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Long term testing of Antioxidants for Industrial Applications (Turbine) in Group I and II base oils

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Executive Summary

Long term tests of various Antioxidants (AO) were evaluated in both Group I and II turbine oils. The AO packages were exposed to a long term (>5,000 Hrs) dry turbine oil stability test (TOST, ASTM D943) in the absence of water. The objective of the testing was to understand the performance of the AO systems in the formulation with Group I & II base oils and to achieve greater than 5,000 hours of service in modified (no water) D943 TOST. Samples were taken at various intervals and were tested for total acid number (TAN), viscosity change and appearance. There are some general trends that were observed with the different AO systems in the different types of bases oils (Group I vs Group II). The resulting (dry) TOST data indicated that Group II oils last significantly longer than Group I oils and with lower treat rates of the AO. The conclusions from the results indicate that a combination of dithiocarbamate (DTC) and a tolutriazole derivative (TD) seems to be the best combination for Group II oils and hindered phenol (HP) and diphenyl amine (DPA) are best for Group I oils. The best AO combination (0.31% DTC; 0.06% TD) for Group II oils lasted more than 10,000 hours with no precipitation, viscosity or colour change. The best AO combination for Group I Oils, 0.25% hindered phenol (HP); 0.25% alkylated diphenylamine (ADPA), also lasted in excess of 10,000 hours with no precipitation or colour change but had a slight viscosity increase. Using the correct combination of AO additives it is possible to optimise the protection of the different base oils and to achieve the same long term performance in the (dry) TOST testing of >5000 hours.

Introduction

Vanderbilt's Petroleum Application Laboratory (PAL) continuously evaluates new AO to prolong the life of Group I base fluids comparable to Group II base fluids for an industrial application (Turbine). Industrial oil formulations containing Vanderbilt AOs were subjected to a dry TOST (modified ASTM D943) for extended time and evaluated for a variety of parameters including appearance, viscosity and TAN. The various additive chemistries and performance data are examined in this article.

Results and Discussion

Group II Formulations

The use of AO is critical to the long term performance of an industrial turbine oil package where the fluid may be in service for several years. It is important that these lubricant/additives systems provide maximum protection and maintain durability of equipment that operates in a variety of environments and operating temperatures. To evaluate these AO, a long term test dry TOST (modified ASTM D943) was setup and run with the goal of lasting at least 5000 hours of service time. The objective was to try to optimise the AO additive type and dosage for each different base oil type in order to reach at least 5,000 hours of service time in the TOST testing.

In order to screen the performance of the Vanderbilt AO, twenty formulations were prepared using ADPA, HP, DTC, and TD chemistries at different treat rates and combinations. Formulations are summarised in tables 1 and 4. As shown in these two tables (1&4) the twenty different formulations (10 formulations of Group I and 10 formulations of Group II) were mixed with at least two different AO and a standard ashless rust inhibitor and/or copper corrosion inhibitor (500 ppm). The treat rates of the AO combinations varied depending on the base oil type (Group I or II) and ranged from 0.37-0.7 wt%. The appearance of the formulation was noted at the beginning when it was made (9/3/2012), at two different intervals (4/10/13 & 12/26/13) and its final appearance (1/22/16). A failure of the fluid was noted by reaching a TAN >2.0 mgKOH/g in the dry TOST (modified ASTM D943). This typically occurred with a noticeable change in viscosity and appearance (precipitate and/or color).

	Formulation #									
	1	2	3	4	5	6	7	8	9	10
Hindered Phenol (HP)	0.15		0.14		0.08	0.2		0.19		0.1
Diphenyl Amine (ADPA)	0.15			0.17	0.08	0.2			0.21	0.1
Dithiocarbamate (DTC)		0.25	0.14	0.17	0.15		0.31	0.19	0.21	0.2
Tolutriazole Derivative (T)		0.05	0.04	0.04	0.04		0.06	0.04	0.04	0.04
Copper Corrosion Inhibitor	0.05					0.05				
Rust Inhibitor	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Group II (ISO VG 32)	99.6	99.65	99.63	99.57	99.6	99.5	99.58	99.53	99.49	99.51
Treat Rate	0.4	0.35	0.37	0.43	0.4	0.5	0.42	0.47	0.51	0.49
	Appearance									
Made 9/3/12	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear
Appearance 4/10/2013	Clear	Fall out	Fall out	Fall out	Clear	Clear	Clear	Clear	Fall out	Clear
Appearance 12/26/2013	Clear	Fall out	Fall out	Fall out	Fall out	Clear	Clear	Clear	Fall out	Fall out
Appearance on 1/22/16	Clear no ppt	Clear dark light ppt	Clear dark light ppt	Clear dark green medium ppt	Clear blue light ppt	Clear no ppt	Clear no ppt	Clear no ppt	Clear green light ppt	Clear blue light ppt

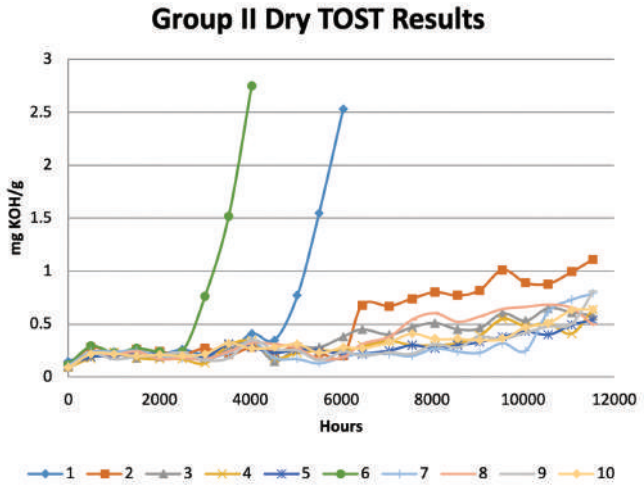
Table 1. *Group II AO Formulations and Appearance.*

The performance results of the TOST test for Group II oils can be seen in Table 2. Nine out of the ten systems (90%) reach 5,000 hours of service time with eight systems (80%) reaching greater than 10,000 hours of service time. Graph 1 shows the failure rate for each of the different formulations to reach the failure specification (>2.0 mg/KOH of TAN) and correlates well with the viscosity increase (Graph 2). It is apparent that the two worst performing systems are samples 1 and 6 which failed much earlier than the other systems and had an increase in viscosity. Both of these systems use HP and DPA which are the standard phenolic and amine type of AO. The difference between the two samples is the amount of the two AO that were used. It's important to note that no benefit was seen when the total amount of AO was increased from 0.15 to 0.2 wt%.

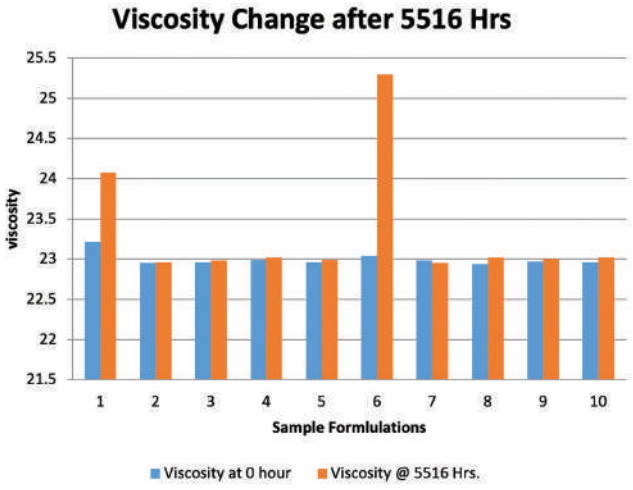
Group II Dry TOST (Modified ASTM D943) Results (mgKOH/g)

	1	2	3	4	5	6	7	8	9	10
Mod D943 (No H_2O)	0.15	0.11	0.09	0.09	0.11	0.12	0.11	0.09	0.08	0.09
500 Hrs.	0.22	0.28	0.23	0.18	0.19	0.29	0.24	0.22	0.22	0.22
1000 Hrs.	0.2	0.22	0.22	0.23	0.2	0.23	0.24	0.21	0.17	0.22
1500 Hrs.	0.24	0.26	0.18	0.18	0.23	0.27	0.25	0.24	0.19	0.2
2000 Hrs.	0.21	0.24	0.19	0.17	0.22	0.24	0.2	0.17	0.21	0.21
2500 Hrs.	0.26	0.21	0.23	0.17	0.22	0.24	0.18	0.18	0.23	0.2
3000 Hrs.	0.21	0.27	0.17	0.13	0.19	0.76	0.17	0.17	0.16	0.22
3524 Hrs.	0.23	0.21	0.26	0.3	0.31	1.52	0.23	0.24	0.18	0.32
4028 Hrs.	0.41	0.28	0.34	0.34	0.28	2.75	0.34	0.32	0.35	0.27
4532 Hrs.	0.35	0.24	0.15	0.18	0.23		0.18	0.31	0.26	0.28
5036 Hrs.	0.77	0.28	0.28	0.23	0.26		0.17	0.27	0.25	0.31
5516/5492 Hrs.	1.55	0.23	0.28	0.25	0.25		0.13	0.17	0.16	0.23
6044 Hrs.	2.53	0.2	0.38	0.25	0.22		0.19	0.19	0.24	0.28
6458 Hrs.		0.68	0.45	0.29	0.22		0.22	0.31	0.2	0.27
7052 Hrs.		0.67	0.4	0.34	0.25		0.22	0.38	0.23	0.33
7556 Hrs.		0.74	0.47	0.3	0.3		0.2	0.54	0.22	0.41
8060 Hrs.		0.8	0.51	0.3	0.27		0.27	0.6	0.31	0.36
8564 Hrs.		0.77	0.45	0.32	0.3		0.24	0.52	0.28	0.36
9044 Hrs.		0.82	0.46	0.39	0.33		0.23	0.57	0.38	0.35
9548 Hrs.		1.01	0.6	0.55	0.38		0.32	0.64	0.36	0.36
10052 Hrs.		0.89	0.53	0.48	0.43		0.25	0.66	0.42	0.47
10556 Hrs.		0.88	0.65	0.51	0.4		0.62	0.68	0.48	0.51
11060 Hrs.		0.99	0.61	0.41	0.49		0.73	0.65	0.5	0.63
11540 Hrs.		1.11	0.58	0.64	0.54		0.79	0.49	0.81	0.64
Hours to Δ 1	5269	11535				2806				
Hours to Fail (2)	5758					3726				

Table 2. *Group II Dry TOST results.*



Graph 1. *Group II Dry TOST Results.*



Graph 2. *Group II Viscosity Change Results.*

The best performing samples for the Group II base oils were samples 7 and 8 which both achieved greater than 10,000 hours of service time and remained clear without any precipitate. These two formulations both contained sulphur and nitrogen based chemistries in the form of DTC and TD as their AO system. The difference between the formulas was the addition of HP in sample 8 which contained less DTC and TD.

Group I Formulations

The objective of this study was to get a Group I oil to optimise the AO for the base oils and achieve the same performance as the Group II formulations. The difficulty in this is that Group I packages tend to breakdown quicker and therefore need higher loadings of AO to get comparable performance. Hence, similar AO types and rust/corrosion inhibitors were used but at slightly higher treat rates compared to Group II based formulations.

Details of these formulations are shown below in Table 4. Five of the ten (50%) formulations make it to the 5,000 hour mark and only three (30%) make it to the 10,000 hour mark (Table 5). The rate of failure (>2.0 mg/KOH of TAN) can be seen in Graph 3 below and its apparent that these Group I systems have a hard time making it to 5,000 hour mark.

The viscosity change before and after 5,000 hours of service time in plotted in Graph 4. All 10 formulations exhibited an increase in viscosity at the end of the test. This is definitely a contrast to the Group II systems where only the failed formulations (1 & 6) showed a viscosity increase. Breakdown of the oil because of oxidation leads to increase of viscosity and forming precipitate/sludge. The three best performing formulations (11, 14, 16) all contained at least 0.25% of the DPA AO. Some further improvement in AO protection was seen when the complimentary HP AO was used in samples 11 & 16.

	Formulation #									
	11	12	13	14	15	16	17	18	19	20
Hindered Phenol (HP)	0.25		0.22		0.12	0.3		0.26		0.14
Diphenyl Amine (ADPA)	0.25			0.26	0.12	0.3			0.3	0.14
Dithiocarbamate (DTC)		0.37	0.22	0.26	0.24		0.42	0.26	0.3	0.28
Tolutriazole Derivative (T)		0.06	0.04	0.04	0.04		0.07	0.04	0.04	0.04
Copper Corrosion Inhibitor	0.05					0.05				
Rust Inhibitor	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Group I (ISO VG 32)	99.4	99.52	99.47	99.39	99.43	99.3	99.46	99.39	99.31	99.35
Treat Rate %	0.6	0.48	0.53	0.61	0.57	0.7	0.54	0.61	0.69	0.65
Appearance										
Made 9/6/12	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear
Appearance 4/10/2013	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear
Appearance 12/26/2013	Clear	Clear	Clear	Clear	Fall out	Clear	Clear	Clear	Clear	Fall out
Appearance on 1/22/16	Clear no ppt	Clear no ppt	Clear no ppt	Clear no ppt	Clear no ppt	Clear no ppt	Clear no ppt	Clear no ppt	Clear very light ppt	Clear no ppt

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Group I Dry TOST (modified ASTM D943) Results (mgKOH/g)										
	11	12	13	14	15	16	17	18	19	20
Mod D943 (No H_2O)	0.12	0.12	0.12	0.11	0.11	0.15	0.13	0.11	0.11	0.12
500 Hrs.	0.28	0.25	0.24	0.24	0.24	0.24	0.18	0.17	0.2	0.2
1000 Hrs.	0.19	0.3	0.22	0.23	0.33	0.31	0.26	0.25	0.24	0.28
1500 Hrs.	0.33	0.23	0.26	0.36	0.23	0.31	0.32	0.29	0.29	0.33
2000 Hrs.	0.43	0.27	0.31	0.4	0.25	0.35	0.2	0.26	0.4	0.3
2500 Hrs.	0.43	0.3	0.28	0.44	0.36	0.4	0.25	0.27	0.36	0.3
3000 Hrs.	0.41	0.58	1.76	0.46	0.41	0.64	0.22	0.23	0.33	0.34
3524 Hrs.	0.58	2.7	2.45	0.6	0.69	0.75	0.2	0.35	0.47	0.37
4028 Hrs.	0.57			0.71	1.24	0.79	1.71	2.17	0.58	0.63
4532 Hrs.	0.57			0.85	1.64	0.63	2.53		0.56	1
5036 Hrs.	0.75			0.95	2.48	0.64			0.74	1.67
5492/5468	0.57			0.82		0.57			0.9	2.54
6068/6044 Hrs.	0.65			0.91		0.76			1.11	
6548/6524 Hrs.	0.64			1.07		0.87			1.41	
7052/7028 Hrs.	0.77			1.16		0.77[b]			1.55	
7556/7532 Hrs.	0.94			1.51		0.95[c]			1.93	
8060/8036 Hrs.	0.96			1.54		0.86[d]			2.65	
8564/8540 Hrs.	0.85			1.44		0.89[e]				
9044 Hrs.	0.94			1.7		0.99[f]				
9548 Hrs.	1.1			1.67		1.04[g]				
10052 Hrs.	1.25			1.89		1.5[h]				
10556 Hrs	1.24			1.93		1.5[i]				
11060 Hrs.	1.97			2.57		1.42[j]				
11540 Hrs.	1.31									
Hours to Δ1	9604	3148	2801	6772	3907	9837	3835	3733	6102	4624
Hours to Fail (2.0)		3357	3194	10611	4748		4206	3979	7606	5109

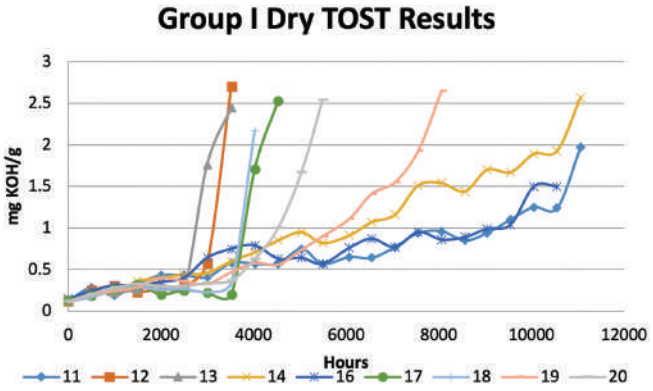
b=6,908 hours; c=7,412 hours; d-7,916 hours; e=8,420 hours; f=8,900 hours; g=9,404 hours; h=9,908 hours; i= 10,432 hours; j= 10,936 hours

Table 5. *Group I Dry TOST results.*

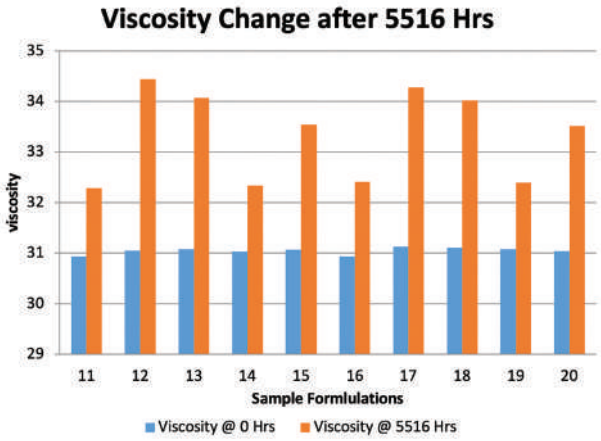
Conclusions

The data shows that the AO system for the different base oils requires selecting the correct type and combination of AO. The data illustrates that using a combination of DTC tolutriazole AO provides the best performance from Group II base oils and long life in the dry TOST. From Table 2 we can see that the formulations 7 & 8 are the best performing oils which lasted greater than 10,000 hours with no discoloration, precipitation of solids or increase in viscosity. The sulphur & nitrogen chemistry of DTC/TD yields the best AO performance in the dry TOST testing with these Group II base oils.

The Group I base oils tell a slightly different story. In order to get the best level of performance, different additive chemistry types and treat rates need to be adjusted for optimal protection against oxidation.



Graph 3. *Group I Dry TOST Results*



Graph 4. *Group I Viscosity Change Results*

The traditional combination of HP and DPA appears to be the best AO combination for these base oils. No discolouration of any of the samples was observed but precipitation of solids and an increase in viscosity was observed in this long term dry TOST test using Group I base oils. From the data in Table 5 samples 11, 14 and 16 were the best performing formulations that lasted for more than 10,000 hours. The data also shows that the use of a sulphur-containing AO (DTC) appears to have no performance advantage in these formulations.

Future Work

In future work, the AO treat rates in both the Group I and II base oils may be further optimised to determine the minimum amount needed to achieve the 10,000 hours dry TOST life. For Group II base oils, less than 0.4 wt% total AO treat rate and for Group I base oils, less than 0.6 wt% total AO treat rate should be explored for further cost reduction. Exploring other AO or multifunctional additives may add additional performance benefits or lower treat rates.

The Group II formulations saw some colour changes, while Group I formulations saw viscosity increase over the testing period. These are both signs that the base oils are breaking down over time which means that further improvements to the additive systems can be made.

None of these fluids were tested for friction or wear performance, so these properties should be determined in order to assess potential ancillary benefits of the DTC/TD AO system compared to the traditional ADPA/HP AO system.

It is possible that the sulphur content of the DTC/TD system may indeed contribute to improved friction & wear when compared to the ADPA/HP system.

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