



**Track or Category:** Lubrication Fundamentals

## Improved Oxidation Stability and Solvency of Naphthenic/Paraffinic Blends – A Parameter Study

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### INTRODUCTION

Base oil blends are frequently encountered in finished lubricant formulations. Nynas has for some time supplied Group I replacement base oils which has proven to fulfil the viscosity and solvency needs for industrial lubricants. One additional key performance aspect of these novel blended base oils is their response to added antioxidants. In the present study, a new test matrix comprising Naphthenic, Group II, Group II and PAO base fluids were investigated with respect to Pour Point, Flash Point, Aniline Point and viscosity. A new set of correlations between added primary and secondary antioxidants and overall base oil sulfur could be established, which serve as useful guidelines for lubricant formulators.

With the Group I base oil production capacity rapidly declining, industrial lubricants are facing new challenges with formulation compatibility, additive 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. One important aspect of these novel base oils is their response to added antioxidants.

The first part of this study was reported at the STLE Annual Meeting in 2017 [1]. In that study, base oil and additive sulfur levels could be correlated to oxidation stability in different laboratory tests. In the present study, a new test matrix comprising Naphthenic, Group II, Group II and PAO base fluids were investigated with respect to Pour Point, Flash Point, Aniline Point and Kinematic Viscosity. This is of general interest to the lubricants formulator, or anyone interested in the properties of blends.

What are the significant changes of properties arising from the gradual increase in the Naphthenic blending component? How fast do key variables like volatility and solvency change? How long does a “synthetic” base fluid retain its properties, before a transition to a semi-synthetic blend can be observed?

A new set of correlations between added primary and secondary antioxidants and overall base oil Sulfur could be established, which serve as useful guidelines for lubricant formulators.

### MATERIALS AND METHODS

The base oils in this study are Naphthenic oils, and paraffinic base oils of Group II and Group III, and fully

synthetic PAO (Group IV), see Table 1 (Low viscosity), Table 2 (Mid viscosity) and Table 3 (Upper mid viscosity)

**Table 1. The low viscosity blends of NYNAS™ T 9 (8.89 cSt) into Group II (HP 2, 10.7 cSt), Group III (NEXBASE 3020, 7.55 cSt) or PAO (SpectraSyn 2, 5 cSt). Viscosity Index (VI) ASTM D 2270, Pour Point ASTM D 7346 (PP); Aniline Point ASTM D 611 (AP).**

	Group II	Group III	PAO
<i>NYN</i>	10.61 cSt	7.58 cSt	5.08 cSt
<i>AST 9,</i>	VI 66.5	VI 95.9	VI 83.9
<i>5% in</i>	PP -39 °C	PP -42 °C	PP -87 °C
	AP 90 °C	AP 94 °C	AP 100 °C
<i>NYN</i>	10.40 cSt	7.69 cSt	5.31 cSt
<i>AST 9,</i>	VI 63.6	VI 89	VI 79.9
<i>15% in</i>	PP -42 °C	PP -42 °C	PP -87 °C
	AP 88 °C	AP 95 °C	AP 97.1 °C
<i>NYN</i>	10.20 cSt	7.86 cSt	5.54 cSt
<i>AST 9,</i>	VI 60.5	VI 93.3	VI 77.7
<i>25% in</i>	PP -42 °C	PP -42 °C	PP -84 °C
	AP 86 °C	AP 92 °C	AP 94.1 °C

More on the properties of the Naphthenic base oil can be found at Nynas web pages, [www.nynas.com](http://www.nynas.com), or in the web app [productfinder.nynas.com](http://productfinder.nynas.com). The key properties of these blends were investigated with respect to Kinematic Viscosity, Viscosity Index (VI), Flash Point, Pour Point and Aniline Point. An oxidation stability study utilizing HP-DSC Oxidation Induction Time (OIT, ASTM D6186) in relation to

added primary and secondary antioxidants, and base oil sulfur levels, was also carried out.

**Table 2. The mid viscosity blends of NYNAS™ T 22 (23.01 cSt) into Group II (HP 4, 19.7 cSt), Group III (NEXBASE 3043, 19.9 cSt) or PAO (SpectraSyn 4, 18.4 cSt). Viscosity Index (VI) ASTM D 2270, Pour Point ASTM D 7346 (PP); Aniline Point ASTM D 611 (AP).**

	Group II	Group III	PAO
NYNAS	19.82 cSt	20.03 cSt	18.47 cSt
T 22,	VI 104	VI 122	VI 123
5% in	PP -18 °C	PP -18 °C	PP -72 °C
	AP 107°C	AP 115 °C	AP 118°C
NYNAS	19.95 cSt	20.06 cSt	18.64 cSt
T 22, 15%	VI 98	VI 116	VI 114
in	PP -21 °C	PP -21 °C	PP -72 °C
	AP 105°C	AP 111 °C	AP 115°C
NYNAS	20.13cSt	20.13 cSt	18.66 cSt
T 22, 25%	VI 90	VI 108	VI 110
in	PP -21 °C	PP -21 °C	PP -69°C
	AP 102 °C	AP 108°C	AP 111°C

**Table 3. The upper mid viscosity blends of NYNAS™ BT 46 (46.51 cSt) into Group II (HP 6, 41.30 cSt), Group III (NEXBASE 3080, 48.48 cSt) or PAO (SpectraSyn 8, 47.53 cSt). Viscosity Index (VI) ASTM D 2270, Pour Point ASTM D 7346 (PP), Aniline Point ASTM D 611 (AP).**

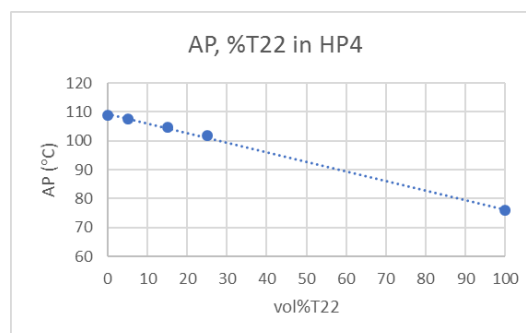
	Group II	Group III	PAO
NYNAS	41.53cSt	48.20 cSt	46.90 cSt
BT 46, 5%	VI 100	VI 131	VI 136
in	PP -21 °C	PP -15 °C	PP -54 °C
	AP 111°C	AP 126 °C	AP 132 °C
NYNAS	41.72 cSt	47.40 cSt	45.85cSt
BT 46,	VI 95	VI 124	VI 129
15% in	PP -24 °C	PP -15 °C	PP -54°C
	AP109°C	AP122°C	AP127°C
NYNAS	41.96 St	46.68 cSt	44.95 cSt
BT 46,	VI 89.5	VI 117	VI 121
25% in	PP -24°C	PP -18 °C	PP -54°C
	AP 106°C	AP 118 °C	AP122°C

## RESULTS AND DISCUSSION

Select results of the properties of these blends are exemplified by the results for NYNAS™ T 22 and Group II (see Table 2).

### Aniline Point

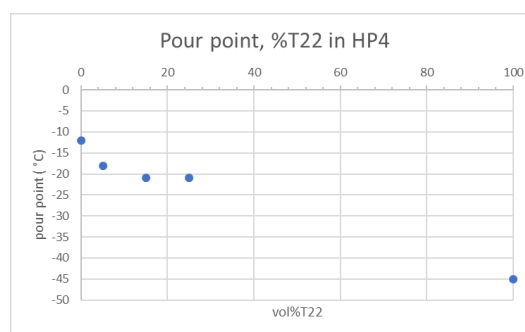
The solvency of the blends is here represented by the Aniline Point (AP) data, Figure 1. The AP drops by seven (7) degrees at 25% T 22 in the blend, and it decreases in a linear fashion towards the AP of T 22 (76 °C). Thus, solvency can be readily tuned by blending.



**Figure 1. The effect on solvency, as expressed by the Aniline Point (AP), of blending NYNAS T 22 into a Group II paraffinic base oil.**

### Pour Point

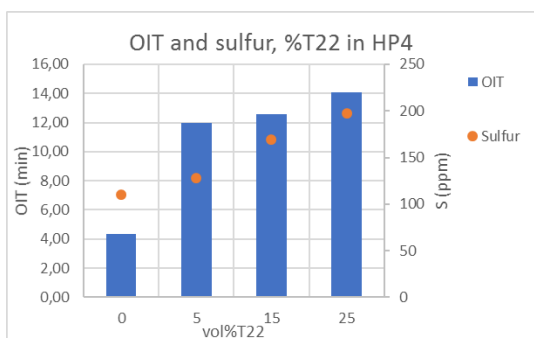
The Pour Point (PP) is a convenient measure of the low temperature flow properties of base oils and lubricants. In this study, the Naphthenic base oils and PAO represent the “wax free” fluids, with excellent low temp properties, and the paraffinic Group II and Group III base oils display Pour Points typical of “wax containing” base oils. The T 22 blends in Figure 2 display a pronounced drop in PP, by six (6) degrees, already after the addition of only 5% T 22, and by nine (9) degrees at 15% addition. This property (PP) shows less linearity across the study, but as low temp properties are more complex phenomena, this is not entirely surprising.



**Figure 2. The effect on low temperature properties, as expressed by the Pour Point (PP), of blending NYNAS T 22 into a Group II paraffinic base oil.**

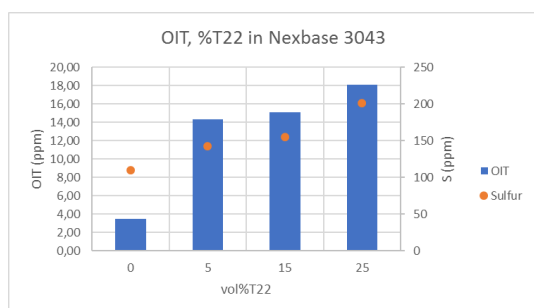
### Oxidation Stability by OIT

The oxidation stability of inhibited blends was studied by the Oxidation Induction Time (OIT). As primary Antioxidants (AO), 0.03% BHT and 0.03% Aryl Amine were used. As an ashless Secondary Antioxidant (Sec. AO), 0.03% Dialkyl Di-Thiocarbamate was utilized to provide some additional Sulfur. The total AO concentration thus was 0.1%. The Group II base oil provides ca 15 ppm Sulfur, the rest of the S comes from the Sec. AO. With each 5% of T 22 in a blend, about 20 ppm additional base oil Sulfur is added, since T 22 has about 400 ppm S. The effect of this is visible in Figure 3, leading to a rapid improvement in OIT, with a real step-up already at 5% T 22, with a factor of 3x, from 4 to 12 minutes.



**Figure 3. OIT of T 22 and Group II (HP 4, 20 cSt). A marked step-up in OIT is explained by a doubling of the base oil Sulfur contribution even at 5% addition of T 22.**

A similar trend is seen in Figure 4 for T 22 and Group III, only slightly larger: the step change in OIT from 3 to 14 minutes (more than 4x) for the initial addition of 5% T 22. At the highest blend rate (25%), a slightly higher OIT can be measured. This is not unexpected, as a more highly refined base oil would respond even better to added antioxidants.



**Figure 4. OIT of T 22 and Group III (NEXBASE 3043, 19.9 cSt). A similarly large step-up in OIT is observed, possibly indicating an even better improvement of the oxidation stability.**

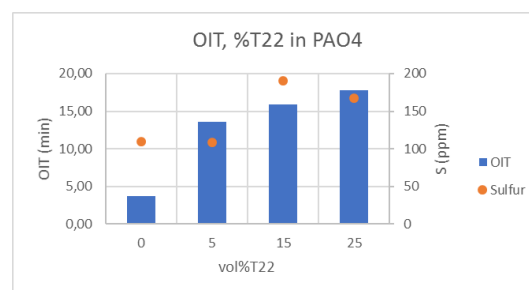
## REFERENCES

- [1] T. Norrby, A.-L. Jonsson, "Base Oil and Antioxidant selection – The role of secondary antioxidants and base oil sulfur content", *Proceedings of the 72<sup>nd</sup> STLE Annual Meeting*, Atlanta, May 21-25, 2017.

## KEYWORDS

Additives: Additive Interaction, Lubricant Chemical Analysis: Oxidation Resistance, Base Stocks: Mineral Base Stocks

The OIT for the PAO blends display a similar pattern, where we observe a step change upon the addition of the T 22 with its additional "payload" of base oil Sulphur; Figure 5. We also observe some scatter in the Sulfur content measurement, which we continue to investigate. The OIT for the 25% blend is similar to that of the Group III blend (see Figure 4); another manifestation of the strong influence of the combined effect of beneficial Sulfur-containing molecules in the base oils and the additive.



**Figure 5. OIT of T 22 and PAO (SpectraSyn 4, 18.4 cSt). A similarly large step-up in OIT is observed, possibly indicating an even better improvement of the oxidation stability.**

The OIT investigations of the T 9 and BT 46 are presently on-going, and the results are not yet available.

## CONCLUSIONS

1. The properties of the blends of Naphthenic base oils in group II, Group II and PAO has been systematically investigated.
2. Improvements of solvency (Lower AP) and low temperature properties (lower PP) can be realized.
3. Oxidation stability improvements can be rationalized by correlation the Sulfur levels to the observed OIT.





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Improved Oxidation stability  
and solvency of naphthenic/  
paraffinic blends – a  
parameter study

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Dr. A.-L. Jonsson  
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Sweden





# Nynas was founded in 1928

- ▶ Nynas is the largest specialty oil producer in Europe
- ▶ Offices in more than 30 countries around the globe
- ▶ Net Sales: 1.5 Billion USD (2016)
- ▶ Average number of employees: 1000
- ▶ Refineries in Nynäshamn (SE), Harburg (DE), Gothenburg (SE), Eastham JV (UK), Antwerp JV (BE)



Nynashamn



Harburg

# A wide scope of applications .....

## 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 transformers, instrument transformers, distribution transformers

## BASE OILS



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

# NSP Blend Study

# Introduction

- ▶ 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
- ▶ The first part of this study was reported at the STLE Annual Meeting in 2017 [1].
- ▶ In that study, base oil and additive sulfur levels could be correlated to oxidation stability in different laboratory tests.
- ▶ In the present study, a new test matrix comprising Naphthenic, Group II, Group II and PAO base fluids were investigated with respect to
- ▶ Pour Point, Flash Point, Aniline Point and Kinematic Viscosity (KV).
- ▶ Hopefully, this study is of general interest to the lubricants formulator, or anyone interested in the properties of blends

[1] T. Norrby, A.-L. Jonsson, "Base Oil and Antioxidant selection – The role of secondary antioxidants and base oil sulfur content", *Proceedings of the 72<sup>nd</sup> STLE Annual Meeting*, Atlanta, May 21-25, 2017.



## Some interesting aspects of base oil blends

- ▶ What are the significant changes of properties arising from the gradual increase in the Naphthenic blending component?
- ▶ How fast do key variables like volatility, pour point and solvency change?
- ▶ How long does a “synthetic” base fluid retain its properties, before a transition to a semi-synthetic blend can be observed?
- ▶ What is the Antioxidant response in this test matrix?
- ▶ What is the correlation to benefits of base oil Sulfur?

## Base oils used in the blending study

- ▶ The base oils in this study are Naphthenic oils, and paraffinic base oils of Group II and Group III, and fully synthetic PAO (Group IV)
- ▶ Three viscosity ranges:
  - Table 1 (Low viscosity, ca. 10 cSt)
  - Table 2 (Mid viscosity, ca. 20 cSt)
  - Table 3 (Upper mid viscosity, ca. 46 cSt)
- ▶ In each viscosity group, Naphthenic base oils have been matched viscosity-wise with the paraffinic base oils
- ▶ The Naphthenic base oil has then been blended in with 5%, 15% and 25 % into each base oil from Group II, Group III or Group IV (PAO )
- ▶ The **key properties** of these blends were investigated with respect to Kinematic Viscosity, Viscosity Index (VI), Flash Point, Pour Point and Aniline Point.
- ▶ An **oxidation stability** study utilizing HP-DSC Oxidation Induction Time (OIT, ASTM D6186) in relation to added primary and secondary antioxidants, and base oil sulfur levels, was also carried out.

Table 1. Low viscosity blends

	<b>Group II</b>	<b>Group III</b>	<b>PAO</b>
<i>NYNAS T 9, 5% in</i>	10.61 cSt	7.58 cSt	5.08 cSt
	VI 66.5	VI 95.9	VI 83.9
	PP -39 °C	PP -42 °C	PP -87 °C
	AP 90 °C	AP 94 °C	AP 100 °C
<i>NYNAS T 9, 15% in</i>	10.40 cSt	7.69 cSt	5.31 cSt
	VI 63.6	VI 89	VI 79.9
	PP -42 °C	PP -42 °C	PP -87 °C
	AP 88 °C	AP 95 °C	AP 97.1 °C
<i>NYNAS T 9, 25% in</i>	10.20 cSt	7.86 cSt	5.54 cSt
	VI 60.5	VI 93.3	VI 77.7
	PP -42 °C	PP -42 °C	PP -84 °C
	AP 86 °C	AP 92 °C	AP 94.1 °C

## Table 2. Mid viscosity blends

	<b>Group II</b>	<b>Group III</b>	<b>PAO</b>
<i>NYNAS T22, 5% in</i>	19.82 cSt	20.03 cSt	18.47 cSt
	VI 104	VI 122	VI 123
	PP -18 °C	PP -18 °C	PP -72 °C
	AP 107 °C	AP 115 °C	AP 118 °C
<i>NYNAS T22, 15% in</i>	19.95 cSt	20.06 cSt	18.64 cSt
	VI 98	VI 116	VI 114
	PP -21 °C	PP -21 °C	PP -72 °C
	AP 105 °C	AP 111 °C	AP 115 °C
<i>NYNAS T22, 25% in</i>	20.13 cSt	20.13 cSt	18.66 cSt
	VI 90	VI 108	VI 110
	PP -21 °C	PP -21 °C	PP -69 °C
	AP 102 °C	AP 108 °C	AP 111 °C



Table 3. Upper mid viscosity blends

	<b>Group II</b>	<b>Group III</b>	<b>PAO</b>
<i>NYNAS BT 46, 5% in</i>	41.53 cSt	48.20 cSt	46.90 cSt
	VI 100	VI 131	VI 136
	PP -21 °C	PP -15 °C	PP -54 °C
	AP 111 °C	AP 126 °C	AP 132 °C
<i>NYNAS BT 46, 15% in</i>	41.72 cSt	47.40 cSt	45.85 cSt
	VI 95	VI 124	VI 129
	PP -24 °C	PP -15 °C	PP -54 °C
	AP 109 °C	AP 122 °C	AP 127 °C
<i>NYNAS BT 46, 25% in</i>	41.96 cSt	46.68 cSt	44.95 cSt
	VI 89.5	VI 117	VI 121
	PP -24 °C	PP -18 °C	PP -54 °C
	AP 106 °C	AP 118 °C	AP 122 °C

# The properties of blends

- ▶ A compilation of the results of the investigations of the properties of these blends are displayed in the following section
- ▶ We have grouped the results by each Naphthenic oil (T 9, T 22 or BT 46), and compare the properties across each viscosity group
- ▶ The results for Kinematic Viscosity of the blends is followed by solvency (Aniline Point), low temperature properties (Pour Point) and volatility (exemplified by the Flash Point)
- ▶ A brief discussion in each sub section outlines the findings, and some general trends are high-lighted.

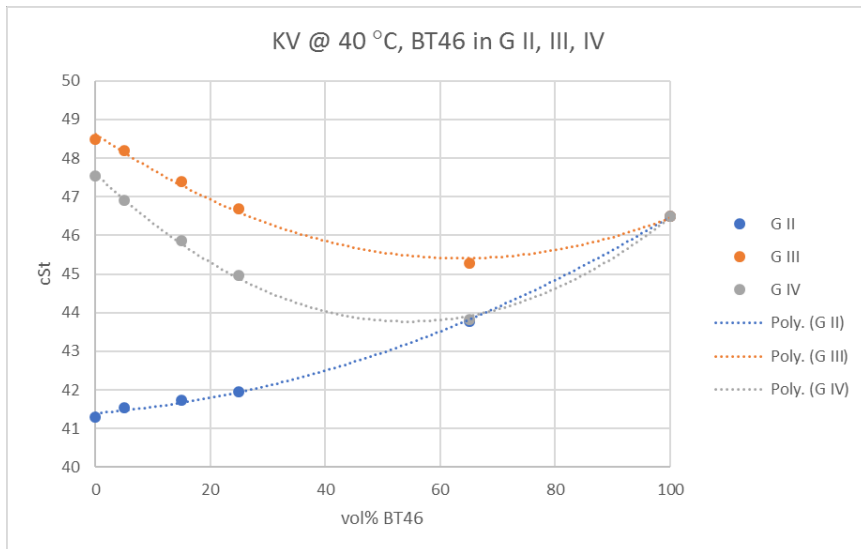
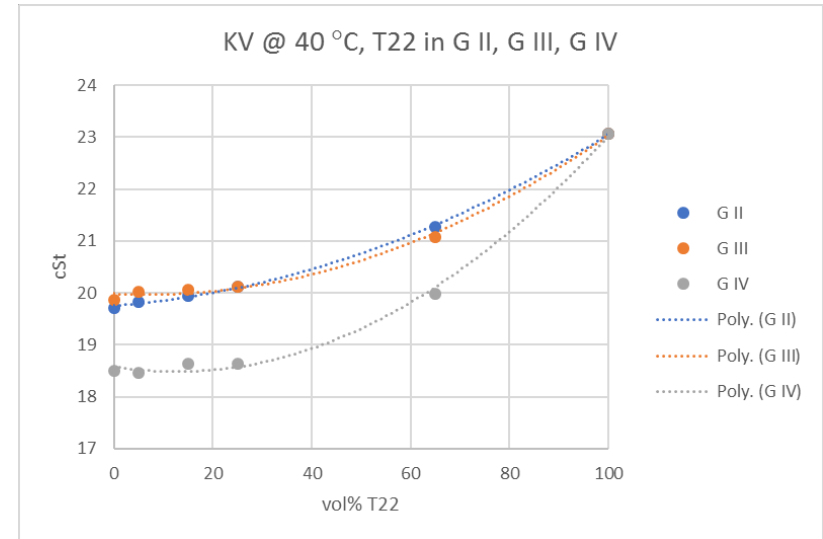
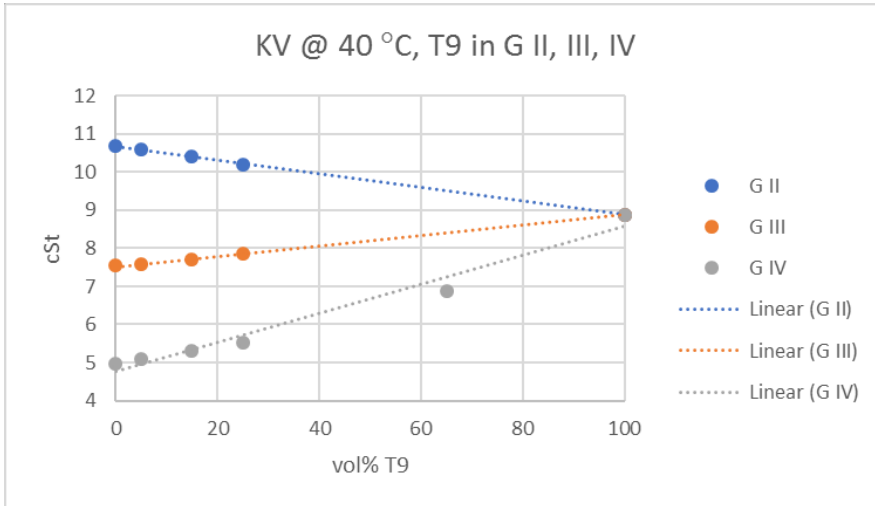
# Kinematic Viscosity

- ▶ The Kinematic Viscosity (KV) of blends of base oils with different properties; e.g. different viscosity and VI; are not trivial to predict, nor can the viscosity behavior be expected to be linear.
- ▶ This phenomenon is particularly visible at 40 °C, why we have displayed the viscosity at that temperature throughout.
- ▶ Large differences in viscosity has been cited as one factor [2, 3], but as we show in Figures 1-3, also base oils with similar KV but very different chemistry, density and VI will show non-linear blends viscosities.

[2] B. Zhmud, "Viscosity Blending Equations", Lube-Tech No. 93, Lube Magazine No. 121, June 2014.

[3] G. Centeno, G. Sánchez-Reyna, J. Ancheyta, J. A. D. Muños, N. Cardona, "Testing various mixing rules for calculation of viscosity of petroleum blends", *Fuel*, Vol. 90, (2011), pp 3561-3570.

# KV of blends of T9, T 22 and BT 46

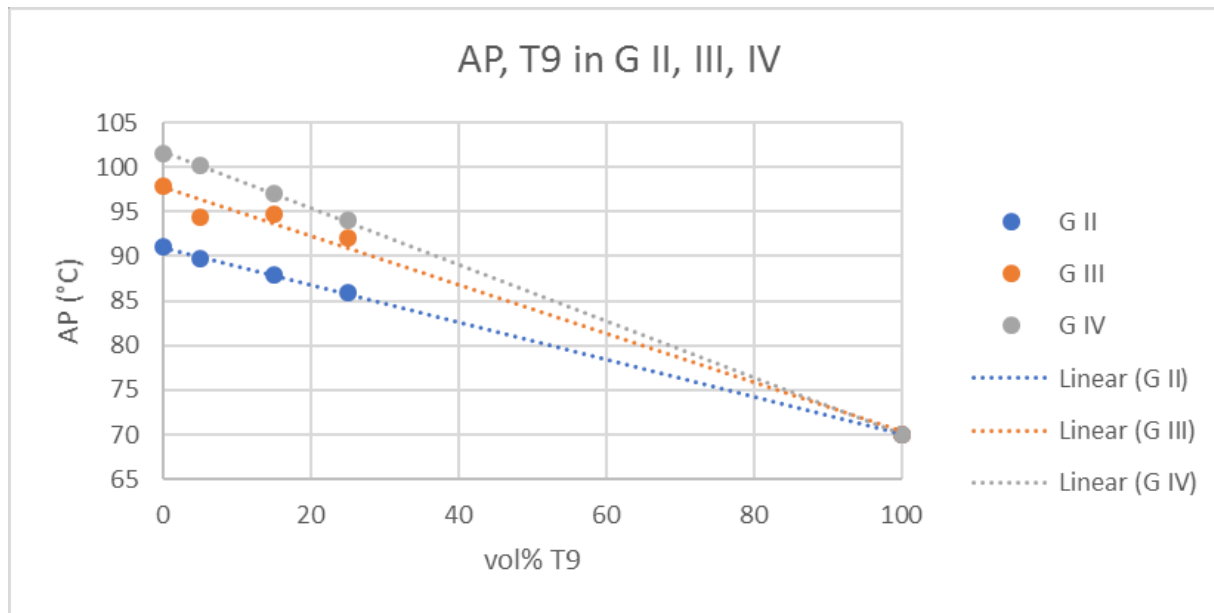


NB Pronounced non-linearity in the blend viscosity diagrams for T 22 and BT 46. (Most visible at 40 degrees)  
An extra data point at 65% blend ratio is shown for illustration purpose.



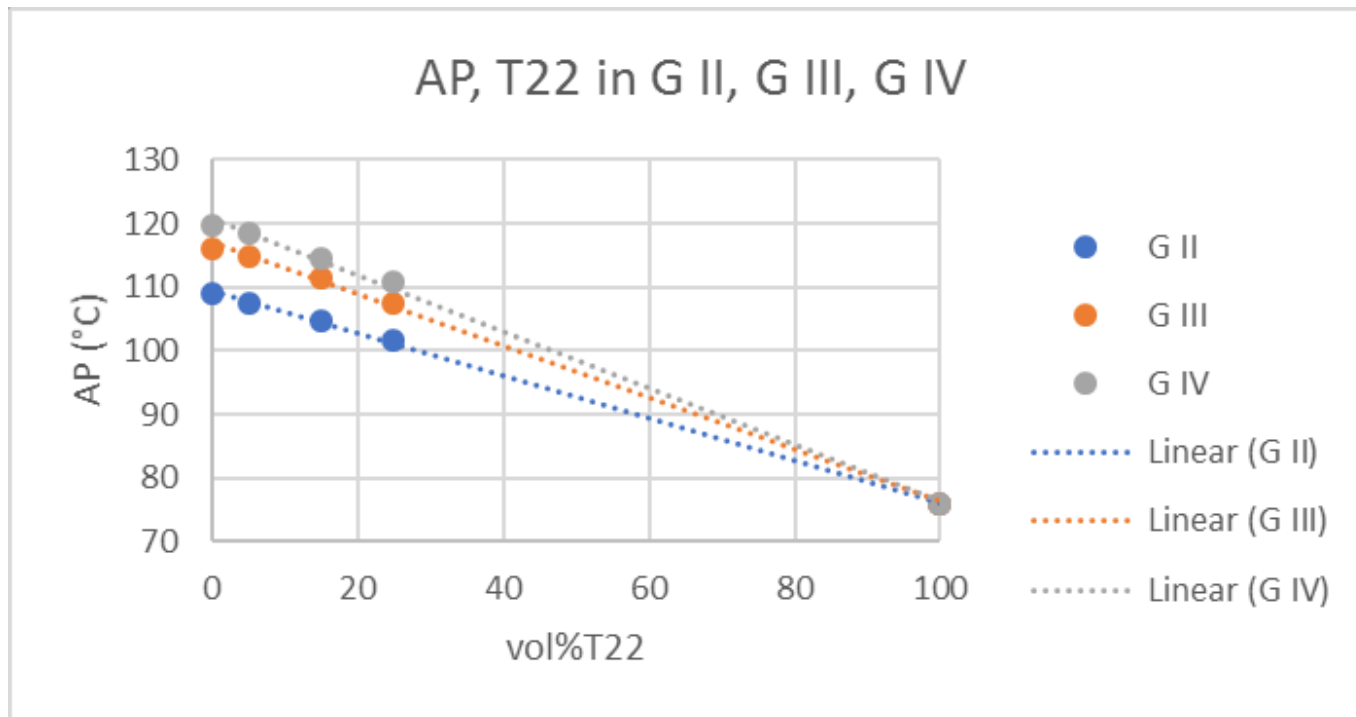
# Aniline Point, T 9

- ▶ The solvency of the blends is here represented by the Aniline Point (AP) data
- ▶ The Aniline Point data fall in on a linear behaviour, thus creating what appears to be a more straight-forward additive behaviour of this property of the blends
- ▶ The large difference in AP between the paraffinic base oils and T9 result in a steep slope and large effect on the AP by blending



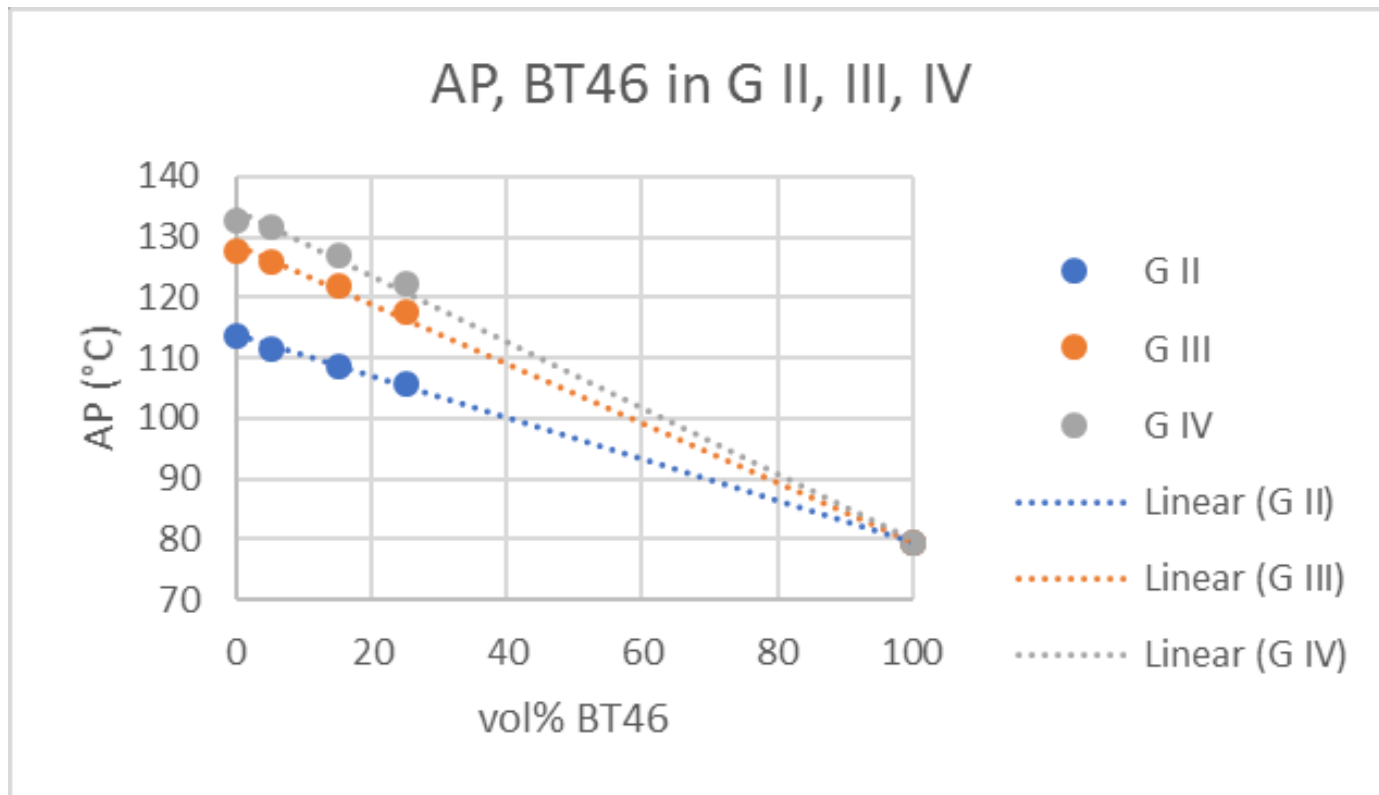
# Aniline Point, T 22

- ▶ In case of the T 22 , the AP drops by 7 °C at 25% T 22 in the blend with Group II, with 8.5 °C in Group III, and by 8.9 °C in the blend with PAO. For all blends, the trend decreases in a linear fashion towards the AP of T 22 (76 °C).



# Aniline Point, BT 46

- ▶ Similarly, for the blends of BT 46, at 25% blend ratio the AP decreases by 8-10 °C, which is twice the gap in AP between neat PAO and Group III, for example.



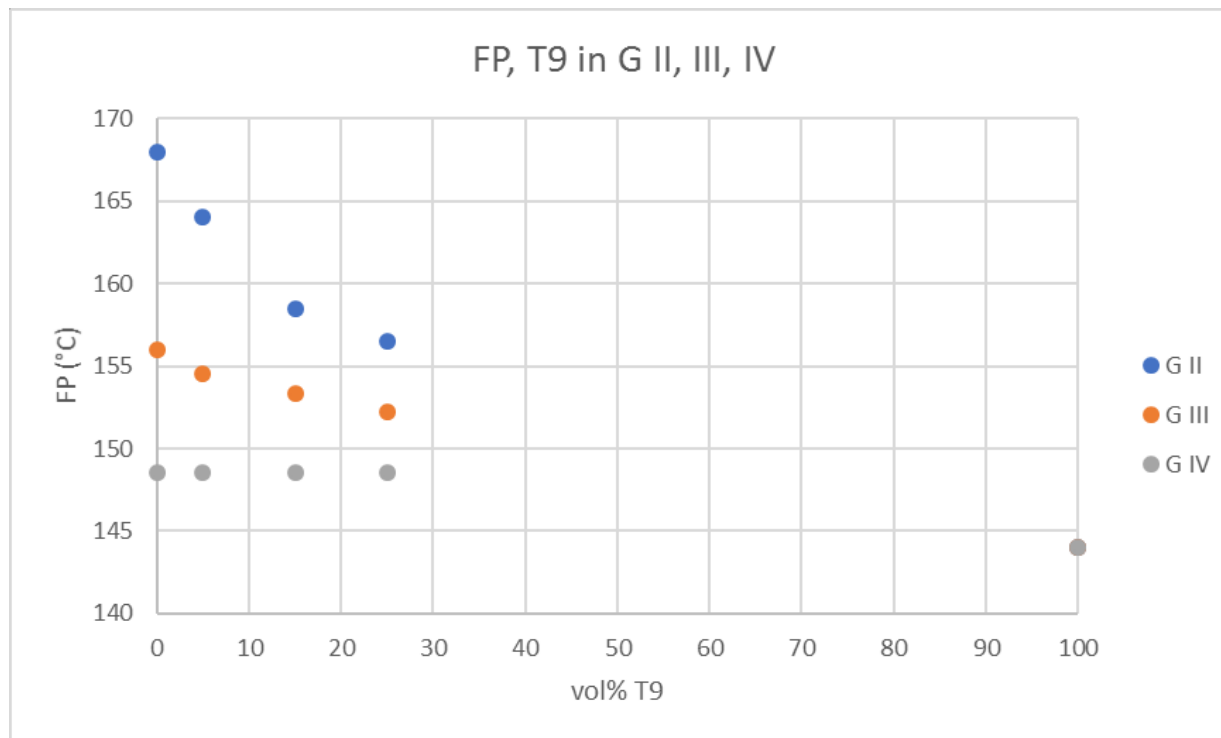
# Flash Point

- ▶ The volatility of a base oil blend is another important property
- ▶ One convenient way to study and compare one aspect of this, is to measure the Flash Point (FP)
- ▶ Here we report the results by Pensky-Martin (PM, ASTM D 93)



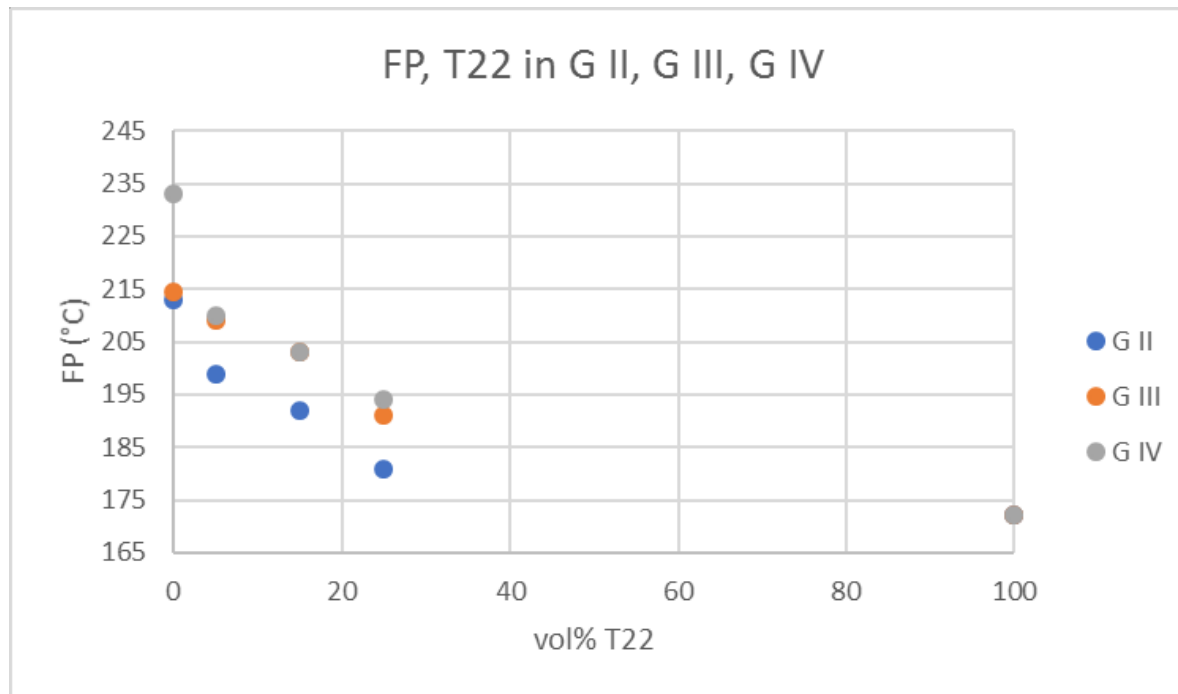
# Flash Point, T 9

- ▶ The FP of the blends of NYNAS T 9 and Gr II, Group III and Group IV (PAO) are shown below
- ▶ The apparently high FP of the Group II base oil must be seen in the relation to its comparatively high KV (10.7 cSt, vs. Gr III 7.5 cSt and PAO, 5.0 cSt), see Table 1



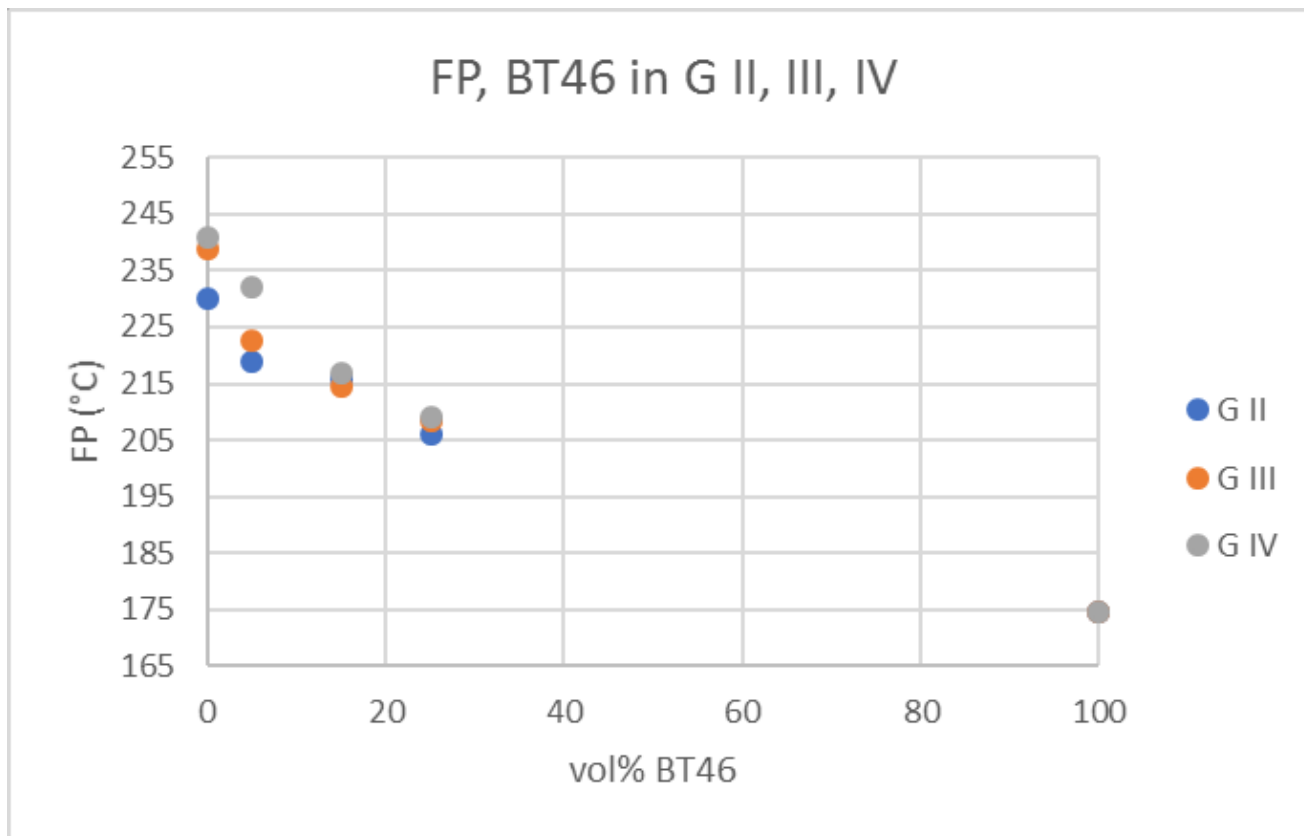
# Flash Point, T 22

- ▶ For the blending of T 22 into the mid viscosity base oils, where the FP difference is rather large, the effect is rather substantial
- ▶ For the 5% blend of T 22, the FP remains above 200 °C.
- ▶ The trend line for the more highly refined Group III and PAO is clearly above that of the Group II blends, which fully reflects the design intention and key requirements on these base oils



# Flash Point, BT 46

- ▶ The Flash points of the upper mid-viscosity blends follow a similar trend, but here all blends studied remain at FPs well above 200 °C



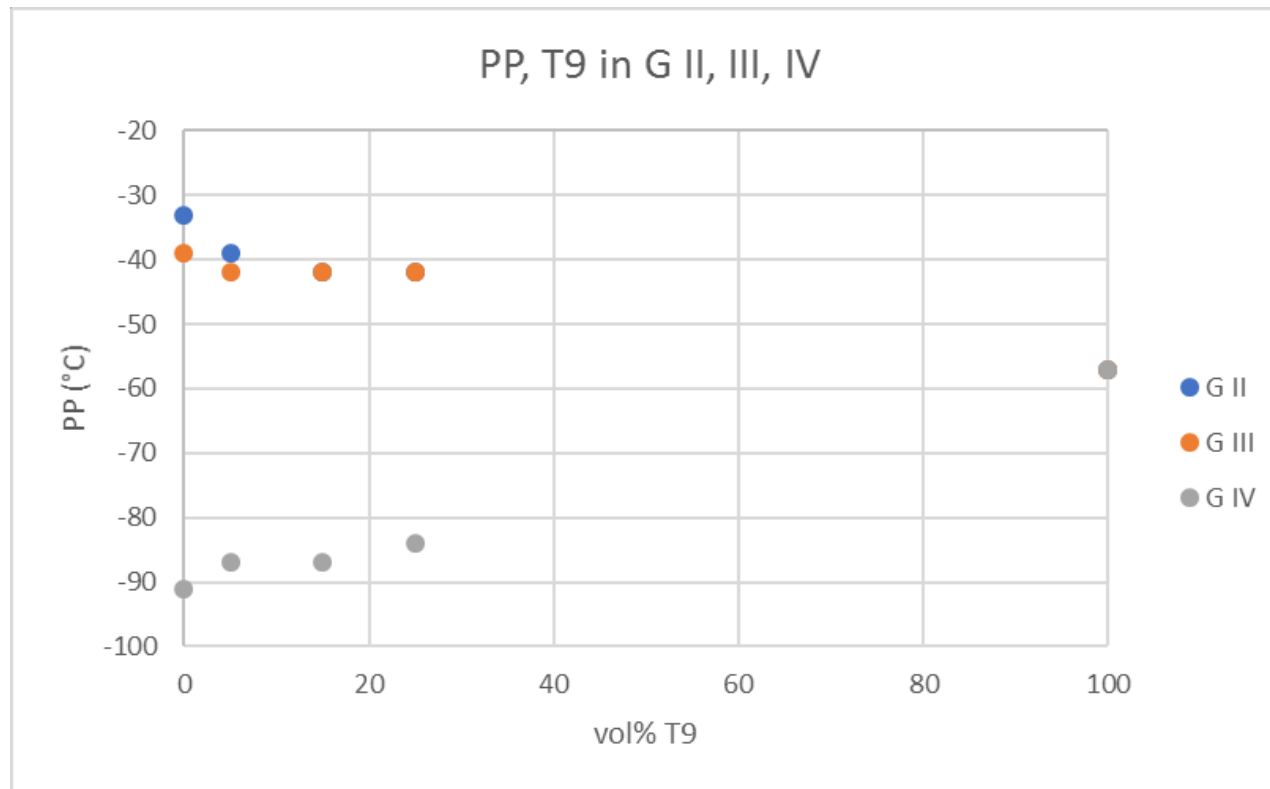
# Pour Point

- ▶ The Pour Point (PP) is a convenient measure of the low temperature flow properties of base oils and lubricants
- ▶ In this study, the Naphthenic base oils and PAO represent the “wax free” fluids, with excellent low temp properties..
- ▶ ..and the paraffinic Group II and Group III base oils display Pour Points typical of “wax containing“ base oils
- ▶ This property (PP) shows less linearity across the study, but as low temperature properties are more complex phenomena, which sum up to a total effect based on different contributing parts, this is not entirely surprising



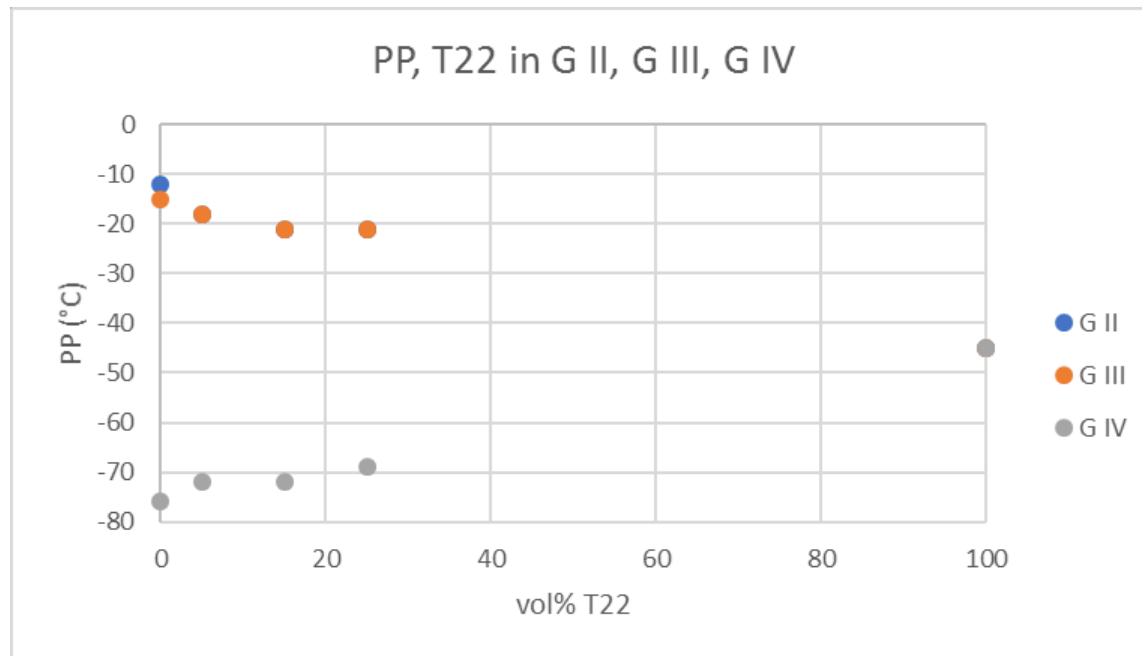
# Pour Point, T 9

- ▶ In the blends of T 9 and PAO, the PP increases in a fairly linear fashion, remaining very low
- ▶ The Group II and III blends each display quick drop at 5% in-blending, which appears to level off



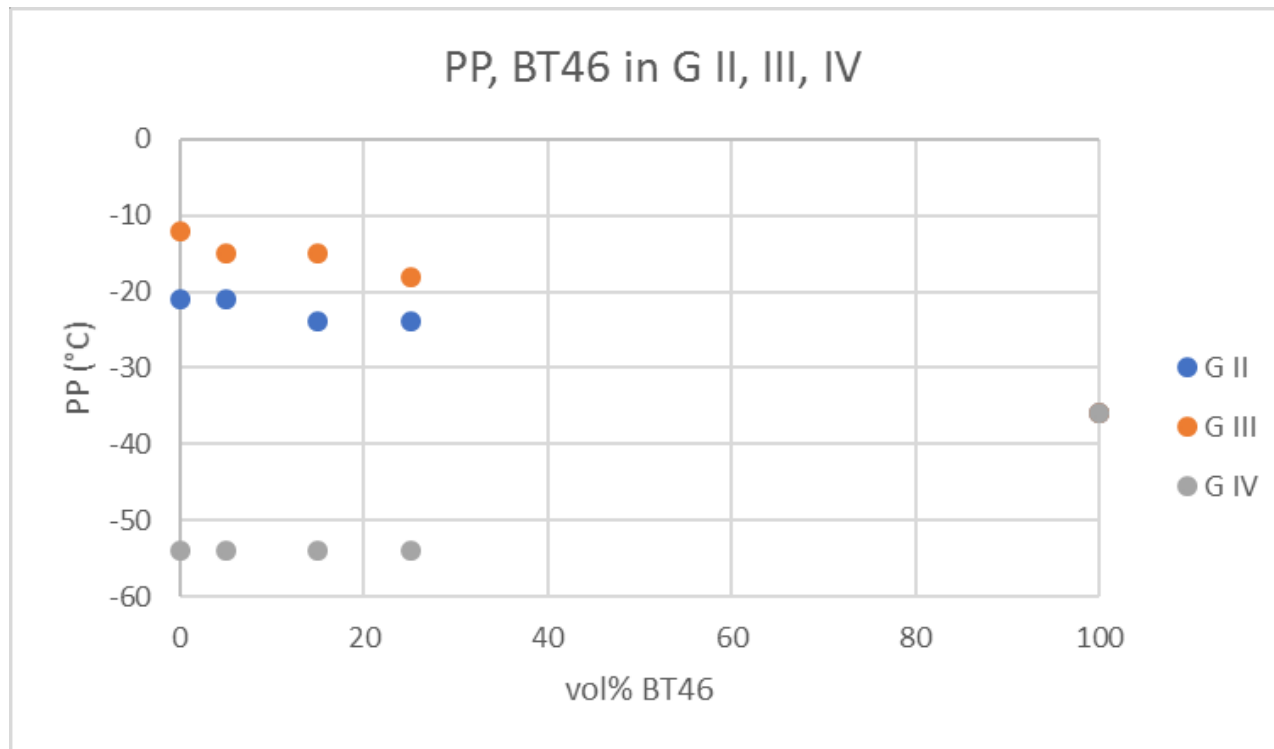
# Pour Point, T 22

- ▶ The T 22 blends with the wax-containing Group II and III fluids display a small drop in PP, by 3 to 6 °C after the addition of 5% T 22, and by nine (9) degrees at 15% addition
- ▶ The blends of the wax-free fluids display a completely different performance range; this is the reason why Naphthenic and PAO blends are frequently utilized in lubricants with extreme demands like aviation hydraulics and advances shock absorber fluids



# Pour Point, BT 46

- ▶ For the blends of BT 46, a similar pattern appears.
- ▶ The PAO blends are dominated by the PAO at 5-25%, which in this case almost fully retain the PP of the neat PAO.

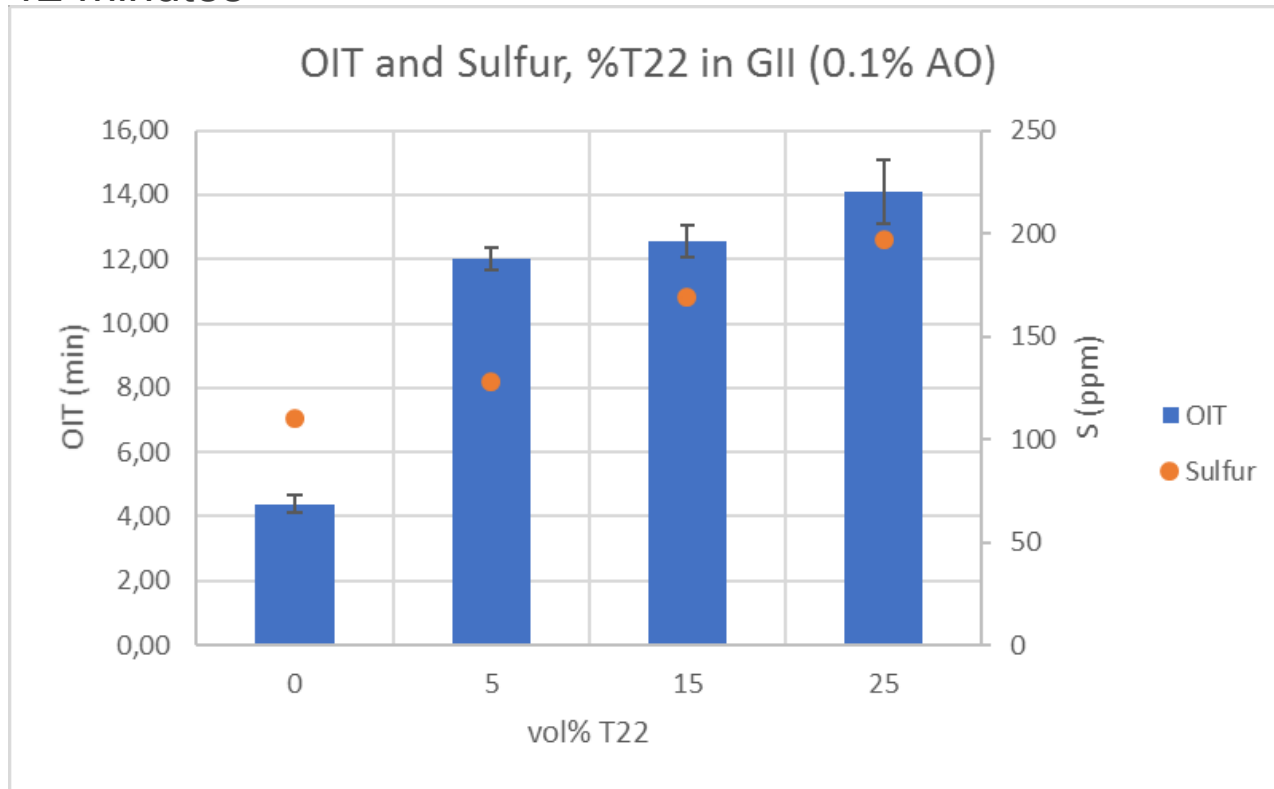


## Oxidation stability and Antioxidant response

- ▶ The oxidation stability of inhibited blends was studied by the Oxidation Induction Time (OIT)
- ▶ As primary Antioxidants (AO), 0.03% BHT and 0.03% Aryl Amine were used
- ▶ As an ashless Secondary Antioxidant (Sec. AO), 0.03% Dialkyl Di-Thiocarbamate was utilized to provide some additional Sulfur
- ▶ The total AO concentration thus was 0.1%.
- ▶ The Group II base oil provides ca 15 ppm Sulfur, the rest of the S comes from the Sec. AO; Group III and PAO similar patterns
- ▶ Importantly, with each 5% of T 22 in a blend, about 20 ppm *additional* base oil Sulfur is added, since T 22 has about 400 ppm S.

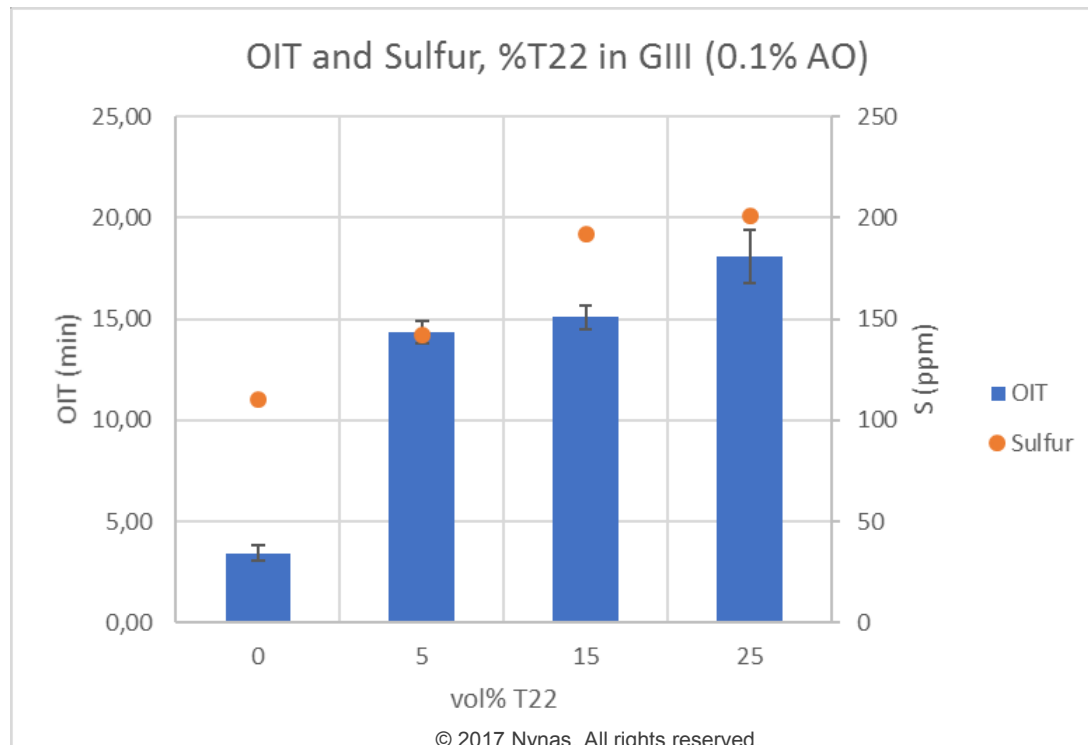
# OIT and Sulfur content, T 22 and Group II

- ▶ OIT of T 22 and Group II (20 cSt)
- ▶ The synergistic and beneficial effect of the increase in Sulfur leads to a rapid improvement in OIT, with a real step-up already at 5% T 22, with a factor of 3x, from 4 to 12 minutes



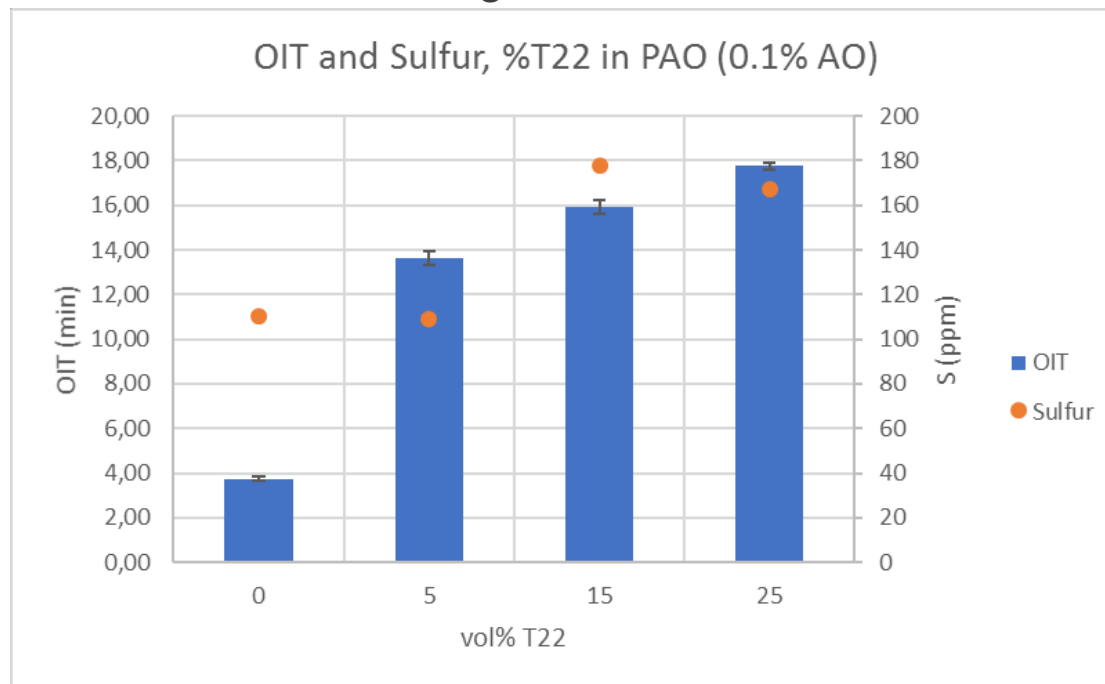
# OIT and Sulfur content, T 22 and Group III

- ▶ A similar trend is seen for T 22 and Group III (19.9 cSt), only slightly larger: the step change in OIT from 3 to 14 minutes (more than 4x) for the initial Addition of 5% T 22
- ▶ At the highest blend rate (25%), a slightly higher OIT can be measured. This is not unexpected, as a more highly refined base oil would respond even better to added antioxidants



# OIT and Sulfur content, T 22 and Group IV (PAO)

- ▶ The OIT for the PAO blends display a similar pattern, where we observe a step change upon the addition of the T 22 with it's additional "payload" of base oil Sulphur
- ▶ We also observe some scatter in the Sulfur content measurement, which we continue to investigate. The OIT for the 25% blend is similar to that of the Group III blend (18 min); another manifestation of the strong influence of the combined effect of beneficial Sulfur-containing molecules in the base oils and the additive



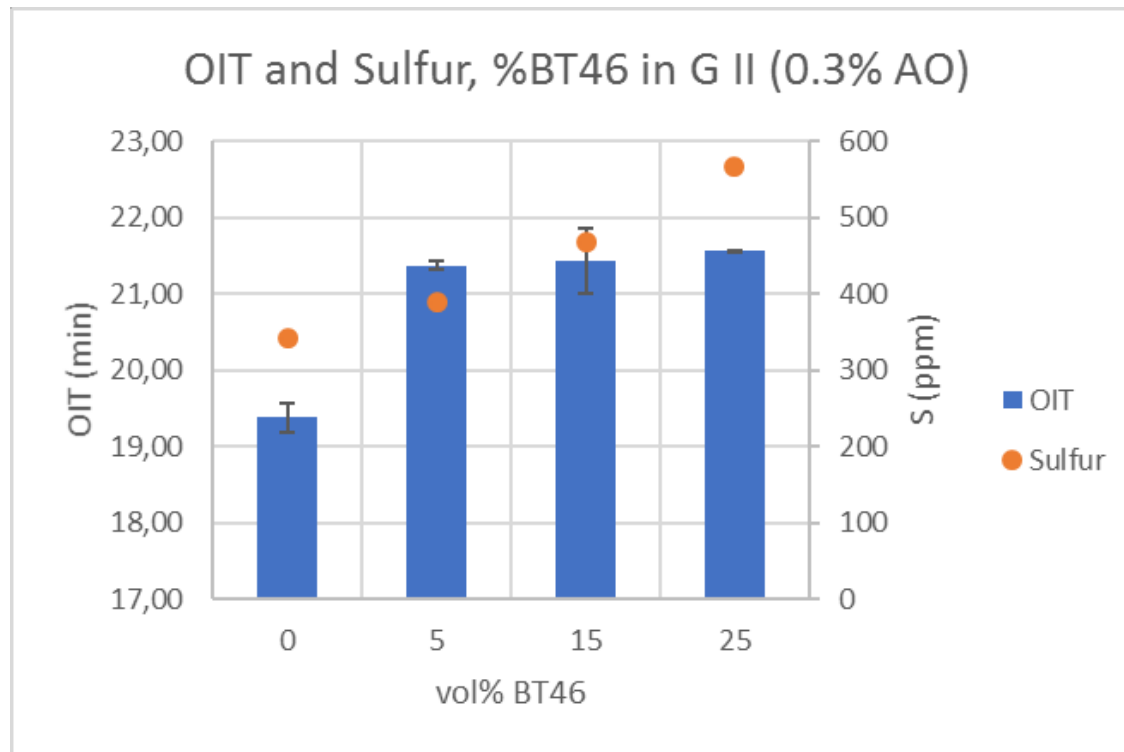


## OIT and Sulfur content, BT 46 and Group II

- ▶ In this part of the study, we found stable result only at a higher AO treat rate (0.3% overall)
- ▶ As primary Antioxidants (AO), 0.1% BHT and 0.1% Aryl Amine were used
- ▶ As an ashless Secondary Antioxidant (Sec. AO), 0.1% Dialkyl Di-Thiocarbamate was utilized to provide some additional Sulfur
- ▶ The total AO concentration thus was 0.3%
- ▶ The Group II base oil provides ca 15 ppm Sulfur, the rest of the S comes from the Sec. AO; Group III and PAO similar patterns
- ▶ Importantly, with each 5% of BT 46 in a blend, about 40 ppm *additional* base oil Sulfur is added, since T 22 has about 880 ppm Sulfur

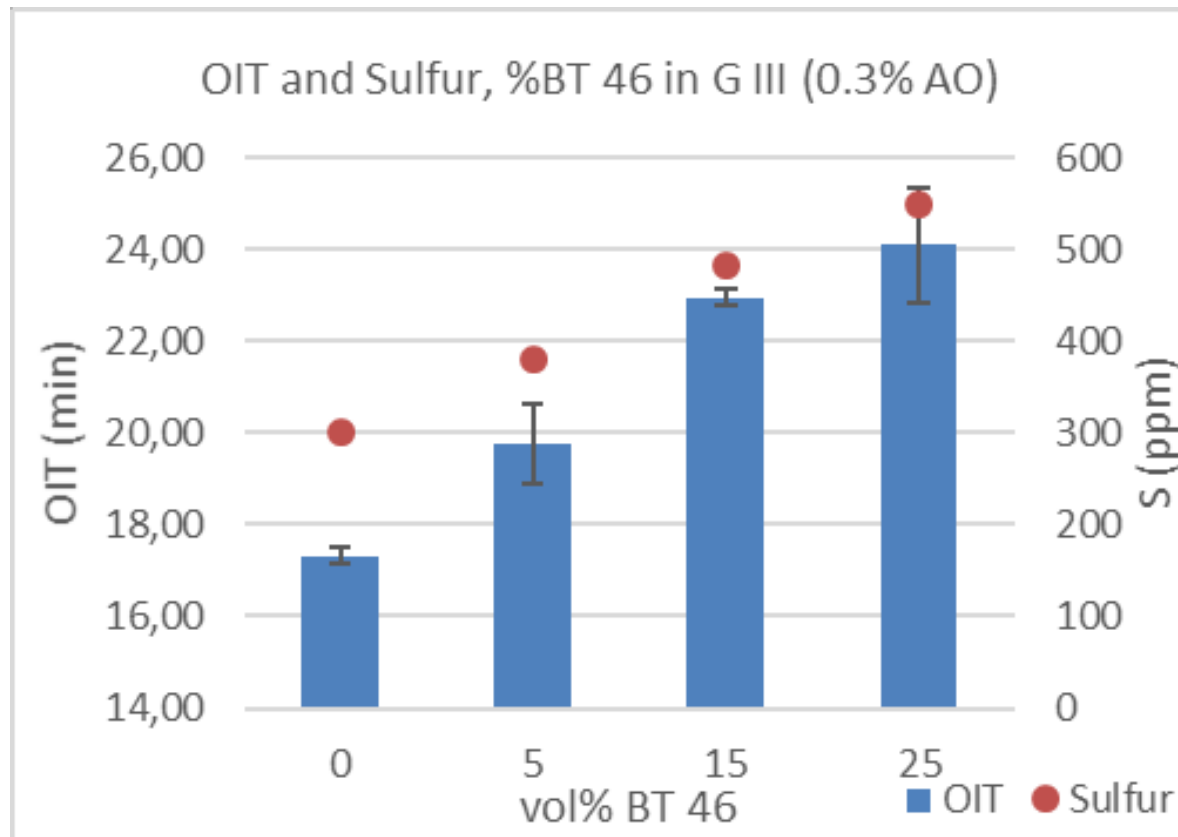
# OIT and Sulfur content, BT 46 and Group II

- ▶ Blends of BT 46 and Group II base oil provides a similar manifestation of the strong influence on oxidation stability of base oil sulfur in combination with sulfur-containing secondary antioxidants
- ▶ Addition of naphthenic oils to paraffinic base oil improves the response to antioxidants, increasing the oxidation induction time



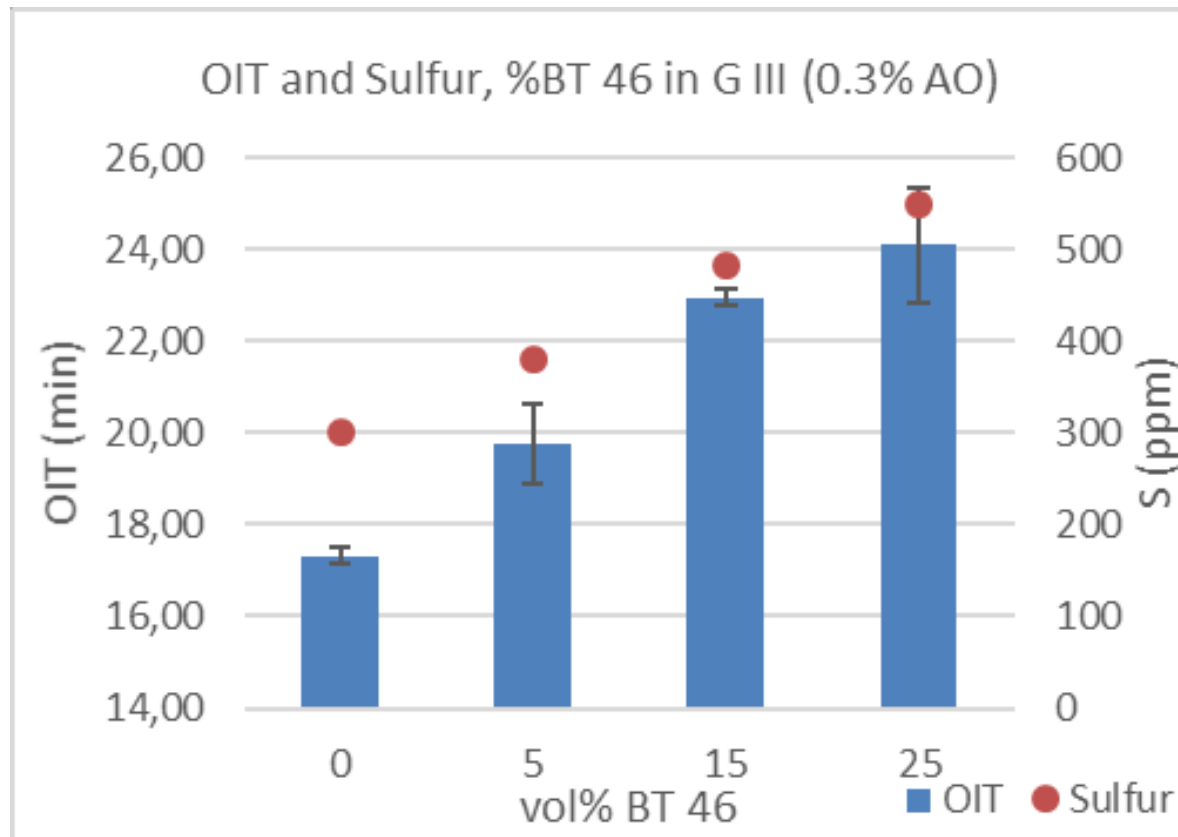
# OIT and Sulfur content, BT 46 and Group III

- ▶ Blends of BT 46 and Group III yield a similar pattern
- ▶ Even higher OIT is reached, compared to the Group II case, supporting the expectation of a better AO response in Group III with Sec. AO and Sulfur



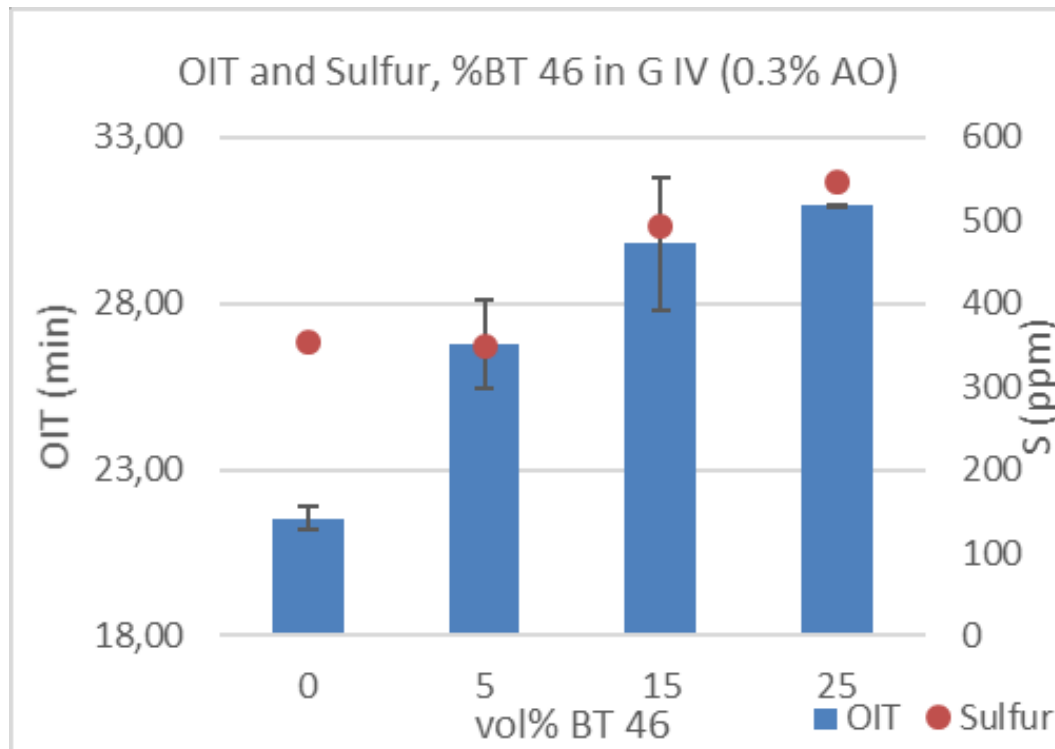
# OIT and Sulfur content, BT 46 and Group III

- ▶ Blends of BT 46 and Group III yield a similar pattern
- ▶ A higher OIT is reached, compared to the Group II case, supporting the expectation of a better AO response in Group III with Sec. AO and Sulfur



# OIT and Sulfur content, BT 46 and Group IV (PAO)

- ▶ Blends of BT 46 and PAO again yield a similar pattern
- ▶ Even higher OIT is reached, compared to the Group III case, displaying an even better AO response in PAO with Sec. AO and Sulfur

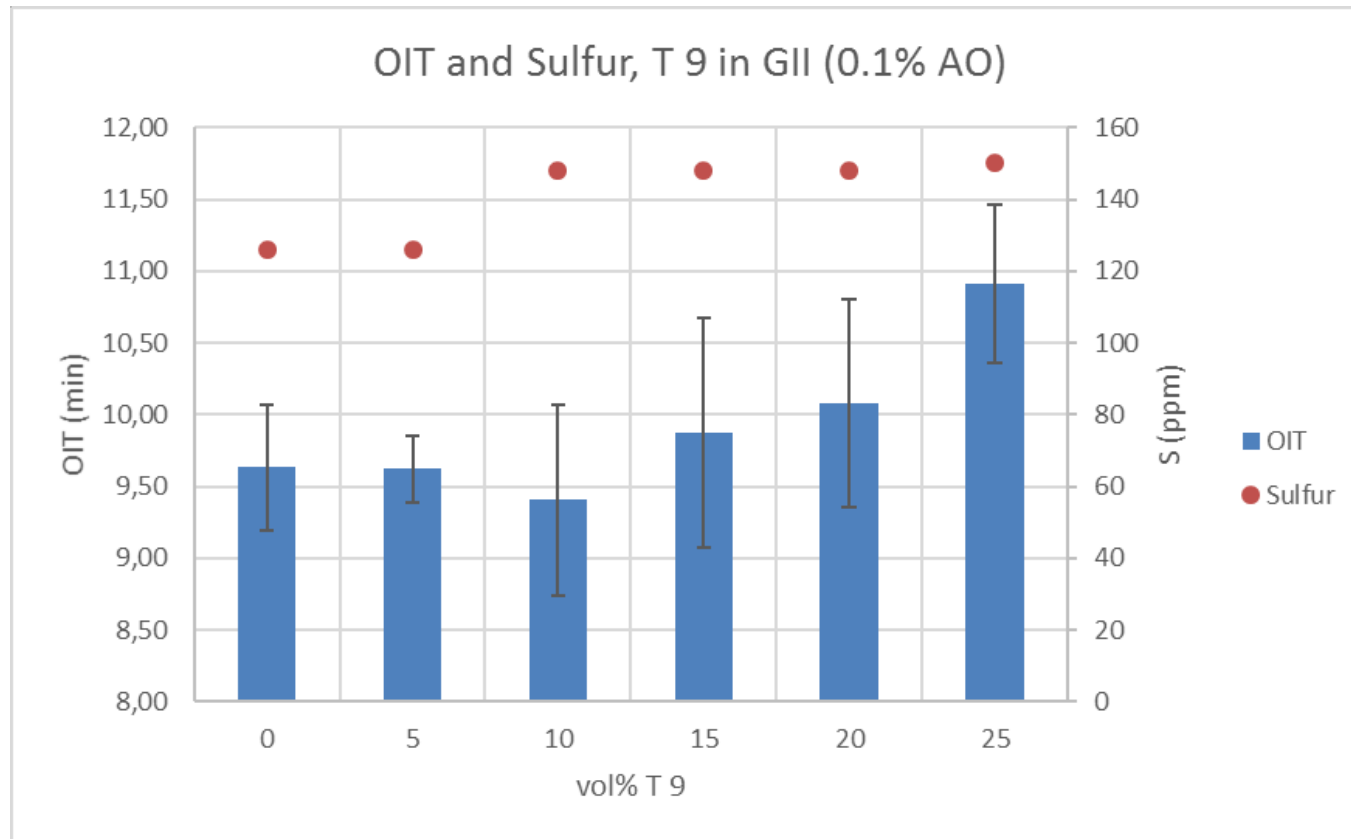


## OIT and Sulfur of T 9 blends

- ▶ The sulfur content of T 9 is low compared to T 22 and BT 46
  - T 9: 80 ppm
  - T 22: 360 ppm
  - BT 46: 880 ppm
- ▶ Although base oil sulfur increase with the addition of T 9 to G II (HP 2), the overall sulfur content is still very low and the secondary AO (dithiocarbamate) will account for the main source of sulfur in the formulated blends used in the OIT-measurements
- ▶ Interestingly, how addition of T 9 to paraffinic base oils affects the oxidation stability **proved much more difficult to assess using OIT** than for the blends of heavier series previously discussed

# OIT and Sulfur of T 9 blends

- Possibly, a difference in OIT between the paraffinic base oil (HP 2) and the blend with 25% T 9 can be distinguished, but otherwise the differences are too small and repeatability way too large for certainty in any assessment





## Some general comment on OIT measurements

- ▶ Clearly OIT determination of low viscosity lubricants is difficult, a problem previously encountered when trying to develop a short oxidation test for transformer oils. It is noted that ASTM D 6186 was not developed encompassing low viscosity lubricants [4]
- ▶ The blends of T9/G III and T9/G IV (PAO 2) display similar behavior when trying to determine OIT
- ▶ Higher treat rates of antioxidant (increasing from 0.1% to 0.3%) did not improve the repeatability or give larger differences in OIT, nor did changing the isothermal temperature (185 °C) to lower (160 °C) or higher (190 °C).
- ▶ One factor which have been mentioned as a source of uncertainty of the method is the sample cups (crucibles) [5], which have been verified in our investigations as well

[4] I.-S. Rhee, "Development of New Oxidation Stability Test Method for Lubricating Oils Using Pressure Differential Scanning Calorimeter (PDSC)", NLGI Spokesman, 2001, 65, 16

[5] B. K. Sharma, A. J. Stipanovic, "Development of new oxidation stability test method for lubricating oils using high-pressure differential scanning calorimetry" Thermochim. Acta, 2003, 402, 1

## Some general comment on OIT measurements (II)

- ▶ Another factor which might impact OIT measurements, particularly with low viscosity oils, is the volatility of the sample. The volatility of T 9 is comparatively much higher than for T 22 and BT 46
- ▶ During OIT measurement, the sample is gradually heated up to the isothermal measurement temperature which normally is ~170–190 °C (range of method 130-210 °C)
- ▶ Although high pressure is applied to minimize evaporation it is possible that this operation still could cause losses for low viscosity samples, thus affecting the accuracy
- ▶ It is possible that the oxidation stability of these blends could be assessed by other methods, specifically by the methods usually employed for **transformer oils** (e.g. IEC 61125, ASTM D 2440, ASTM D 2112), but this was not investigated within the scope of this project

## Summary and conclusions

- ▶ The impact of naphthenic oil addition to base fluids of paraffinic character in terms of oxidation stability, flammability, solvency and cold temperature properties have systematically been investigated
- ▶ Results give that addition of naphthenic base oils to paraffinic base fluids can improve pour point and aniline point, without unjustified sacrifices in e.g. flash point
- ▶ The non-linear relationship of blending base oils of different viscosity index and chemistry is specifically highlighted
- ▶ The correlation of base oil sulfur with increased oxidation stability and response to antioxidants have been further corroborated.

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