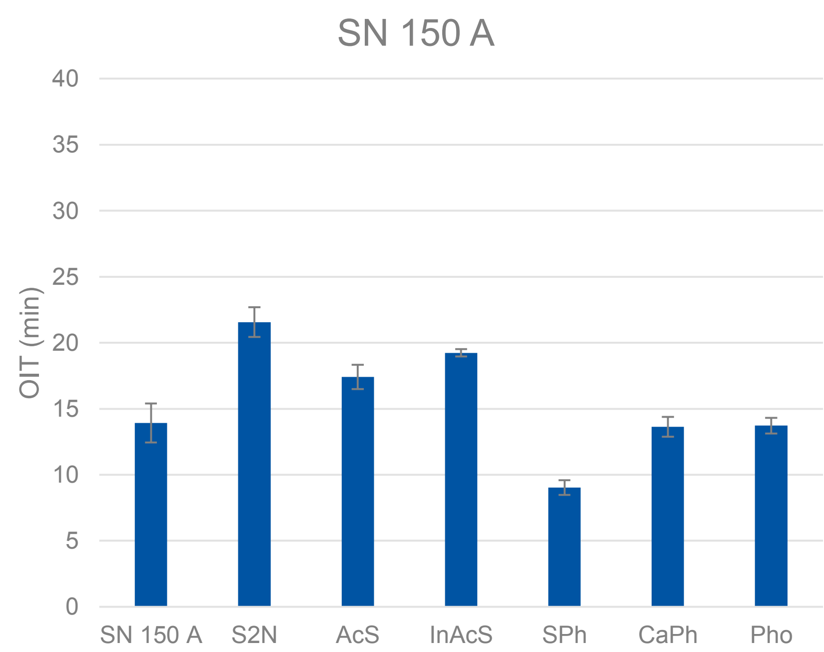


Primary AO: BHT (0.2 wt%), diphenylamine (0.2 wt%) Secondary AO: (0.2 wt%)

Antioxidant response of New Range oils to Sec. AO

- New Range 150 displays a **better** Sec AO-response compared to SN 150
- The same **order** of effectiveness amongst the 6 different Sec. AO's for the two base oils

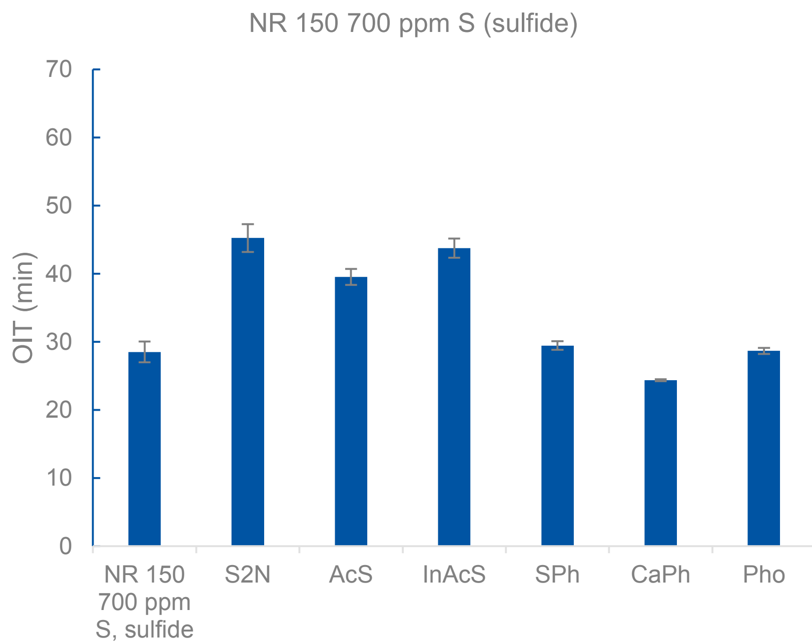


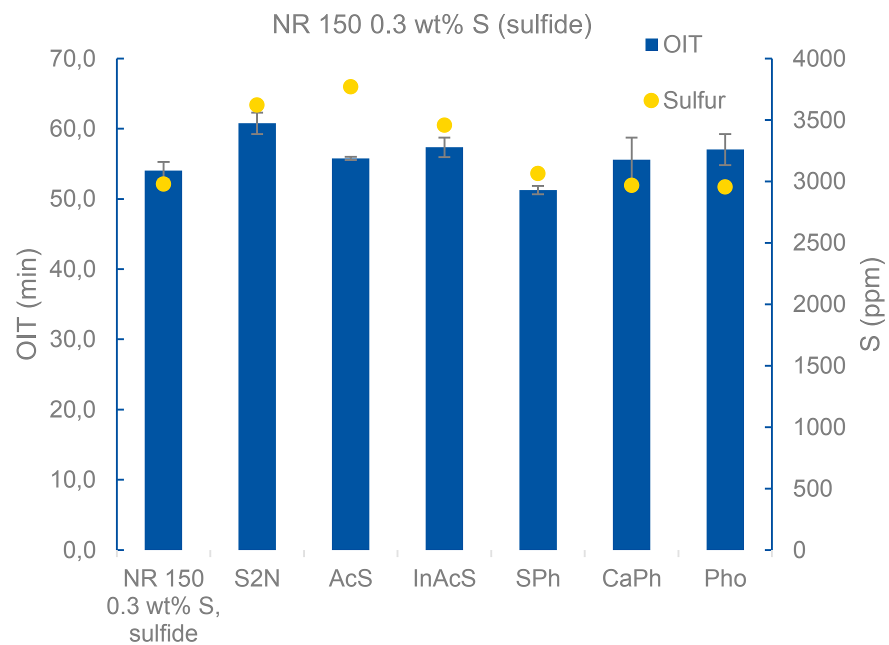


Primary AO: BHT (0.2 wt%), diphenylamine (0.2 wt%) Secondary AO: (0.2 wt%)

Base oil Sulfur influence of AO response of New Range base oils to Sec. AO

- Similar, but less marked behaviour for low-dose sulfide doped New Range150 (NR 150, 700 ppm S). With increasing sulfide levels (NR 150, 0.3 wt% S) the effect of secondary AO is eliminated, indicating a plateau sulfur levels for AO-effect is reached

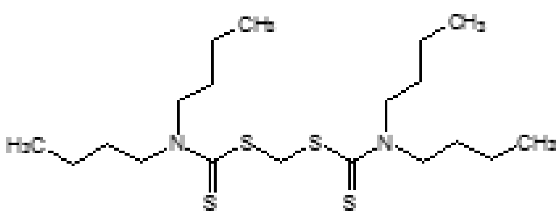


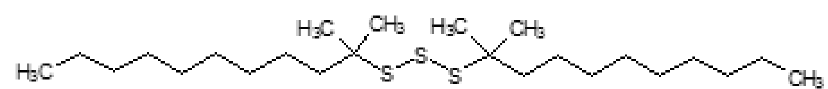


Primary AO: BHT (0.2 wt%), diphenylamine (0.2 wt%) Secondary AO: (0.2 wt%)

Results: AO response of New Range oils to Sec. AO

- With addition of sulfur-containing **secondary antioxidants**, New Range 150 perform better than Group I oils in RPVOT and HPDSC oxidation tests
- A combination of BHT + diphenylamine and secondary antioxidant, either dithiocarbamate (S2N) or inactive sulfur carrier (InAcS), would provide **excellent oxidation stability** of New Range150
  - We have previously shown very good AO response in ZDDP-containing formulations (See e.g. our STLE paper from 2016, [3])





[3] "Substitution of Group I base oils in industrial lubricants- applications in model hydraulic fluid formulations", Norrby, T., Malm, L., Salomonsson, P., 71st STLE Annual Meeting of the STLE, Lase Vegas 2016

Conclusion

- The New Range Group I replacement base oils have lower response to primary antioxidants than Group I oils
- With addition of sulfur-containing secondary antioxidants, New Range 150 perform better than Group I oils in RPVOT and HPDSC oxidation tests
- The results support the theory that the low intrinsic sulfur in the New Range series is at least partly responsible for the poor response to primary antioxidants
- The HPDSC and RPVOT results in this study clearly demonstrate how antioxidant response and ranking can change based on the oxidation test employed

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