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Combination of novel antioxidant system and thermally stable esters for high temperature greases

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Introduction

High temperature lubricating greases can be described as long service life products suitable for use at elevated temperatures. These products may be found in a variety of equipment running at high temperatures: plain and roller bearings, slideways, transmission axles, gears, chains… Such greases are normally expected to show the following general features:

- High dropping point
- High resistance to oxidation
- Low evaporation rate at high temperatures
- Controlled oil separation at high temperatures
- Good mechanical stability (even though this is desirable for any type of grease)

In order to obtain the above properties, base fluids (as main constituents of greases) are generally chosen from high quality group IV or V synthetic products: PAO, esters, silicones, or fluorinated compounds, for instance. These fluids will indeed show good to outstanding resistance to oxidation, and low to extremely low volatility properties. The quality of resulting greases will largely depend on the performance of base fluids, especially under extreme conditions.

The thickening agent is usually selected between products like (amongst other things):

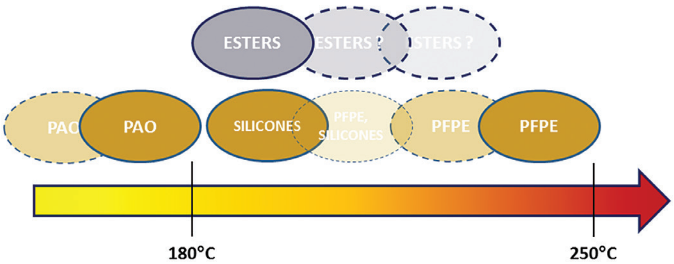
- Polyurea, for its inherently good resistance to oxidation
- Organically modified clays or silica, as they do not melt
- Polytetrafluoroethylene (PTFE), for its remarkable oxidative inertia.

However, even though these compounds all show favourable features as far as high temperature resistance is concerned, their performance in terms of thickening quality needs to be evaluated.

NYCO, as a manufacturer of synthetic esters and speciality lubricants, has been investigating the possibility of producing greases capable of withstanding elevated temperatures, on the basis of thermally stable synthetic esters treated with high performance antioxidant systems.

Of course, the term "elevated temperature" deserves a more explicit description. When looking at commercially available greases, it appears like the majority of them claim to be usable at temperatures up to 150°C, sometimes 170°C, but only a few would claim to sustain higher temperatures. Therefore, for this study, we would like to consider operating temperatures covering the range of 180°C to 250°C. Such a rather extreme range is envisaged because at such temperatures, thermo-oxidative stability is the main concern. Also, it is a temperature area where ester based greases would not usually venture.

Whilst PAO based greases generally show maximum service temperatures of about 170 to 180°C, at the other end of the scope we will find Perfluoropolyether (PFPE) based greases, sustaining temperatures of up to 250°C – sometimes even more. Silicone and fluorosilicone based greases may be found in the intermediate area of this temperature range.



Esters, and neopolyol esters in particular, are well known for their high thermo-oxidative stability. We would like to investigate the relevance of using ester based greases in temperature areas above 180°C, where PAO based greases start being insufficiently resistant, and silicone or fluorinated products may not yet be necessary. Ultimately, our goal for this study is to better understand where exactly ester based greases fit on the temperature chart, if we can push them further left on the chart, and broadly speaking, how we can make the most of synthetic esters as base fluids for high temperature greases.

In order to explore that area, we designed greases by carefully selecting a base ester fluid, treating it with a high performance antioxidant system, thickening it with an inorganic compound, and eventually evaluating high temperature performance of resulting products. An area of particular interest in this study is our ability to efficiently thicken a highly thermally stable ester, as the question is actually not so much if such a base fluid can be thickened, but if mechanical stability will be of a satisfactory level.

Optimizing thermo-oxidative resistance of base fluid

Synthetic esters, which are known for their high performance at higher temperatures, were considered and tested as possible base fluids for this work. Some basic features were used as good indicators of the performance under extreme conditions, like flash point and evaporation rate for instance.

Thermogravimetry analysis proved to be a very interesting tool to evaluate behaviour of base fluids (and resulting greases) and better understand volatility phenomena.

We also used the ASTM D4636 test, designed for jet engine oils, which evaluates the resistance of a lubricant fluid to catalysed oxidation at elevated temperatures, in the presence of metal coupons and with air bubbling (204°C, 72 h). Viscosity and acid number changes are measured after the test. This test is a stringent oxidation and corrosion test.

Another useful test is the GFC-Lu-27-T-07 micro-coking test, which was initially designed by the automotive industry to evaluate the coking propensity and the detergency ability and of oils in contact with hot metal surfaces, where a gradient of temperature is applied.

As synthetic products, the structure of esters can be tailored and designed to maximize thermo-oxidative stability and minimize volatility, which is one of the reasons why they are used in jet engine lubricants, amongst other applications.

In particular, neopolyol esters, a specific class of esters, are known to show excellent resistance to oxidation, thermal degradation and coking, thanks to their structure (Figure 1). They all have in common the presence of a quaternary carbon in their carbon chain that makes them particularly robust under higher temperatures: the absence of hydrogen in β of alcohol oxygen does inhibit thermal decomposition resulting from elimination reactions.

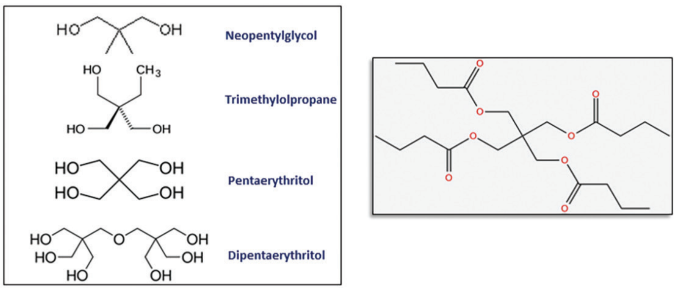


Figure 1. *Neopolyols, neopolyol ester (Pentaerythritol ester)*

By carefully selecting acids that are reacted with neopolyols, it is possible to further optimize resistance to thermo-oxidation, and eventually obtain a high viscosity ester demonstrating very low volatility and maximized thermo-oxidative stability (Table 1, Figure 2 - NYCOBASE 9600X). Tables 2 and 3 show ASTM D4636 oxidation and corrosion test results and GFC-Lu-27-T-07 micro-coking test results, in comparison with PAO of similar viscosity (400 mm2/s at 40°C).

Properties	Results	Units	Test methods
Kinematic viscosity at 40°C	380	mm²/s	ISO 3104
Kinematic viscosity at 100°C	26	mm²/s	ISO 3104
Flash point COC	290	°C	ISO 2592
Volatility, 6h – 200°C	2.2	mass %	ASTM D972
Volatility, 1h – 250°C	0.3	mass %	ASTM D6375
Thermogravimetric analysis Onset temperature, O_2	280	°C	-

Table 1. *NYCOBASE 9600X*

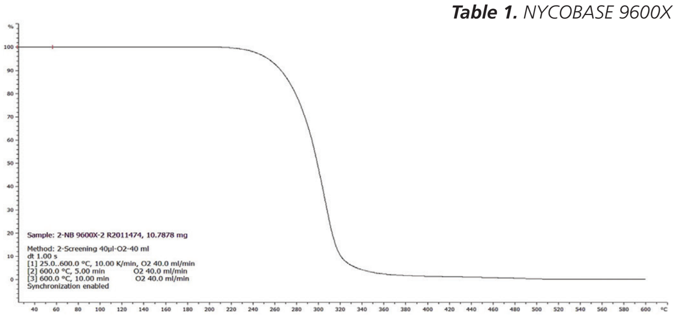


Figure 2. *NYCOBASE 9600X - Thermogravimetry (dynamic)*

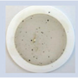
Nycobase 9600X - ASTM D4636 Oxidation and corrosion catalysed test 204°C – 72 h – 5 l/h O_2 – Formulated				Nycobase 9600X - GFC-Lu-27-T-07 Micro-coking test 230-280°C, 90 min	
Initial Viscosity : 100°C 40°C	mm²/s	26 380		Deposit temperature	273°C
Δ KV 40°C	%	30		Average Merit	8.8
Δ Acid number	mg KOH/g	0.2			
Deposit	mg/100 ml	1.7			
					

Table 2. *NYCOBASE 9600X – General properties, Dynamic thermogravimetric analysis under oxygen (10°C/min)*

PAO 40 - ASTM D4636 Oxidation and corrosion catalysed test 204°C – 72 h – 5 l/h O_2 – Formulated				PAO 40 - GFC-Lu-27-T-07 Micro-coking test 230-280°C, 90 min	
Initial Viscosity : 100°C 40°C	mm²/s	39.5 403		Deposit temperature	<230°C
Δ KV 40°C	%	39		Average Merit	6.6
Δ Acid number	mg KOH/g	5.7		Metal plate	
Deposit	mg/100 ml	Filter clogged			

Table 3. *NYCOBASE 9600X and PAO 40, Thermo-oxidative stability, coking propensity*

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NYCOBASE 9600X appears to be an interesting candidate for the purpose of the study, as it demonstrates:

- A very low volatility, which translates into little evaporation in operation
- An outstanding resistance to oxidation, resulting in a low tendency to polymerize
- A low coking propensity, which means that the oil will eventually burn – cleanly.

In a second step, NYCO utilized its expertise in the formulation of last generation, high temperature jet engine oils to design a specific antioxidant system showing excellent response in neopolyol esters. This technology provides superior protection against thermo-oxidative degradation.

Comparison between this technology (NYCOPERF AO 337) and traditional combinations of aminic anti-oxidants (dioctyl diphenylamine, octylated phenyl alpha-naphthylamine, for instance) clearly demonstrates superior performance of NYCO's technology, as shown in aluminium pan evaporation test results at 200°C on 2 formulated esters, and on micro-coking test results (Figure 3).

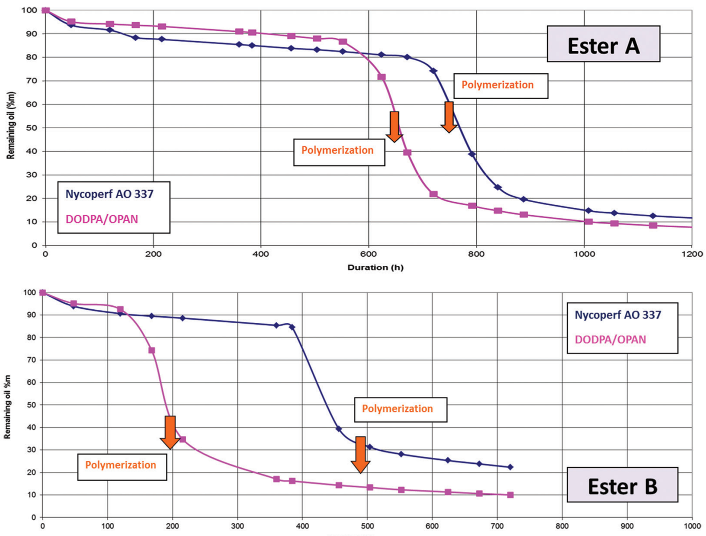


Figure 3. *Pan test, evaporation graphs, 200°C.*

GFC-Lu-27-T-07 Micro-coking test 230-280°C, 90 min		
	5 mm²/s Turbine oil Aminic AO technology	5 mm²/s Turbine oil Nycoperf AO 337
Deposit temperature	<260°C	302°C
Average Merit	8.5	9.7
Metal plates		

Micro-coking test, 230-280°C, Comparison of AO systems - Formulated oils.

The expected phenomena taking place on severely heated oils are:

- Evaporation, resulting in mass loss
- Thermal decomposition, resulting in lighter, volatile compounds and mass loss
- Oxidation, resulting in a variety of oxygen containing products
- Polymerization of degradation products, resulting in deposit and varnish

True evaporation is most probably a negligible phenomenon compared to thermo-oxidative mechanisms. It is noticeable that NYCOBASE 9600X, because of its chemical nature, seems to have an inherenty low coking propensity.

Antioxidants, through their inhibiting action on thermal decomposition and oxidation, seem to delay the induction time, when rapid decomposition starts increasing exponentially. They probably do not change the way the product degrades. This seems to be confirmed by the general profile of the evaporation curves that remains unchanged whatever the type of anti-oxidant.

In order to obtain the best possible base fluid for the formulation of high temperature greases and maximize thermo-oxidative properties, we quite naturally chose to combine highly thermally stable ester NYCOBASE 9600X with NYCO's high performance anti-oxidant system NYCOPERF AO 337.

Oxidation tests confirm such a combination leads to outstanding results in terms of resistance to thermo-oxidative degradation and coking propensity (Figure 4, Table 4: thermal stability of formulated fluid). Such properties are taken advantage of in applications like high temperature chain oils for instance, where temperatures sometimes as high as 300°C can be met. This technology is patented as a high performance anti-oxidant system in high temperature chain oils (1).

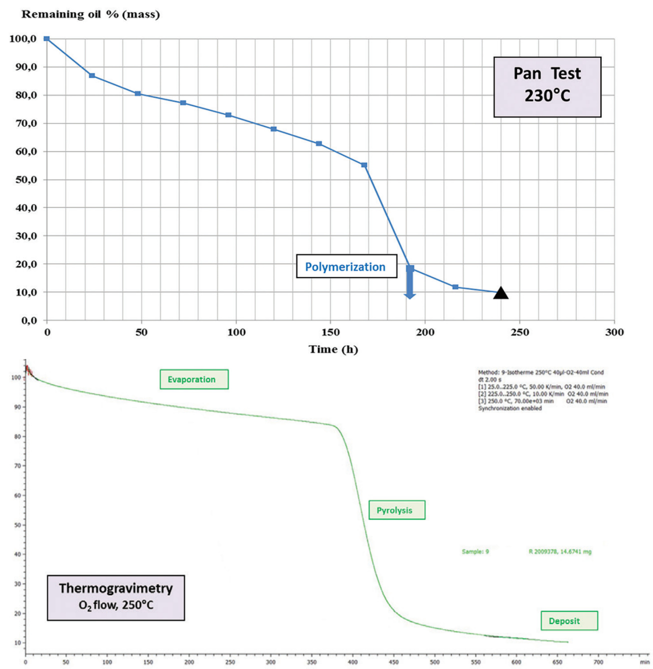


Figure 4. *Pan test at 230°C and thermogravimety of NYCOBASE 9600X with NYCOPERF AO337.*

	Micro-coking test 230-280°C
Deposit temperature	> 280
Merit A	10
Merit B	10
Average	10
Picture	

Table 4. *NYCOBASE 9600X/NYCOPERF AO 337, fully formulated fluid, Pan evaporation test, 230°C, Thermogravimetric analysis, 250°C, Micro-coking test, 230-280°C*

The TGA graph clearly shows 3 phases that outline the properties that we are looking for in such a base fluid:

- A slow evaporation phase
- A rapid decomposition phase (pyrolysis)
- A polymerization phase, leaving very little residue

Efficiently thickening the selected base fluid

One fundamental aspect of this study is to ascertain that the selected base fluid can be properly thickened to produce mechanically stable greases. Inorganic thickeners were preferred for this project, as they are easy to handle, cost-effective and suitable for extreme temperatures. The selected base fluid was therefore thickened with bentonite clay and silica, and the resulting greases were fully formulated with antioxidants, Phosphorus and Sulfur additives, and metal deactivator (Table 5).

		Nycobase 9600X	74,33	80,36	80,94	73,85
		Bentonite clay	11,62	12,59	-	-
		Silica	-	-	12,01	12,12
		Nycoperf AO 337	10,00	-	-	9,98
		OPAN	-	1,50	1,50	-
		DODPA	-	1,50	1,50	-
		P additive	2,00	2,00	2,00	2,00
		Metal deactivator	0,05	0,05	0,05	0,05
		S additive	2,00	2,00	2,00	2,00
		TOTAL	100,00	100,00	100,00	100,00
PROPERTIES	**TEST METHODS**	**UNITS**				
P0	ASTM D 217	1/10 mm	343	322	169	182
P60	ASTM D 217	1/10 mm	346	330	210	223
Delta P60-P0			3	8	41	41
P100000	ASTM D 217	1/10 mm	319	320	244	Liquid
Delta P100000-P60			-27	-10	34	--
Roller Test	ASTM D 1831	1/10 mm	4	6	64	--

Table 5. *Consistency and mechanical stability of clay and silica thickened greases*

NYCOPERF AO 337 contains 30% active material, it was therefore compared with a 3% treat rate of aminic anti-oxidants. It was possible to achieve a remarkably stable NLGI 1 grease, either in P100,000 worked penetration or in the Roller test. Bentonite clay, however, must be carefully selected to match the polarity of the medium, as some bentonite thickeners did result in mechanically unstable greases.

Hydrophilic fumed silica, as expected, resulted in greases that were not as stable mechanically. However, these greases were evaluated all the same to understand the impact of thickening agents on thermal stability.

Evaluation of grease performance at high temperatures

As a first step usual properties were tested on the obtained greases: dropping point, oil separation and evaporation rate at 200°C (Table 6).

				Bentonite clay	Bentonite clay	Silica	Silica
PROPERTIES	**TEST METHODS**	**CONDITIONS**	**UNITS**	Nycoperf AO 337	Aminic antoxidants	Nycoperf AO 337	Aminic Antioxidants
P0	ASTM D 217	--	1/10 mm	343	322	169	182
P60	ASTM D 217	--	1/10 mm	346	330	210	223
Dropping point	ASTM D 2265	--	°C	>300	>300	>300	>300
Oil separation	ASTM D 6184	30h - 200°C	%m	6,9	5,9	1,5	0,8
Evaporation	ASTM D 2595	22h - 200°C	%m	4,2	4,6	3,4	3,6

Table 6. *High temperature properties*

As expected from infusible thickeners, dropping points are very high. They are in fact more of an oil separation phenomenon. Oil separations are of a very satisfactory level, even though slightly on the high side.

Evaporation rates are partly due to Sulfur additive that contributes to roughly 2% mass loss, but still show very satisfactory levels.

Thermo-gravimetric analysis at 230°C and 250°C, under oxygen flow, was used to assess the thermo-oxidative stability. Such measurements may be used to provide an indication of relative grease life in operation (2) – but the severity of the test (high temperature, small quantity of grease, pure oxygen flow) must be taken into account.

In addition:

- Commercially available 345 mm2/s PFPE based, PTFE thickened grease and
- Laboratory PAO 40 based greases, thickened with bentonite clays, and treated with same additive systems (NYCOPERF AO 337/aminic antioxidants)

were compared with ester based greases.

Results lead to the following conclusions:

- Profile of curves is similar to those of base fluids, and shows the 3 distinct phases observed earlier (evaporation, decomposition, deposit formation). A notion of induction time is clearly visible (Figure 5).
- It is confirmed NYCOPERF AO 337 provides better thermal stability than traditional aminic anti-oxidant system (Figure 5).
- Silica seems to be more neutral at high temperatures, compared to bentonite clay, thus showing slightly better results (Figure 5). This is attributable to the partially organic nature of bentonite clay contributing to thermal instability.
- Commercially available PFPE/PTFE grease shows remarkable inertia at 250°C (Figure 5), as expected.

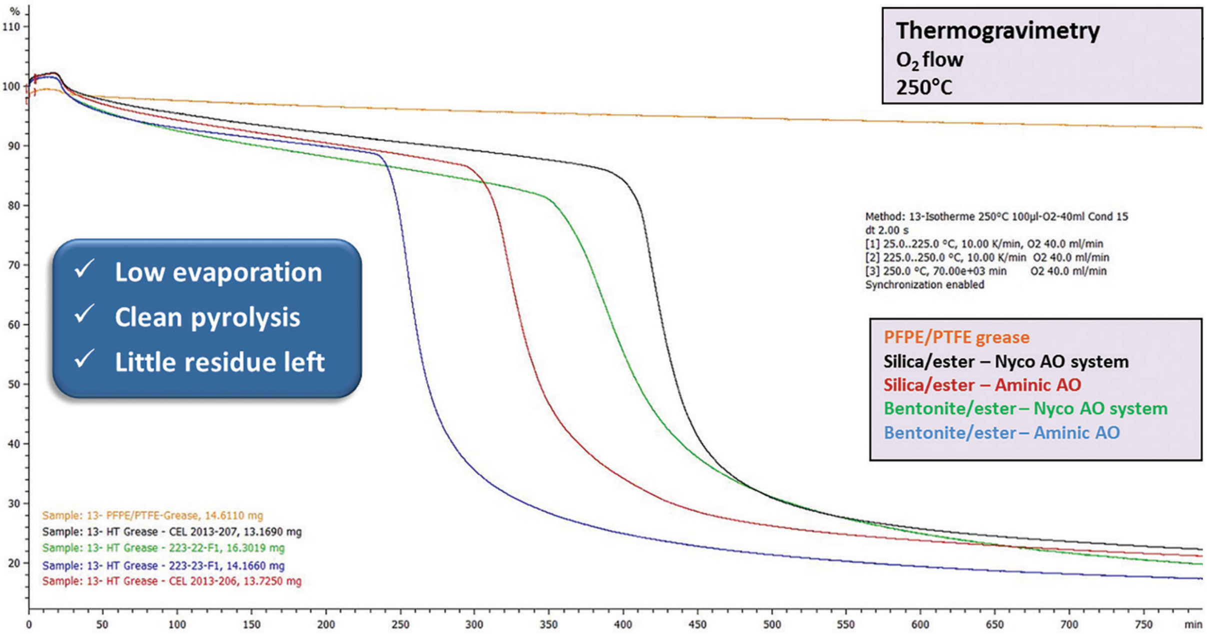


Figure 5. *Thermogravimetric analysis, 250°C*

However, TGA curves do not quite show a complete picture, as they do not say anything about the consistency of the greases throughout the process – which is obviously an essential feature of their lubricating function.

In order to find out about this, we interrupted the test a few times to check the aspect of the grease. We confirmed that even though they had turned black, they remained soft and plastic: they kept their lubricating consistency up to their induction time, after which not much matter was left but bentonite clay, judging from the cracked aspect in the bottom of metal cups (Figure 6), thus confirming the clean burning propensity of such products.

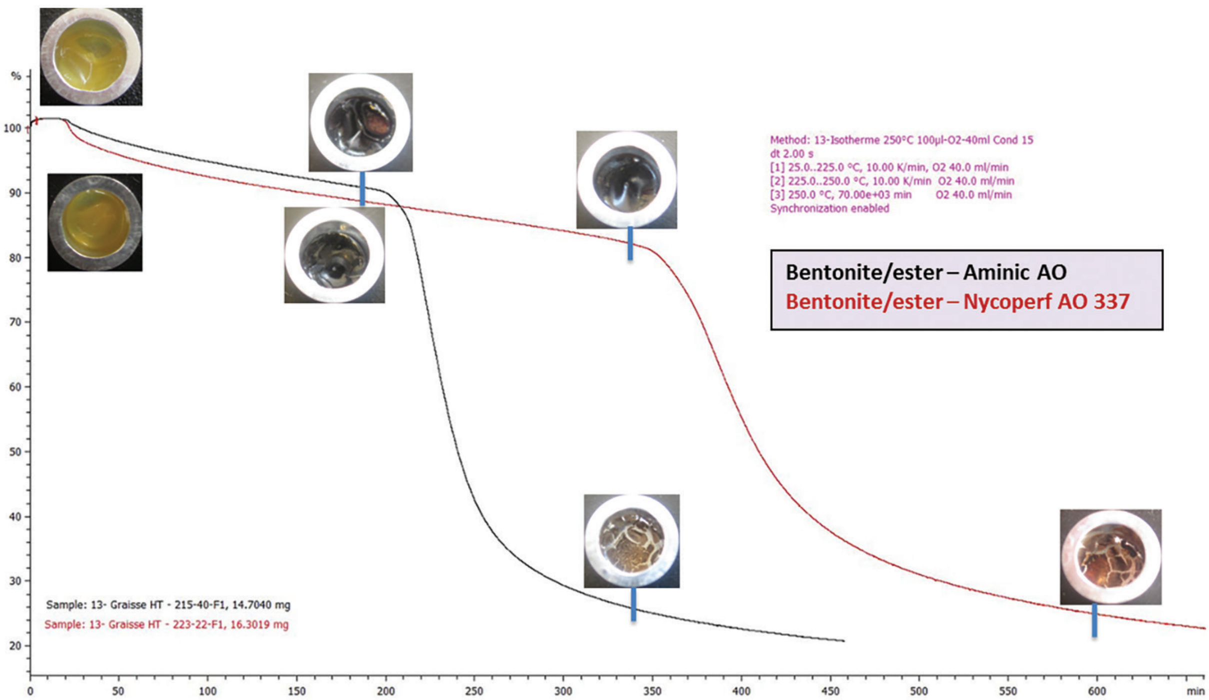


Figure 6. *Ester based grease aspect before and after Induction Time, 250°C*

PAO 40 based bentonite clay greases, treated with same additive systems, show high rates of evaporation and thermal degradation (Figure 7) right from the beginning of test. Thermo-oxidative degradation quickly generates high amounts of hard deposit, leaving approximately 60% residue.

The curves also confirm the evaporation/decomposition profile is related to the chemistry of base fluid rather than additive system.

Use of an oligomer-based additive for stabilizing a lubricating composition for a conveyor chain, patent US 8492321 B2, Gérard Goujon, Florence Severac, Marc Borel-Garin, NYCO.

(2) Prediction of high temperature grease life using a decomposition kinetic model, In-Sik Rhee, Presented at the NLGI 76th Annual Meeting, Tucson, Arizona, USA, June 13-16, 2009.

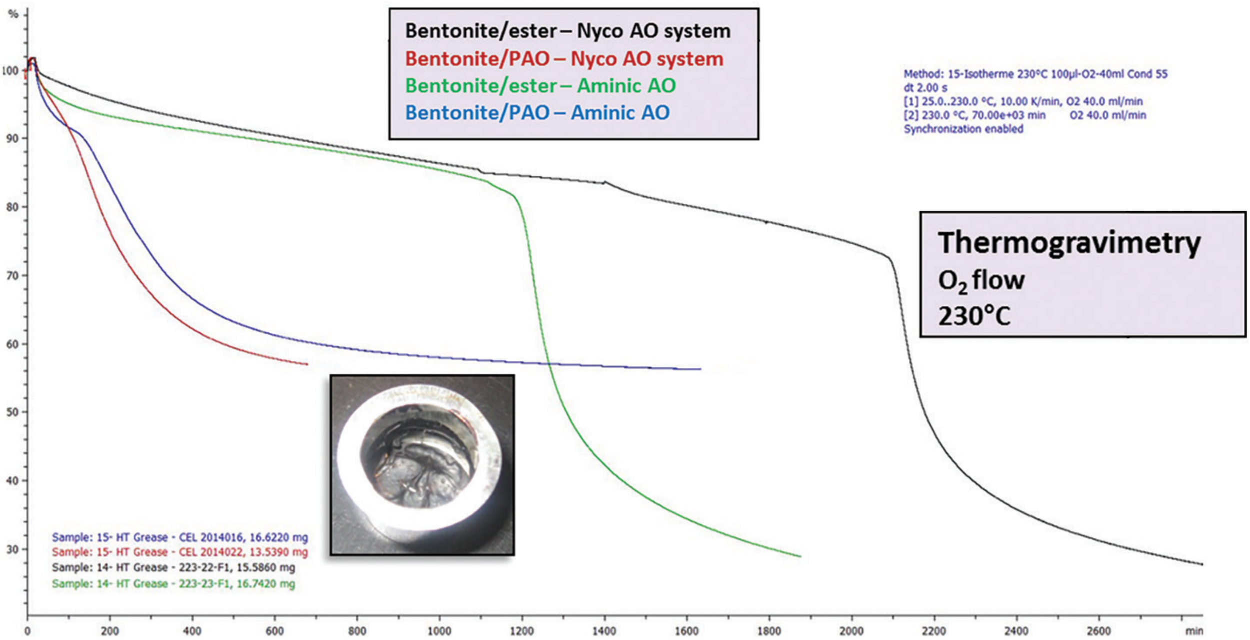
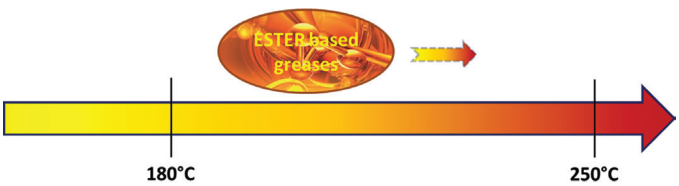


Figure 7. *PAO 40 and ester based greases, thermogravimetric analysis, 230°C*

Conclusion

By selecting a specifically designed thermally stable ester, treating it with a high performance anti-oxidant system, and thickening it with a carefully selected bentonite clay, it is possible to produce a mechanically stable NLGI 1 grease. This grease shows remarkably low evaporation rates and unchanged consistency up to its induction time, measured at 2100 min at 230°C and 400 min at 250°C on TGA equipment under oxygen flow. It leaves very little residue after decomposition.
These results suggest such a grease could be used at operating temperatures of 180°C to 230°C. We can confirm it should perform well where PAO based greases stop being suitable, and should be able to replace silicone/fluorinated fluid based products over a wider than initially expected temperature range.



(1) Use of an oligomer-based additive for stabilizing a lubricating composition for a conveyor chain, patent EP 2350241 A1, Gérard Goujon, Florence Severac, Marc Borel-Garin, NYCO.

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