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Oxidation stability and base oil sulphur

a dynamic relationship of additive response factors

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Summary

The world base oil landscape is currently going through rapid structural changes. The rate of change is unparalleled in modern times, with Group I base oil production capacity rapidly declining, and Group II capacity rapidly expanding. The main technical and commercial driver for this change is the technical needs of the automotive engine oil applications. Industrial lubricants, however, have a technical need firmly based in the Group I base oils, mainly due to viscosity and solvency needs. Thus, the rapid decline of Group I availability poses a great challenge for industrial lubricants formulators. Based on our Naphthenic base oil technology, Nynas has developed a new range of Group I replacement base oils. The properties of these closely mimic those of Group I base oils, and we have investigated the low temperature performance, and elastomer material compatibility of these. A key property of fully formulated lubricants is oxidation stability. In this study, we have utilised HP-DSC to explore the oxidation stability of naphthenic-paraffinic base oil blends in model formulations with primary and secondary antioxidants. Correlations between added primary and secondary antioxidants and overall base oil Sulphur could be established, which serve as useful guidelines for lubricant formulators.

Introduction

The world base oil market is currently undergoing rapid change. Very large projects for the production of Group II and Group III have been completed in recent years in different regions of the world. Some estimates of the base oil market indicate that, by name plate capacity, the world market would be between 6 and 10 million metric tonnes per annum. This base oil glut spills over onto the Group I producers, which in 2015 alone has resulted in the announced closures in Western Europe of ca. 1.5 million metric tonnes, ca 20 % of the total regional base oil production. Thus, rapid changes in the base oil market, driven mainly by the technical demand from high performance automotive engine oil applications, are impacting all lubricant applications.

As these highly paraffinic Group II and Group III base oils make their way into industrial lubricant formulations, it is important to pay attention to the many important chemical and physical differences exist between these base oil types. The viscosity range covered in Group I is far wider, providing much needed high viscosity to industrial gear oils, greases and engine oils, Table 1.

API Group	Light neutral	Medium neutral	Heavy neutral	Bright Stock
Group I	38%	13%	33%	16%
Group II	55%	25%	20%	none
Group III	80%	20%	none	none

Table 1. *Typical base oil yield in different viscosity grades.*

The solvency offered by Group II and Group III, with rapidly increasing aniline points, and lower aromatic carbon type content, is far lower than that of Group I base oils. Thus, some negative effect on the blending of industrial lubricants based on Group II or Group III base oils with existing Group I based industrial product can be foreseen and have indeed been reported from the field of industrial turbine and hydraulic oils during the last decade.

Industrial lubricant blenders are facing new challenges with formulation compatibility, additive solubility and are struggling with extensive re-formulations. Could naphthenic-paraphinic blends of base oils provide a Group I replacement, which has the proven ability to fulfill the viscosity and solvency needs for industrial lubricants. In addition, we developed and tested model hydraulic fluids, metalworking fluids and lubricating greases based on these new oils [1]. One important property of these novel base oils is their response to added antioxidants, as this has wide-ranging consequences for the usefulness and customer acceptance.

For different reasons, most of the modern base oils have a low Sulphur content. All highly refined base oils end up with a low Sulphur content, compared to traditional solvent neutral Group I base oils, as a consequence of hydrotreatment reaction design. The ultra-low Sulphur level is a design feature of base oils for all modern engine oil uses, especially for all types of "Mid-SAPS" and "Low-SAPS" formulations (SAPS= Sulphated Ash, Phosphorus and Sulphur). In the case of naphthenic specialty products (NSP), the process step of deep hydrogenation is designed to convert aromatics to naphthenics, and to remove Sulphur and Nitrogen organic compounds. Some of these contribute to smell and colour instability and are thus targeted for removal by the refining and hydrotreatment processes. But some Sulphur-containing organic molecules are actually very beneficial, acting as natural antioxidants in un-inhibited oils (i.e. base oils without added antioxidant additives). These Sulphur species are actually crucial as primary and secondary antioxidants, working in conjuncture with added primary antioxidants (AO) like the commonly used alkyl-phenol (BHT-type) and aryl-naphthyl-alkyl amines. The ability of various types of Sulphur-organic molecules to function as primary and secondary antioxidants is well-known text book chemistry but remains a challenge to compensate for in many industrial lubricant formulations!

Interestingly, it is also well-know that the AO response is considered to be higher, or better, in highly refined, low-Sulphur base oils. Obviously, there are chemical reaction processes running in opposite directions, with opposing effects, synergies and antagonisms, benefits and liabilities. Finding the correct level and chemical nature (structure) of secondary antioxidants for base oil and formulated lubricants might appear as a game of chance, but fortunately there are some very helpful tools out there for the formulator.

Some ways of controlling the base oil Sulphur are only open to the base oil refiners themselves. For the lubricant formulator, many options still exist for the successful formulation of the finished lubricant product. Some pluripotent additives, like the very frequently utilised Zink Di-Thio Phosphate (ZDDP) type, bring multiple benefits to the lubricant formulation, not least by acting as a secondary antioxidant. Many types of Sulphur-containing extreme pressure (EP) and anti-wear (AW) additives for industrial lubricants and MWFs are utilised in finished lubricants "anyway", thus imparting much improved oxidation stability as an additional benefit, see Figure 1, AO molecules.

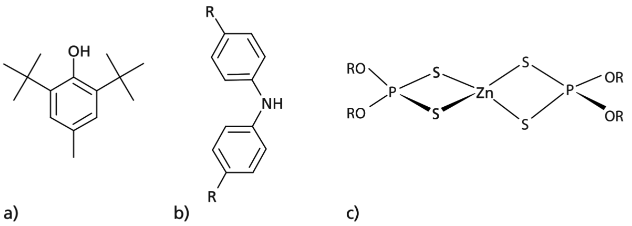

***Figure 1**. Primary antioxidants AO and ZDDP, a) BHT, b) Di(Alkyl-phenyl)-amine, c) ZDDP. R = alkyl chain.*

Thus, the purpose of this present study is to highlight this crucial, but often (sometimes) overlooked role of base oil or additive Sulphur for superior antioxidant expression, and enhanced oxidation stability during the use phase of the finished lubricant.

The first part of Nynas' work on the properties of NSP + PSP Blends ("Nybase") was reported at the Esslingen Colloquium in January 2016 and was subsequently published in T + S [1].

A study specifically investigated the oxidation stability properties of naphthenic-paraffinic base oil blends was published at the Esslingen Colloquium 2018 [2]. In that study, base oil and additive Sulphur levels could be correlated to oxidation stability in different laboratory tests. A second, free-standing part was presented STLE Annual Meeting in Minneapolis in 2018 [3]. In that study, a new test matrix comprising Naphthenic, Group II, Group III and PAO base fluids were investigated with respect to different chemical and physical properties, including oxidation stability. An additional set of correlations between added primary and secondary antioxidants and overall base oil Sulphur could be established, which we hope might serve as useful guidelines for lubricant formulators, or anyone interested in the properties of blends.

Experiments and tests

Methodology

The oxidation stability behaviour of Nynas' Naphthenic-paraffinic blend base oil Nybase 150 was compared to that of several different Group I Solvent Neutral 150 base oils. Additional comparisons were made to NYNAS T 22 and a Group II paraffinic base oil of similar viscosity (20 cSt at 40 °C). All base oils were formulated with primary antioxidants. In some samples, additional "base oil" type Sulphur was added, molecular species that are not necessarily identified, or commonly utilised as, lubricant additives. Six different secondary antioxidants (AO) were investigated as well, since most base oil buyer or lubricant formulator readily can obtain these additives from different commercial suppliers. We also tested samples containing a combination of primary and secondary antioxidants and additional "base oil" Sulphur had been boosted.

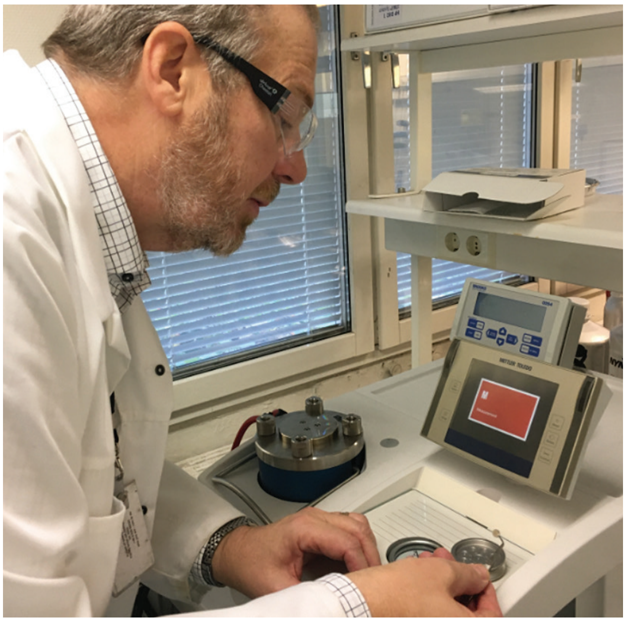

***Figure 2**. The HP-DSC test equipment.*

The effect of the Sulphur content in base oils was investigated in a thin-film oxidation study, using High Pressure Differential Scanning Calorimetry (HP-DSC) [4]. The oxidation induction time (OIT) of HP-DSC is determined at 35 bar O2, 200 °C and with 3.0-3.3 mg sample size, Figure 2.

Antioxidant selection

Primary Antioxidants

The primary antioxidants, BHT and Diphenyl amine (Figure 1) were dosed at 0.1% each. This corresponds to a fairly modest treat rate, suitable for generating OIT results under reasonably mild conditions.

Secondary Antioxidants

A selection of six different, commercially readily available, additives, known or expected to display (also) a secondary antioxidant effect is shown in Figure 3.

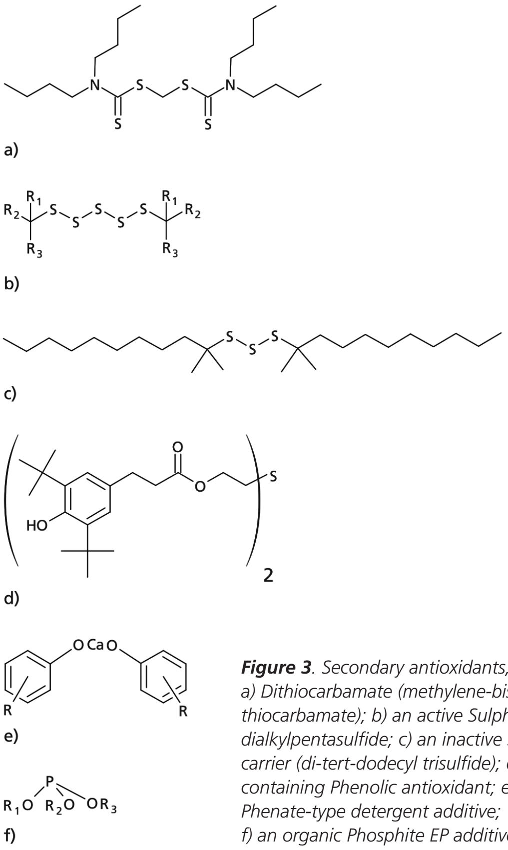

***Figure 3**. Secondary antioxidants,*
a) Dithiocarbamate (methylene-bis-(N,N'-dibutyl) thiocarbamate); b) an active Sulphur carrier, dialkylpentasulfide; c) an inactive Sulphur carrier (di-tert-dodecyl trisulfide); d) a Sulphur-containing Phenolic antioxidant; e) a Calcium Phenate-type detergent additive;
f) an organic Phosphite EP additive.

Results

Response to primary antioxidants

The HPDSC-Oxidation Induction Time (OIT) measures how long time the inhibited oil can withstand severe oxidation at the chosen elevated temperature (isothermal measurement) and oxygen pressure. When the inhibitor is depleted, the oil is subjected to rapid oxidation and a strong exothermic reaction is noted (Figure 4) and the onset time can thus be determined.

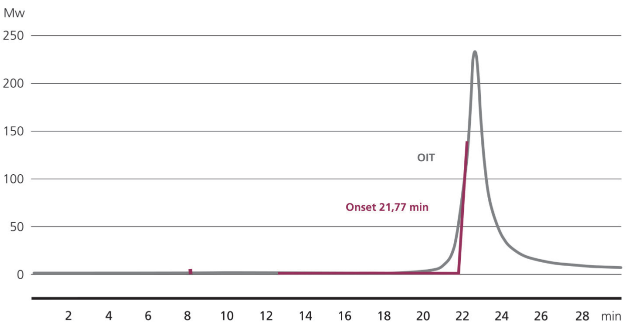

***Figure 4**. Oxidation Induction time, OIT.*

Initially, Nybase 150 was doped with a sulfide model compound to correspond to the Sulphur levels of a typical Group I base oils. A low dose and high dose Nybase 150 was prepared, 700 ppm Sulphur, and 0.3 wt% (3000 ppm) Sulphur, respectively. The results outlined in Figure 5 contains several important leads. The initial base oil Sulphur shapes the overall oxidation stability behaviour. A lower total base oil Sulphur gives a shorter OIT. The Nybase at 300 ppm has an OIT of 3.74 min, and is followed by the SN 150 base oil A with 700 ppm Sulphur and an OIT of 6.36 min. A Nybase with 700 ppm Sulphur, whereof 400 ppm in the form of added benzothiophene, clocks in at an OIT of 4.23 minutes. So evidently benzothiophenic Sulphur is not the key to improved antioxidation in this chemical system [5]. At an OIT of 20.10 minutes, Nybase with 700 ppm Sulphur doped up with sulfidic species displays about five times (5x) higher oxidation stability. Finally, at a proposed "saturation level", the Nybase with 3000 ppm overall Sulphur yields an OIT of 45.39 minutes, with some peak broadening.

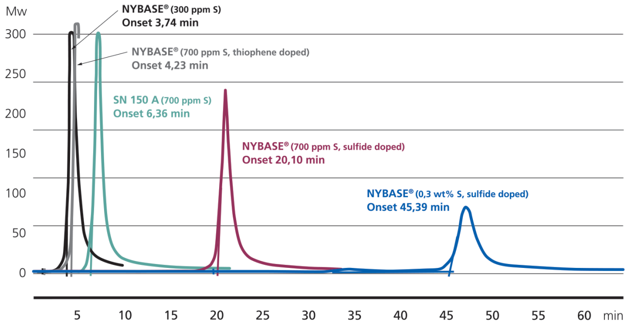

Figure 5. *Effect on OIT of base oil Sulphur content and speciation. The samples all contain primary AO, with additional "base oil" Sulphur species of different types.*

In Figure 6, the OIT is plotted against the overall Sulphur content. The strong OIT response of the sulfidic-type "base oil" Sulphur is contrasted against the absence of any effect by the addition of thiophene Sulphur.

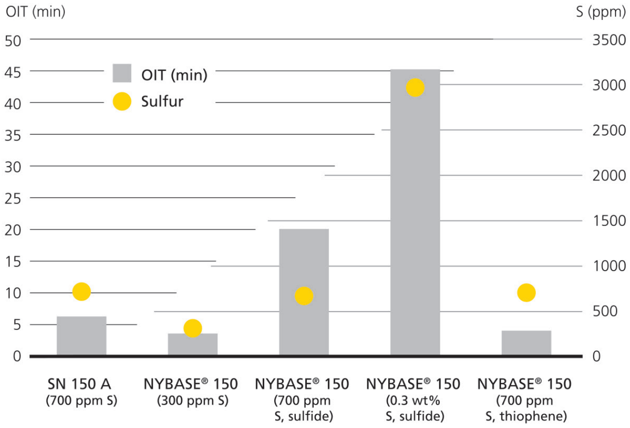

Figure 6. *The effect on OIT of overall Sulphur content, and the specific effect of different Sulphur carriers.*

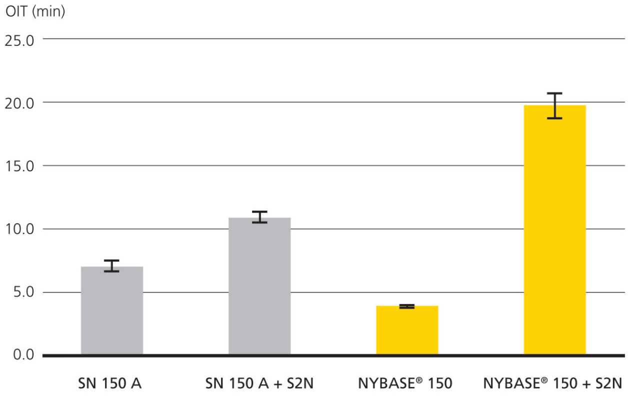

Figure 7. *The effect on OIT by the addition of Sulphur in the form of a Dithiocarbamate additive employed as a secondary antioxidant.*

The effect of an added secondary antioxidant in the form of an additive of Dithiocarbamate type is seen in Figure 7. The response to this secondary antioxidant is far more pronounced in Nybase 150 than in the reference Group I SN 150 A base oil. The OIT was increased by a factor of five for Nybase 150, and by about 1.5 times for SN 150 A. This example shows how a more highly refined, low-sulphur base oil displays a better response to antioxidant additives, which is what is often taught in textbooks [6].

In Figure 8, the combination effect from "base oil" sulphur, primary antioxidants and a secondary antioxidant is explored. For low-sulphur doped Nybase 150, N (700 ppm S, sulfide type) the combined response of the sulphur carriers is an improved OIT by a factor of about 1.5. For the next step, increase of total sulphur to the "normal Group I level" of 3 000 ppm Sulphur, an OIT of nearly 50 minutes is reached, which more than doubles the OIT value before "base oil Sulphur" was being added. After reaching about 3 000 ppm, a saturation level effect is observed also here.

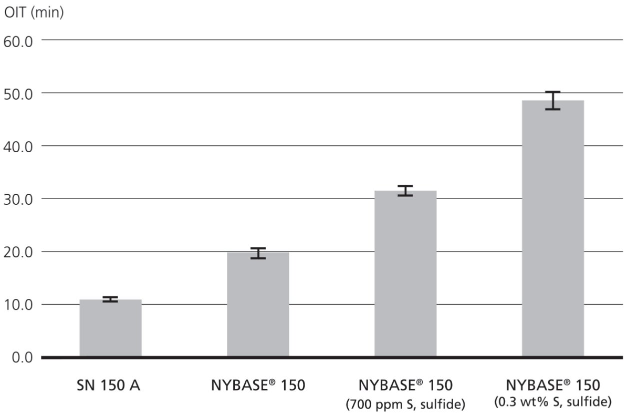

Figure 8. *The effect on OIT during incremental addition "base oil" sulphur to an oil inhibited with primary and secondary antioxidants. The OIT approached 50 minutes for the blend where the total sulphur is ca 3000 ppm. The contribution from the Dithiocarbamate additive alone at 0.1 % is ca. 200 ppm Sulphur.*

In Figure 9, a look across the base oil groups reveal that a baseline response behaviour to the combination of primary and secondary antioxidants can be observed, at an OIT of ca. 10 minutes. This value is obtained for the reference Group I base oil (SN 150A), the Group II base oil, and for the naphthenic base oil NYNAS T 22. The Nybase 150 displays a better AO response at 20 min OIT, and when "base oil" Sulphur is brought in for a total 700 ppm, the OIT jumps to over 30 minutes.

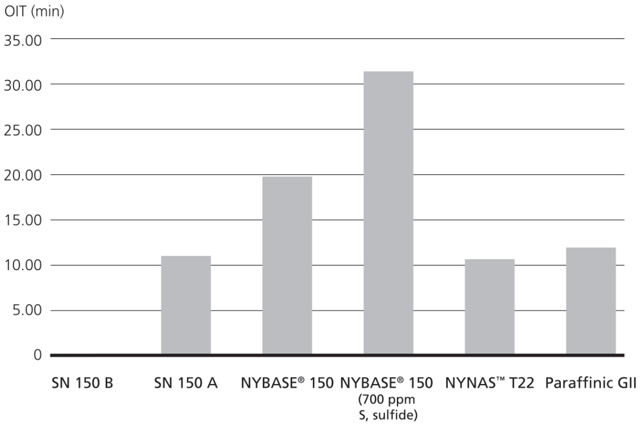

***Figure 9**. A comparison of OITs obtained for SN 150 A, Nybase 150, Nynas T 22 and a Group II base oil of 20 cSt (4 cSt at 100 °C).*

The results of a side by side comparison of the six different additives selected as candidates for secondary antioxidant behaviour is shown in Figure 10.

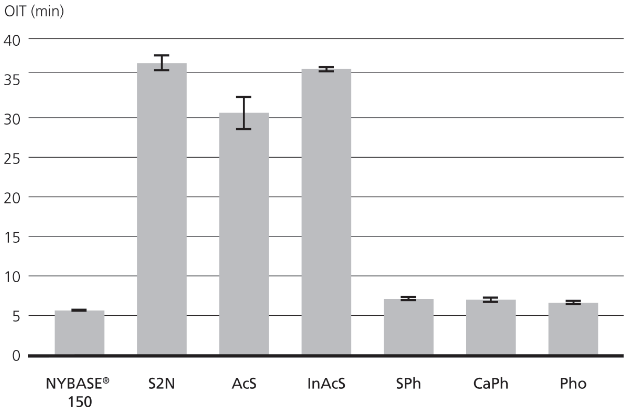

***Figure 10**. A screening of six different secondary antioxidant candidates. From left to right: Dithiocarbamate (S2N), active Sulphur carrier (AcS), inactive Sulphur carrier (InAcS), Sulphur-containing Phenolic (SPh), Calcium Phenate (CaPh), Phosphite (Pho). (For chemical structures, please see Figure 3).*

The six additives were shown in Figure 3, and were characterised by their OIT response, in this experiment at a twice as high treat rate (0.2% of each antioxidant). The resulting OIT:s, from left to right, for the six different secondary antioxidant candidates fall into two groups:

- Dithiocarbamate (S2N), active Sulphur carrier (AcS), inactive Sulphur carrier (InAcS) → **good** response, OIT in the range of 30 to 35 minutes
- S-containing Phenolic (SPh), Calcium Phenate (CaPh), Phosphite (Pho) → **poor** response, very little difference versus the baseline behaviour of Nybase 150 at an OIT of around 5 minutes

Part II Oxidation stability of generic naphthenic-paraffinic blends

The oxidation stability of another range of antioxidant-inhibited blends of naphthenic and paraffinic base oils was studied by the Oxidation Induction Time (OIT) [3]. Here, we share a small selection of these results, for blends of NYNAS T 22 and Group II and Group III base oils. 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 utilised to provide some additional Sulphur. The total AO concentration thus was 0.1%. The Group II base oil provides ca 15 ppm Sulphur, the rest of the Sulphur thus comes from the secondary antioxidant added. With each 5% of T 22 in a blend, about 20 ppm additional base oil Sulphur is carried into the blends, as NYNAS T 22 has about 400 ppm base oil Sulphur. The effect of this is visible in Figure 11, 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.

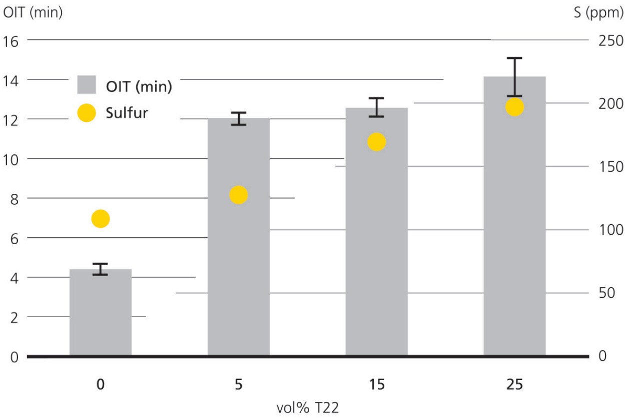

***Figure 11**. OIT of NYNAS T 22 and Group II (KV@40 °C, 19.7 cSt, KV @ 100 °C, 4.1 cSt). A marked step-up in OIT is explained by a doubling of the base oil Sulphur contribution even at 5% addition of T 22.*

A similar trend is seen in Figure 12 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% NYNAS 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.

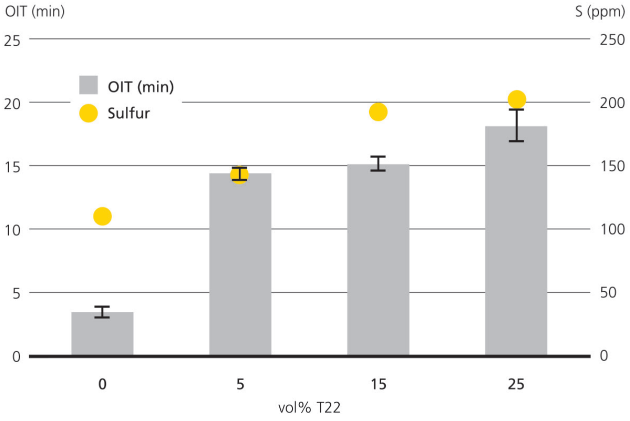

***Figure 12**. OIT of NYNAS T 22 and Group III (KV@40°C, 19.9 cSt, KV @ 100°C, 4.3 cSt). A similarly large step-up in OIT is observed, possibly indicating an even better improvement of the oxidation stability.*

Conclusions and Outlook

In this work, we have tried to elucidate the effects of primary and secondary antioxidants in relation to overall system Sulphur levels: "base oil" Sulphur and additive Sulphur. We found that the effect on the OIT obtained by HP-DSC gave us a tool to clearly discriminate between the effect of different types of added "base oil" Sulphur, and from six different secondary antioxidant candidate additives. The result was that Sulfide-type and thiocarbamate structures clearly contribute to the improvement in oxidation stability, and that several other types of known secondary antioxidants displayed no effect in the systems studied by HP-DSC.

Thus, oxidation stability improvements can be rationalised by correlation of the Sulphur levels to the observed OIT. Interestingly, adding a Naphthenic base oil to these low-Sulphur Group II and Group III base oils clearly improves the OIT results. We also note that for many types of finished lubricants, additives of the type showing good effect in this study already are commonly utilised, and good antioxidant response thus is obtained.

For many other formulations, keeping an eye of the overall Sulphur levels, and perhaps trying one of these functional additives, might be a useful strategy for improving the finished lubricant property.

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