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Anilinosilanes as thermo-oxidation stabilizers of commercial lubricating base oils

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Abstract

Anilinosilanes with different substituents on the benzene ring and on the silicon atom were prepared and used as antioxidants for lubricating base oil. The prepared antioxidants were compared with a commercial antioxidant termed MOX. The base oil before and after MOX addition starts oxidation at 218 and 265°C, respectively; while addition of anilinosilanes with *p*-methyl and *p*-methoxy groups increased its oxidation stability up to 298 and 308°C, respectively. Silylation of the amino groups also improved the solubility in oils; most anilines used were insoluble while most anilinosilanes prepared were oil soluble. In addition, silylation increased the antioxidancy of amines; addition of *p*-toluidine or its silylated product for example stabilized the oil up to 251 and 298°C, respectively. Para substituents were more effective than their meta analogues. DSC technique were more sensitive test than TG method towards antioxidation effect. © 1997 Elsevier Science B.V.

Keywords: Anilinosilanes; Antioxidants; Additives

1. Introduction

Oxidation by atmospheric oxygen produces adverse changes in lubricating oils in service at elevated temperatures. The speed and the temperature at which oil deterioration occurs can be retarded by using antioxidants. Oil soluble phenols [1], amines [2], organosulphur [2] and organophosphorus [3] compounds are frequently used. Organometallics and complexes of different metals especially those of Cu, Fe and Zn have been used as antioxidants [3]. Polysiloxanes containing phenolic antioxidants have also been employed [4].

On continuation of our work in the synthesis and application of organometallics, a series of *m* and *p* substituted anilinosilanes have been prepared and tested as antioxidants for lubricating base oils. Aminosilanes are known, in general, to be thermally stable [5] and the synthesis of a number of anilinosilanes have been reported [6]. The onset temperature in a differential scanning calorimetry (DSC) [7] and the thermogravimetry (TG) [8] methods can be used under static conditions to determine the thermo-oxidation stability of oils with and without the addition of

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oxidation inhibitors. These methods are used and compared to evaluate the efficiency of the prepared anilinosilane antioxidants.

2. Experimental

The two base oils used in this study were obtained from Petrolube, Jeddah, Kingdom of Saudi Arabia, and designated 300 SN and 300 SN+MOX. The former base oil was without any additives, while the latter was with the antioxidant additives used by the manufacturer. The physical properties of the 300 SN have been reported [7]. Air sensitive trimethyl chlorosilane and dimethylphenyl chlorosilane were manipulated under dry nitrogen atmosphere. Triethylamine was dried over KOH and distilled. Other chemicals used were of a reagent grade.

TA 3000 Mettler system was used for DSC, TG and DTG measurements under atmospheric air (static condition) or under purging nitrogen gas (dynamic condition). The operation condition was: initial temperature, 50°C; final temperature, 550°C and heating rate, 10°C $\min^{-1}$. Open crucibles were used for TG measurements, while for DSC analysis sealed pans with lids containing a hole pierced with a thick pin were used. The onset temperatures were taken from DSC curves at the intersection of the extrapolated base line before transition with a tangent to the deflected peak.

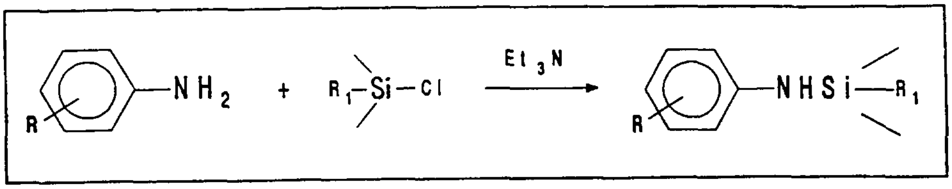
^{1}H NMR spectra were recorded by using Varian EM 390 NMR Spectrometer and $CDCl_3$ as a solvent. IR spectra were obtained by use of a Pye Unicam SP3-100 grating IR spectrometer.

2.1. Preparation of anilinosilanes

A 4 g of amine was dissolved in dried triethylamine. While the solution being stirred and cooled to −5°C, 7 ml of the appropriate chlorosilane was added slowly via syringe under dry nitrogen. The reaction mixture was stirred for 3 h then filtered and washed with dry ether. The solvents were evaporated and the product was distilled under reduced pressure reported previously [9].

3. Results and discussion

Anilinosilanes were prepared by direct reaction of the substituted anilines with trimethyl chlorosilane or dimethylphenyl chlorosilane in the presence of triethylamine, which was used as a base and a solvent as indicated in the following equation.



1. R=H, R_1=Me
2. R=*p*-Me, R_1=Me
3. R=*p*-Cl, R_1=Me
4. R=*p*-Br, R_1=Me
5. R=*p*-OMe, R_1=Me
6. R=*p*-COOEt, R_1=Me
7. R=*m*-Me, R_1=Me
8. R=*m*-Cl, R_1=Me
9. R=*p*-OMe, R_1=Ph

The striking feature in the ^{1}H NMR spectra of anilinosilanes is the shielding position of the SiMe protons (0.13–0.46 ppm), while the NH protons fell in the region 3.22–4.02 ppm. Para ethylcarboxylate substituents in compound 6 had the most deshielding effect on both SiMe and NH protons which appeared at 0.46 and 4.02 ppm, respectively. IR spectra of these compounds are characterized by the Si–Me and Si–N stretching bands in the regions 1230–1260 and 1170–1190 cm^{-1}, respectively. ^{1}H NMR and IR data of anilinosilanes are summarized in Tables 1 and 2, respectively.

Different amines have been used as antioxidants to protect lubricating base oils from oxidation. However,

Table 1
^{1}H NMR data of the prepared anilinosilanes [a]

Compound	SiMe	NH	R [b]	Aromatic protons
1	0.14(9H,s)	3.23(s)	—	6.60(3H,m)
				7.01(2H,m) [c]
2	0.20(9H,s)	3.22(s)	2.16(3H,s)	6.18(2H,d)
				6.89(2H,d) [c]
3	0.13(9H,s)	3.23(s)	—	6.38(2H,d) [c]
				6.90(2H,d)
4	0.18(9H,s)	3.53(s)	—	6.38(2H,d) [c]
				7.06(2H,d)
5	0.13(9H,s)	3.30(s)	3.57(3H,s)	6.41(2H,d) [c]
				6.60(2H,d)
6	0.46(9H,s)	4.02(s)	1.50(3H,t)	6.73(2H,d) [c]
			4.43(2H,q)	7.94(2H,d)
7	0.10(9H,s)	3.57(s)	2.23(3H,s)	6.48(3H,m)
				7.00(H,m) [c]
8	0.10(9H,s)	3.32(s)	—	6.53(3H,m)
				6.93(H,m) [c]
9	0.33(6H,s)	3.34(s)	3.67(3H,s)	6.63(5H,m) [d]
				7.36(2H,d) [c]
				7.60(2H,d)

[a] Chemical shift in ppm.
[b] Protons of *m* or *p* substituted groups.
[c] Ortho protons to the amino groups.
[d] For Si–Ph protons.

Table 2
IR data of the prepared anilinosilanes [a]

Compound	N–H str.	Aromatic C–H str.	Methyl C–H str.	C=C str.	C–N str.	Si–Me Si–N	others
1	3400	3050	2980	1600	—	12660	—
				1460		—	
2	3400	3050	2980	1610	1290	1255	—
			2940	1440		1190	
3	3400	—	—	1600	1270	1240	1096 C–Cl str.
				1465		1170	
4	3400	3028	2980	1590	1290	1255	1085 C–Br str.
			2920	1440		1185	
5	3440	3030	2980	1620	—	1230	1045 C–O str.
			2930	1450		1180	
6	3400	3010	2950	1600	—	1270	1690 C=O str.
				1510		1190	1110 C–O str.
7	3360	3060	2980	1600	1290	1260	—
			2940	1465		1175	
8	3410	3040	2970	1570	—	1260	1090 C–Cl str.
			2920	14		1170	
9	3400	3045	2980	1600	—	1230	1040 C–O str.
		3020	2930	1430		1182	

[a] KBr pellets were used for compounds 3, 5 and 6; neat films were used for the others.

Table 3
DSC and TG data of lubricating base oils and anilinosilanes

Entry	Sample	DSC data (°C)			DTG data (°C)	
		Pure anilinosilanes [a]	Oil + antioxidant [b]		Oil + antioxidant [c]	
			1st	2nd	1st	2nd
1	Oil		218	400	293	446
2	Oil + MOX		265	417	298	451
3	Oil [d]		358	—	364	—
4	Oil + MOX [d]		339	—	380	—
5	Oil + 1	141	275	437	292	448
6	Oil + 2	169	298	432	310	468
7	Oil + toluidine		251	425	292	479
8	Oil + 3	162	262	430	302	453
9	Oil + 4	179	243	435	305	473
10	Oil + 5	198	308	420	312	471
11	Oil + 7	148	250	413	290	423
12	Oil + 8	184	228	—	301	—
13	Oil + 9	168	277	436	294	455

[a] Onset temperatures of the endothermic evaporation peaks of pure anilinosilanes.
[b] Onset temperatures of the oil alone or with antioxidant additives. All peaks are exothermic except the first peaks in entires 4, 10 are endothermic.
[c] Temperatures of the maximum weight-loss rates.
[d] Under dynamic condition, the others are under atmospheric oxygen.

one limitation of their use is their low solubility in oils. All starting amines used, except *p*-toluidine, were insoluble and most of them caused turbidity of the oil. On the other hand, all anilinosilanes prepared were oil soluble except trimethy-4-ethoxycarbonyl-anilinosilane 6 which was excluded from the thermo-oxidation stability study for this reason. DSC and TG curves of pure anilinosilanes showed their thermal stability up to their complete evaporation. The onset temperatures of the endothermic evaporation peaks in the DSC thermograms are listed in Table 3.

The onset temperatures of the DSC peaks and the temperature of the maximum weight-loss rates in the DTG curves of base oil 300 SN alone and with different additives are presented in Table 3. Under static condition (atmospheric air) most samples showed two exothermic peaks in their DSC curves and two weight-loss steps in their TG thermograms. The oil alone for example, as presented in Fig. 1, showed two exothermic peaks with onset temperatures at 218°C and 400°C. During the first DSC peak (218–400°C) the first weight-loss step in the TG curve appeared with maximum rate at temperature 293°C; the sample evaporated completely by the end of the second step. In most cases more than 85% of the oil weight-loss occurs in the first TG step, while by the end of the second step more than 97% of the oil evaporated. Oil with compound 8 showed only one step in both DSC and TG curves. Addition of MOX or other antioxidants enhanced the oil stability as indicated by the increased onset temperatures of the first DSC peaks.

Under dynamic condition (nitrogen atmosphere) the oil alone or with MOX additive gave single peak in both DSC and DTG thermograms during which 100% of the oil evaporated. The oil alone gave an exothermic peak started at 358°C due to the thermal degradation of oil constituents, at much higher temperature than that of the oil under static air (218°C). Oil with MOX gave an endothermic peak at 339°C, which indicates its thermal stability up to its evaporation (an endothermic process). These results confirms that the exothermic peaks under static air were due to the thermal oxidation by atmospheric oxygen, which is accompanied by weight-loss of the samples. A weight-loss change in two steps with, the first step being the major and a slight difference between DTG and DTA peak temperatures were also observed for pyrolysis heavy oil [10].

The onset temperatures of the DSC peaks were more sensitive towards oil oxidation than those of the weight loss rates given by DTG curves and there-

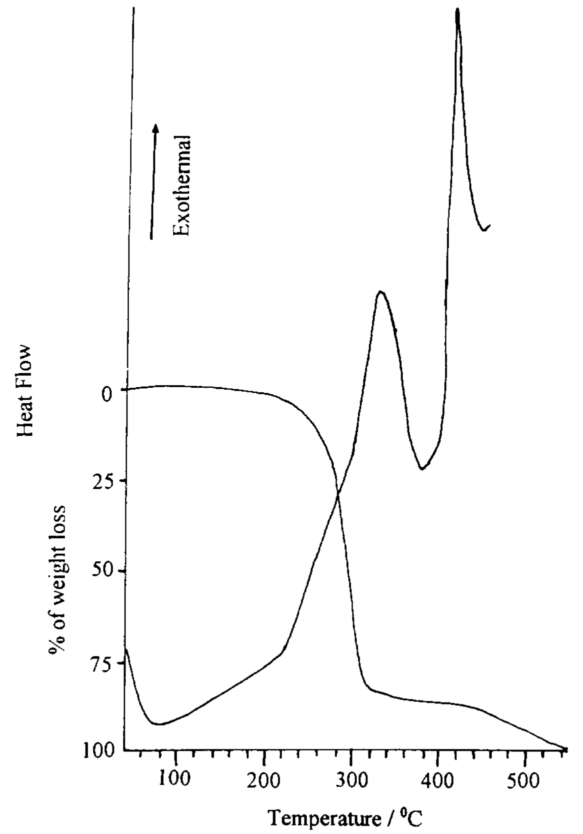


Fig. 1. DSC and TG curves of the base oil 300 SN under static air.

fore were tas a oilstability. The maximum weight-loss rates for example of oil alone or with addition of MOX, *p*-toluidine, 1, 7 or 9 were at very close temperatures (293, 298, 292, 292, 290 or 294°C, respectively), while their oxidation start at varied temperatures as indicated by the onset of their first DSC peaks (218, 265, 251, 275, 250 or 277°C, respectively).

The oil starts oxidation at 218°C while addition of MOX delayed oxidation to 265°C which indicates that the commercial additive increased the thermo-oxidation stability by 47°C. All anilinosilanes used stabilized the base oil against oxidation but at different extends. Anilinosilanes with *p*-methyl (2) and *p*-methoxy (5) substituents gave the best stabilization up to 298 and 308°C, respectively. These temperatures were higher than that of the base oil alone (218°C) by 80 and 90°C, respectively. Fig. 2 presents the first peaks in the DSC curves of oil 300 SN alone or with the additives MOX, 2 and 5 for comparison. Anilinosilanes with *p*-methyl and *p*-chloro substituents provided more stabilization (298 and 262°C, respectively) than those with the corresponding meta substituents (250 and 228°C, respectively).

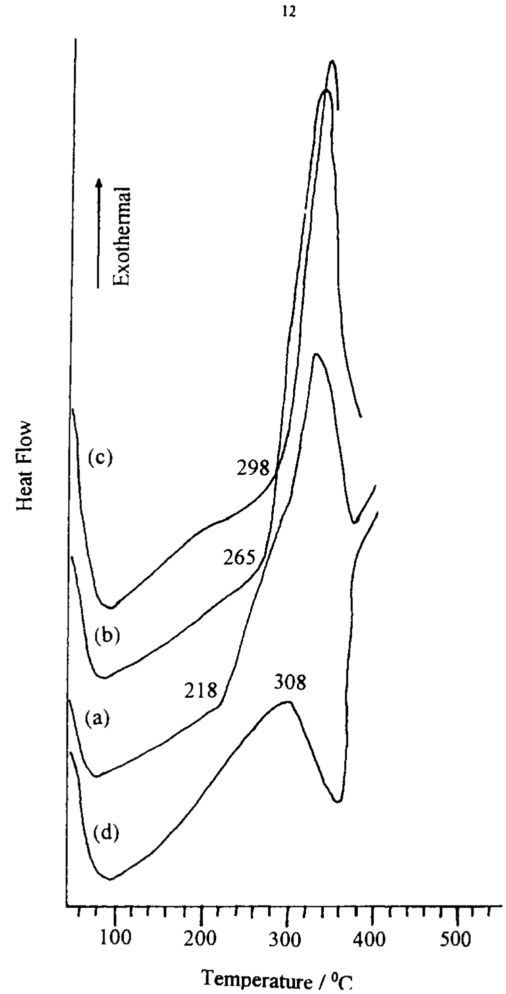


Fig. 2. DSC curves showing the onset temperatures of the first peak of (a) oil, (b) oil + MOX, (c) oil + 2, (d) oil + 5.

Amine antioxidants are known to act by tying up the peroxy radicals, formed at elevated processing temperatures in the working engines under atmospheric oxygen, so that they are incapable of propagating the reaction chain [11]. Oil with *p*-toluidine or with the corresponding anilinosilane 2 gave oxidation peaks start at 251 and 298°C, respectively. This indicates that silylation of the amino groups increased their antioxidation effect despite the fact that *p*-toluidine is solid with m.p. 45°C and b.p. 200°C, while its silylated form (2) is liquid which starts evaporation at 162°C as indicated in Table 3. Therefore, although *p*-toluidine should be more stable in the oil, its silylated form has more antioxidation effect on the oil. Comparison of compounds 5 and 9 (308 and 277°C, respectively) provided that anilinosilane with trimetylsilyl group was better stabilizer than that with dimethylphenylsilyl group. Further examination of the antioxidancy of these anilinosilanes and others is required and under investigation.

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