DOI 10.1007/s12182-014-0328-3

Synthesis and evaluation of some novel additives as antioxidants and corrosion inhibitors for petroleum fractions

Ahmed El-Mekabaty* and Osman M. O. Habib

Department of Chemistry, Faculty of Science, Mansoura University, Mansoura 35516, Egypt

© China University of Petroleum (Beijing) and Springer-Verlag Berlin Heidelberg 2014

Abstract: Benzoxazinone **2** was prepared and reacted with formamide, acetamide, some primary aromatic amines and heterocyclic amines giving the corresponding quinazolone derivatives **3-15** respectively. The reaction of benzoxazinone **2** with hydrazine hydrate and phenyl hydrazine was also studied. Representative compounds of the synthesized products were evaluated as antioxidants and corrosion inhibitors for gasoline engine lubricating oil. The highest antioxidant activities were obtained with compounds **10-15**. The optimum concentration recommended for these new additives was found to be 0.1g for 1L of oil for compounds **13-15**. In addition, some of the highly effective antioxidant additives, namely **10-15**, were thermally analyzed by using thermogravimetric analysis (TGA) and differential thermal gravimetric analysis (DTGA) techniques and the results indicated that compounds are thermally stable and could be used under thermal conditions. Moreover, a comparison of the oxidation stability between the tested oil containing the prepared products and lubricating oil containing commercial additives was also studied.

Key words: Benzoxazinone, quinazolinone, thermal stability, antioxidant additives, anticorrosive additives

1 Introduction

It has been reported that, some heterocyclic compounds, especially those containing nitrogen or sulphur in their compact and stable structures, possess excellent tribological performance (Singh and Chandrasekharan, 1993; Huang et al, 2000; 2001; Xu et al, 2000; Huang, 2003; Singh et al, 1990; Singh et al, 1989; Ren et al, 1995; 1994; Wan et al, 1996; Zhang et al, 1998; Zhang et al, 1999a; Zhang et al, 1999b). Because some of these compounds do not contain P and Zn, they can meet environmental requirements (Xu et al, 2000). Oxidation stability is a major requirement for synthetic lubricants, especially for those used in aircraft gas turbine engines. A large number of experiments have been carried out for investigation of oil oxidation stability (Hsu, 1981). The differential scanning calorimetric technique is now widely used to screen lubricants (Wesolowski, 1981; Zeman, 1982; Zeman et al, 1984; Branes and Bell, 1989).

The present work is in conjunction with our ongoing programme on the utilizing of readily obtainable starting materials for synthesis of heterocyclic systems (Habib et al, 2012) with antioxidant and anticorrosive activities (Habib et al, 2012; El-Mekabaty, 2012; Hassan et al, 2010; Hassan, 2011; Habib et al, 2010; Hassan, 1998; Amer et al, 2011). In this paper, benzoxazinone derivative **2** as building block for synthesis of functionalized quinazoline derivatives is reported and their efficiency as oxidation and corrosion inhibitors for local lubricating oils was evaluated.

2 Experimental

2.1 Synthesis

All melting points were determined on an electrothermal Gallenkamp apparatus. The IR spectra were measured on a Mattson 5000 FTIR Spectrometer in potassium bromide discs. The ^{1}H NMR spectra was recorded in DMSO-d_6 on a Bruker WP spectrometer (300 MHz) and the chemical shifts δ downfield from TMS as an internal standard. The mass spectra was recorded on Finnegan MAT 212 instrument, the ionizing voltage was 70 eV, at Faculty of Science, Cairo University. Elemental analyses were carried out by the Micro analytical unit of Faculty of Science, Mansoura University, Masoura, Egypt. All reactions were followed by TLC (Silica gel, aluminum sheets 60 F254, Merck).

2.1.1 Synthesis of 4-(2-(4-oxo-4*H*-benzo[d][1,3]oxazin-2-yl)vinyl)phenyl benzene sulfonate (2)

A mixture of aldehyde **(1)** (0.01 mole) and 2-methyl-4*H*-benzo[d][1,3] oxazin-4-one (0.01 mole) was fused in a sand

*Corresponding author. email: a_el_m11@yahoo.com
Received November 29, 2012

bath at 170-175 °C in the presence of anhydrous $ZnCl_2$ (1g) for 5 hours. The reaction mixture was triturated with ice/HCl. The solid product was filtered off, washed with water several times, dried and recrystallized from methanol to give (**2**).

2.1.2 Synthesis of 4-(2-(3,4-dihydro-4-oxoquinazolin-2-yl)vinyl)phenylbenzene sulfonate (3) and 4-(2-(3-acetyl-3,4-dihydro-4-oxoquinazolin-2-yl)vinyl)phenyl benzenesulfonate (4)

A mixture of (**2**) (0.01 mole), formamide and/or acetamide (0.01 mole) was fused in a sand bath at 170-175 °C in the presence of anhydrous $ZnCl_2$ (1 g) for 5-7 hours. The reaction mixture was triturated with ice/HCl. The solid product was filtered off, washed with water several times, dried and recrystallized from methanol to give (**3**) and (**4**) respectively.

2.1.3 Synthesis of 4-(2-(4-oxo-3-aryl-3,4-dihydroquinazolin-2-yl)vinyl)phenyl benzenesulfonate (5a-e)

A mixture of (**2**) (0.01 mole) and primary aromatic amines namely, aniline, *p*-toluidine, *o*-anisidine, ethyl *p*-aminobenzoate and *p*-aminophenol (0.01 mole) was fused in a sand bath at 170-175 °C in the presence of anhydrous $ZnCl_2$ (1 g) for 7-9 hours. The reaction mixture was triturated with ice/HCl. The solid product was filtered off, washed with water several times, dried and recrystallized from ethanol to give (**5a-e**) respectively.

2.1.4 Synthesis of 4-(4-oxo-2-(4-((phenylsulfonyl)oxy) styryl)quinazolin-3(4H)-yl)aryl (6a-c)

A mixture (**5e**) (0.01 mole) and acetic anhydride or benzoylchloride or benzenesulfonylchloride (30 mL) was heated under reflux for 2 hours. The reaction mixture was concentrated and the separated solid was filtered off, dried and recrystallized from ethanol to give (**6a-c**), respectively.

2.1.5 Synthesis of ethyl-2-(4-(4-oxo-2-(4-((phenylsulfonyl) oxy)styryl) quinazolin-3(4*H*)-yl)phenoxy)acetate (7)

A mixture of (**5e**) (0.01mole), ethylchloroacetate (0.03 mole) and potassium carbonate (0.03 mole) in dry acetone (50 ml) were refluxed on a water bath for 15 hours. The reaction mixture was poured onto ice water and the separated product was filtered off, dried, and recrystallized from ethanol to afford (**7**).

2.1.6 Synthesis of (*E*)-4-(4-oxo-2-(4-(phenylsulfonyloxy) styryl)quinazolin-3 (4*H*)-yl)phenyl 2-chloroacetate (8)

A mixture of (**5e**) (0.01mole), chloroacetylchloride (0.03 mole) in dry pyridine (50 mL) were heated on a water bath for 7 hours. The reaction mixture was poured onto ice water and the separated product was washed with water several times, filtered off, dried, and recrystallized from methanol to afford (**8**).

2.1.7 Synthesis of 4-(2-(4-oxo-3-aryl-3,4-dihydroquinazolin-2-yl)vinyl)phenyl benzenesulfonate (9-15)

A mixture of (**2**) (0.01 mole) and heterocyclic aromatic amines namely, 3-aminopyridine, 2-aminothiazole, 2-aminobenzothiazole, ethyl 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylate and 5-amino-4-(aryldiazenyl)-4*H*-pyrazol-3-ol (0.01 mole) were fused in a sand bath at 170-175 °C in the presence of anhydrous $ZnCl_2$ (1 g) for 8-11 hours. The reaction mixture was triturated with ice/HCl. The solid product was filtered off, washed with water several times, dried and recrystallized from DMF to give (**9-15**), respectively.

2.1.8 Synthesis of 4-(2-(3-amino-4-oxo-3,4-dihydroquinazolin-2-yl)vinyl)phenyl benzenesulfonate (16)

A solution of (**2**) (0.01 mole) in ethanol (30 mL) was heated under reflux with hydrazine hydrate (0.015 mole) for 8 hours. The solid that separated after concentration and cooling of the reaction mixture was filtered off, dried and recrystallized from ethanol to give (**16**).

2.1.9 Synthesis of 4-(2-(3-(4-arylideneamino)-3,4-dihydro-4-oxoquinazolin-2-yl)vinyl)phenylbenzenesulfonate (17a-d)

A solution of (**16**) (0.01 mole) in ethanol (30 mL) containing few drops of piperidine (3 drops) was heated under reflux with some aromatic aldehydes namely, benzaldehyde, *p*-anisaldehyde, *o*-hydroxybenzaldehyde and *p*-chlorobenzaldehyde (0.01 mole) for 5-6 hours. The solid that separated after concentration and cooling of the reaction mixture was filtered off, dried and recrystallized from ethanol to give (**17a-d**).

2.1.10 Synthesis of 4-(2-(3-(acetamido/phenylsulfonamido)-4-oxo-3,4-dihydro quinazolin-2-yl) vinyl)phenyl benzenesulfonate (18a-b)

A mixture (**16**) (0.01 mole) and acetic anhydride (20 mL) and/or benzenesulfonylchloride (30 mL) was heated under reflux for 2 hours. The reaction mixture was concentrated and the separated solid was filtered off, dried and recrystallized from methanol to give (**18a-b**), respectively.

2.1.11 Synthesis of 4-(2-(3-(1,3-dioxoisoindolin-2-yl)-4-oxo-3,4-dihydro quinazolin-2-yl)vinyl)phenyl benzenesulfonate (19) and (*E*)-4-(2-(4-oxo-3-(phenylamino)-3,4-dihydroquinazolin-2-yl)vinyl)phenylbenzenesulfonate (20)

A mixture of (**16**) (0.01 mole), phthalic anhydride and/or phenyl hydrazine (0.01 mole) was fused in a sand bath at 170-175 °C in the presence of anhydrous $ZnCl_2$ (1 g) for 3 hours. The reaction mixture was triturated with ice/HCl. The solid product was filtered off, washed with water several times, dried and recrystallized from ethanol to give (**19**) and (**20**), respectively.

The characterization data and spectral data of the prepared compounds **2-20** are shown in Table 1 and Table 2.

2.2 Evaluation of the prepared compounds as lubricating oil additives

2.2.1 As antioxidant additives for the tested lubricating oil

A lubricating oil sample free from additives, as well as lubricating oil samples containing different concentrations of prepared products, were subjected to severe oxidation at 155 °C for 36 h. Samples were taken at regular intervals in 3-36 h of oxidation. The oxidation stability of these samples is expressed in terms of total acid number (TAN) according to (ASTMD-3242) (Figs. 1-6)

2.2.2 As corrosion inhibitor additives for the tested lubricating oil

In order to evaluate the corrosion inhibition of the tested lubricating oil samples containing the prepared compounds, strips of seven metals with surface areas of 1 cm^2 were used

Table 1 Characterization data of the prepared compounds

Compound No.	Melting point, °C	Yield (%), Color	Molecular formula (Wt.)	Elemental analysis Calculated (Found)		
				C%	H%	N%
2	158-160	50, grey crystals	$C_{22}H_{15}NO_5S$ (405.42)	65.18 (65.12)	3.73 (3.71)	3.45 (3.41)
3	210-212	61, brown crystals	$C_{22}H_{16}N_2O_4S$ (404.44)	65.33 (65.13)	3.99 (4.00)	6.93 (6.80)
4	190-192	50, brown crystals	$C_{24}H_{18}N_2O_5S$ (446.48)	64.56 (64.26)	4.06 (4.01)	6.27 (6.17)
5a	210-212	55, brown crystals	$C_{28}H_{20}N_2O_4S$ (480.53)	69.98 (69.70)	4.20 (4.28)	5.83 (5.74)
5b	200-202	33, grey crystals	$C_{29}H_{22}N_2O_4S$ (494.56)	70.43 (70.41)	4.48 (4.44)	5.66 (5.55)
5c	240-242	55, buff crystals	$C_{29}H_{22}N_2O_5S$ (510.56)	68.22 (68.15)	4.34 (4.36)	5.49 (5.26)
5d	262-264	83, grey crystals	$C_{31}H_{24}N_2O_6S$ (552.60)	67.38 (67.33)	4.38 (4.28)	5.07 (5.03)
5e	182-184	68, black crystals	$C_{28}H_{20}N_2O_5S$ (496.53)	67.73 (67.64)	4.06 (4.06)	5.64 (5.58)
6a	220-222	79, brown crystals	$C_{30}H_{22}N_2O_6S$ (538.57)	66.90 (66.32)	4.12 (3.99)	5.20 (5.17)
6b	250-252	38, yellow crystals	$C_{35}H_{24}N_2O_6S$ (600.64)	69.99 (69.48)	4.03 (3.90)	4.66 (4.44)
6c	270-272	62, brown crystals	$C_{34}H_{24}N_2O_7S_2$ (636.69)	64.14 (64.16)	3.80 (4.00)	4.40 (4.34)
7	253-255	60, brown crystals	$C_{32}H_{26}N_2O_7S$ (582.62)	65.97 (65.80)	4.50 (4.30)	4.81 (4.72)
8	240-242	42, yellow crystals	$C_{30}H_{21}ClN_2O_6S$ (573.02)	62.88 (62.71)	3.69 (3.49)	4.89 (4.59)
9	135-137	62, brown crystals	$C_{27}H_{19}N_3O_4S$ (481.52)	67.35 (67.56)	3.98 (4.00)	8.73 (8.72)
10	200-202	42, brown crystals	$C_{25}H_{17}N_3O_4S_2$ (487.55)	61.59 (61.51)	3.51 (3.44)	8.62 (8.52)
11	100-102	47, buff crystals	$C_{29}H_{19}N_3O_4S_2$ (537.61)	64.79 (64.55)	3.56 (3.50)	7.82 (7.72)
12	230-232	82, brown crystals	$C_{33}H_{28}N_2O_6S_2$ (612.72)	64.69 (64.54)	4.61 (4.65)	4.57 (4.42)
13	295-297	84, brown crystals	$C_{31}H_{22}N_6O_5S$ (590.61)	63.04 (63.02)	3.75 (3.70)	14.23 (14.12)
14	>300	65, brown crystals	$C_{32}H_{24}N_6O_5S$ (604.64)	63.57 (63.56)	4.00 (3.99)	13.90 (13.80)
15	280-282	35, brown crystals	$C_{31}H_{21}N_7O_7S$ (635.61)	58.58 (58.56)	3.33 (3.31)	15.43 (15.32)
16	160-162	44, orange crystals	$C_{22}H_{17}N_3O_4S$ (419.45)	63.00 (63.06)	4.09 (4.09)	10.02 (10.00)
17a	200-202	66, yellow crystals	$C_{29}H_{21}N_3O_4S$ (507.56)	68.62 (68.45)	4.17 (4.07)	8.28 (8.21)
17b	130-132	71, yellow crystals	$C_{30}H_{23}N_3O_5S$ (537.59)	67.03 (67.00)	4.31 (4.01)	7.82 (7.72)
17c	158-160	75, yellow crystals	$C_{29}H_{21}N_3O_5S$ (523.56)	66.53 (66.43)	4.04 (4.00)	8.03 (8.00)
17d	170-172	58, yellow crystals	$C_{29}H_{20}ClN_3O_4S$ (542)	64.26 (64.16)	3.72 (3.42)	7.75 (7.55)
18a	180-182	65, buff crystals	$C_{24}H_{19}N_3O_5S$ (461.49)	62.46 (62.36)	4.15 (4.19)	9.11 (9.12)
18b	170-172	15, buff crystals	$C_{28}H_{21}N_3O_6S_2$ (559.61)	60.10 (60.16)	3.78 (3.49)	7.51 (7.32)
19	260-262	23, brown crystals	$C_{30}H_{19}N_3O_6S$ (549.55)	65.57 (65.56)	3.48 (3.39)	7.65 (7.52)
20	160-162	68, brown crystals	$C_{28}H_{21}N_3O_4S$ (495.55)	67.86 (67.76)	4.27 (4.13)	8.48 (8.22)

Table 2 Spectral data of the prepared compounds

Compound No.	Spectral data
2	IR (KBr)$\nu_{max.}$ cm^{-1}: 1756 (CO of lactone), 1637 (C=N), 1596 (CH=CH), 1373 (SO_3). MS: *m/z* (%), 405 (M^+, 4.3), 374 (22.5), 263 (34.0), 177 (33.5), 104 (22.3.3), 76 (100). ^{1}H-NMR (DMSO-d_6) δ_{ppm}: 5.5 (d, 1H, CH=), 7.3 (d, 1H, =CH), 6.9-8.2 (m, 13H, Ar-H).
3	IR (KBr)$\nu_{max.}$ cm^{-1}: 3432 (OH), 1612 (C=N), 3336 (NH), 1596 (CH=CH), 1370 (SO_3). MS: *m/z* (%), 404 (M^+, 0.96), 354 (11.4), 255 (13.4), 167 (55.8), 105 (15.8), 91 (100). ^{1}H-NMR (DMSO-d_6) δ_{ppm}: 5.5 (d, 1H, CH=), 7.3 (d, 1H, =CH), 6.9-8.2 (m, 14H, Ar-H, NH).
4	IR (KBr)$\nu_{max.}$ cm^{-1}: 1664 (CON), 1595 ($COCH_3$),1637 (C=N), 1596 (CH=CH), 1368 (SO_3). MS: *m/z* (%), 446 (M^+, 17.8), 356 (22.3), 261 (14.3), 174 (10.0), 109 (30.5), 77 (100). ^{1}H-NMR (DMSO-d_6) δ_{ppm}: 5.5 (d, 1H, CH=), 7.3 (d, 1H, =CH), 2.6 (s, 3H, CH_3CO), 6.9-8.2 (m, 13H, Ar-H).
5a	IR (KBr)$\nu_{max.}$ cm^{-1}: 1664 (CON), 1637 (C=N), 1596 (CH=CH), 1369 (SO_3). MS: *m/z* (%), 481 (M^+, 10.3), 315 (12.8), 221 (15.4), 144 (15.4), 109 (20.5), 77 (100).
5b	IR (KBr)$\nu_{max.}$ cm^{-1}: 1664 (CON), 1637 (C=N), 1596 (CH=CH), 1369 (SO_3). MS: *m/z* (%), 494.4 (M^+, 5.9), 300.7 (100.0), 292 (25.4), 164 (4.4), 129 (22.2), 86 (10.0). ^{1}H-NMR (DMSO-d_6) δ_{ppm}: 5.5 (d, 1H, CH=), 7.3 (d, 1H, =CH), 2.1 (s, 3H, CH_3), 6.9-8.2 (m, 17H, Ar-H).
5c	IR (KBr)$\nu_{max.}$ cm^{-1}: 1664 (CON), 1637 (C=N), 1596 (CH=CH), 1369 (SO_3). MS: *m/z* (%), 510 (M^+, 67.35), 356 (4.6), 287 (55.3), 178 (13.4), 105 (100), 85 (34.5).-
5d	IR (KBr)$\nu_{max.}$ cm^{-1}: 1664 (CON), 1770 (CO of ester), 1637 (C=N), 1596 (CH=CH), 1369 (SO_3). MS: *m/z* (%), 552 (M^+, 4.00), 445 (16.5), 397 (44.2), 258 (35.3), 175 (100), 117 (25.7).
5e	IR (KBr)$\nu_{max.}$ cm^{-1}: 3422-3480 (OH),1664 (CON), 1595 (C=N), 1608 (CH=CH), 1366 (SO_3).-MS: *m/z* (%), 496 (M^+, 3.24), 433 (6.7), 356 (55.7), 248 (25.5), 105 (100), 86 (33.8). ^{1}H-NMR (DMSO-d_6) δ_{ppm}: 5.5 (d, 1H, CH=), 7.3 (d, 1H, =CH), 12.2 (s, 1H, OH), 6.9-8.2 (m, 17H, Ar-H).
6a	IR (KBr)$_{vmax.}$ cm^{-1}: 1740 (O-C=O), 1671 (CON), 1605 (C=N), 1369 (SO_3). MS: *m/z* (%), 538 (M^+, 5.88), 446 (13.3), 366 (37.6), 237 (38.5), 165 (100), 112 (43.7). ^{1}H-NMR (DMSO-d_6) δ_{ppm}: 5.5 (d, 1H, CH=), 7.3 (d, 1H, =CH), 2.4 (s, 3H, CH_3CO), 6.9-8.2 (m, 17H, Ar-H).
6b	IR (KBr)$_{vmax.}$ cm^{-1}: 1740 (O-C=O), 1685 (CON), 1597 (C=N), 1374 (SO_3). MS: *m/z* (%), 600 (M^+, 24.46), 385 (24.5), 256 (7.8), 227 (42.6), 187 (100), 91 (33.5).
6c	IR (KBr)$_{vmax.}$ cm^{-1}: 1685 (CON), 1606 (C=N), 1369 (SO_3). MS: *m/z* (%), 636 (M^+, 5.70), 356 (4.15), 243 (23.4), 167 (53.2), 105 (100), 86 (24.7).
7	IR (KBr)$\nu_{max.}$ cm^{-1}: 1664 (CON), 1770 (CO of ester), 1637 (C=N), 1596 (CH=CH), 1369 (SO_3). MS: *m/z* (%), 582 (M^+, 100), 386 (15.65), 158 (11.2), 115 (10.1), 85 (34.3). ^{1}H-NMR (DMSO-d_6) δ_{ppm}: 5.5 (d, 1H, CH=), 7.3 (d, 1H, =CH), 1.3 (t, 3H, CH_3-ester), 4.3 (q, 2H, CH_2-ester), 4.8 (s, 2H, OCH_2), 6.9-8.2 (m, 17H, Ar-H).
8	IR (KBr)$_{vmax.}$ cm^{-1}: 1678 (CON), 1740 (O-C=O), 1365 (SO_3). MS: *m/z* (%), 574.56 (M^++1, 18.3), 415 (100), 345 (13.3), 193.34 (10.8), 105 (34.3), 68.53 (46.3). ^{1}H-NMR (DMSO-d_6) δ_{ppm}: 5.5 (d, 1H, CH=), 7.3 (d, 1H, =CH), 4.5 (s, 2H, CH_2Cl), 6.9-8.2 (m, 17H, Ar-H).
9	IR (KBr)$_{vmax.}$ cm^{-1}: 1680 (CON), 1591 (C=N), 1372 (SO_3). MS: *m/z* (%), 480 (M^+, 7.1), 326 (12.9), 250.9 (10.6), 155.6 (7.1), 103 (24.7), 77 (100).
10	IR (KBr)$_{vmax.}$ cm^{-1}: 1678 (CON), 1609 (C=N), 1369 (SO_3). MS: *m/z* (%), 487.9 (M^+, 11.7), 455 (100), 346.66 (11.7), 182.77 (1.1), 105 (4.3), 68.29 (96.8).
11	IR (KBr)$_{vmax.}$ cm^{-1}: 1678 (CON), 1596 (C=N), 1365 (SO_3). MS: *m/z* (%), 536 (M^+-1, 27.8), 345 (4.1), 195 (8.0), 149.98 (100), 105.69 (3.2), 68. 19 (30.2).
12	IR (KBr)$\nu_{max.}$ cm^{-1}: 1664 (CON), 1770 (CO of ester), 1637 (C=N), 1596 (CH=CH). MS: *m/z* (%), 612.05 (M^+, 0.51), 283.10 (78.79), 143.25 (100), 96.25 (0.56).
13	IR (KBr)$_{vmax.}$ cm^{-1}: 3328-3378 (OH), 1675 (CON), 1596 (C=N), 1365 (SO_3). MS: *m/z* (%), 590 (M^+, 10.34), 397 (23.18), 288 (51.2), 185 (100), 91 (24.2).
14	IR (KBr)$_{vmax.}$ cm^{-1}: 3353-3419 (OH), 1675 (CON), 1596 (C=N), 1365 (SO_3).MS: *m/z* (%), 604 (M^+, 10.34), 497 (23.18), 388 (51.2), 185 (100), 91 (24.2).
15	IR (KBr)$_{vmax.}$ cm^{-1}: 3354-3380 (OH), 1670 (CON), 1635 (C=N), 1371 (SO_3). MS: *m/z* (%), 635 (M^+, 38.9), 423.24 (92.6), 386 (100), 172 (24.2), 104 (3.2).
16	IR (KBr)$_{vmax.}$ cm^{-1}: 3370-3397(NH_2), 1652 (CON), 1596 (C=N), 1360 (SO_3). MS: *m/z* (%), 419 (M^+, 9.1), 371.3 (100), 280.01 (30.3), 147.12 (27.3), 73.5 (27.2). ^{1}H-NMR (DMSO-d_6) δ_{ppm}: 5.5 (d, 1H, CH=), 7.3 (d, 1H, =CH), 6.9-8.2 (m, 15H, Ar-H, NH_2).
17a	IR (KBr)$_{vmax.}$ cm^{-1}: 1678 (CON), 1596 (C=N), 1365 (SO_3). MS: *m/z* (%), 507 (M^+, 2.3), 415 (12.6), 298 (6.4), 139.11 (100), 98 (11.0), 68. 19 (6.2). ^{1}H-NMR (DMSO-d_6) δ_{ppm}: 5.5 (d, 1H, CH=), 7.3 (d, 1H, =CH), 9.1 (s, 1H, N=CH), 6.9-8.2 (m, 18H, Ar-H).
17b	IR (KBr)$_{vmax.}$ cm^{-1}: 1678 (CON), 1596 (C=N), 1365 (SO_3). MS: *m/z* (%), 537 (M^+, 0.99), 445 (1.3), 275 (6.4), 185.31 (100), 95 (24.6).
17c	IR (KBr)$_{vmax.}$ cm^{-1}: 3354-3380 (OH), 1678 (CON), 1596 (C=N), 1365 (SO_3). MS: *m/z* (%), 523.5 (M^+, 1.02), 453.11 (100.0), 383.50 (1.88), 196.56 (23.35), 55.00 (12.14).
17d	IR (KBr)$_{vmax.}$ cm^{-1}: 1678 (CON), 1596 (C=N), 1365 (SO_3). MS: *m/z* (%), 542.00 (M^++1, 1.02), 421.75 (100.0), 361.00 (2.81), 126.10 (19.54), 47.00 (2.06).
18a	IR (KBr)$_{vmax.}$ cm^{-1}: 3470(NH), 1652 (CON), 1603 (C=N), 1372 (SO_3). MS: *m/z* (%), 461.25 (M^+, 9.21), 395.30 (25.38), 350.50 (100), 213.00 (96.75), 100.00 (5.19).
18b	IR (KBr)$_{vmax.}$ cm^{-1}: 3470(NH), 1652 (CON), 1603 (C=N), 1372 (SO_3). MS: *m/z* (%), 559.00 (M^+, 23.85), 484.00 (22.12), 326.00 (17.17), 235.90 (100), 74.00 (11.33).
19	IR (KBr)$_{vmax.}$ cm^{-1}: 1678 (CON), 1592 (C=N), 1370 (SO_3). MS: *m/z* (%), 549.6 (M^+, 0.23), 545.50 (100.00), 222.10 (1.31), 175.95 (2.97), 99.80 (3.01). ^{1}H-NMR (DMSO-d_6) δ_{ppm}: 5.5 (d, 1H, CH=), 7.3 (d, 1H, =CH), 6.9-8.2 (m, 17H, Ar-H).
20	IR (KBr)$_{vmax.}$ cm^{-1}: 3353 (NH), 1675 (CON), 1596 (C=N), 1365 (SO_3).MS: m/z (%),495.75 (M^+, 16.52), 398.75 (24.23), 234.75 (30.50), 184.75 (100.0). ^{1}H-NMR (DMSO-d_6) δ_{ppm}: 5.5 (d, 1H, CH=), 7.3 (d, 1H, =CH), 6.9-8.2 (m, 19H, Ar-H, NH).

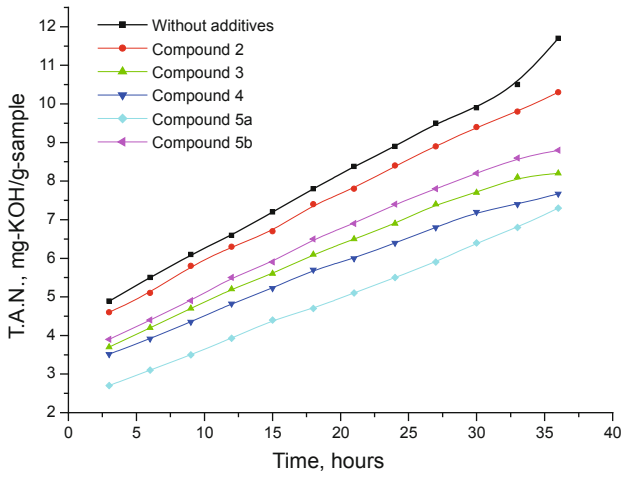


Fig. 1 Variation of the TAN with oxidation time of the tested lubricating oil sample without and with additives (**2-5b**) at 0.1 g/L concentration at 155 ºC up to 36 hours

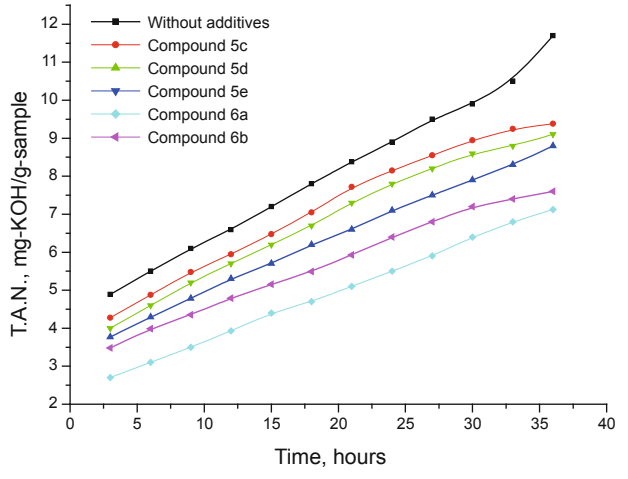


Fig. 2 Variation of the TAN with oxidation time of the tested lubricating oil sample without and with additives (**5c-6b**) at 0.1 g/L concentration at 155 ºC up to 36 hours

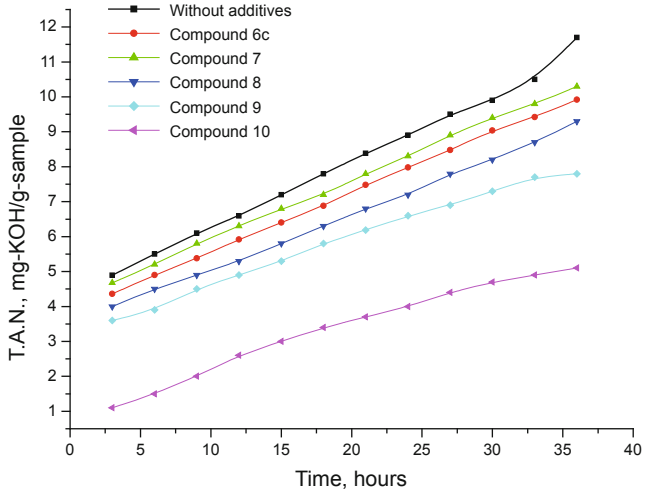


Fig. 3 Variation of the T.A.N. with oxidation time of the tested lubricating oil sample without and with additives (**6c-10**) at 0.1 g/L concentration at 155 ºC up to 36 hours

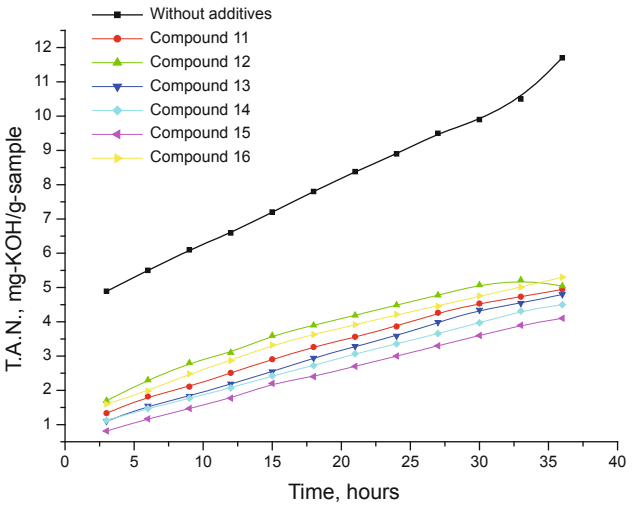


Fig. 4 Variation of the T.A.N. with oxidation time of the tested lubricating oil sample without and with additives (11-16) at 0.1 g/L concentration at 155 ºC up to 36 hours

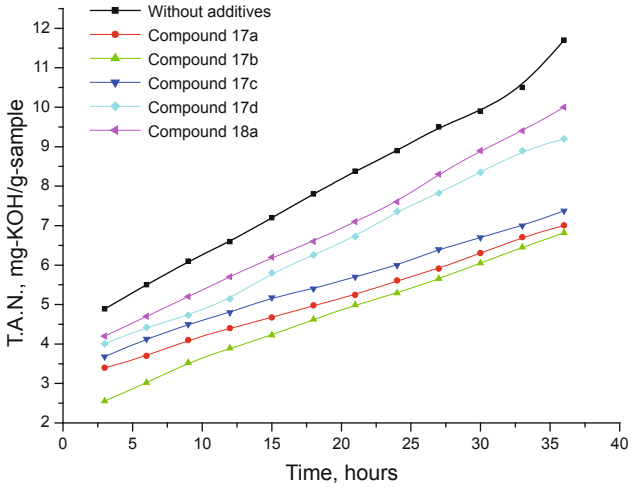


Fig. 5 Variation of the T.A.N. with oxidation time of the tested lubricating oil sample without and with additives (**17a-18a**) at 0.1 g/L concentration at 155 ºC up to 36 hours

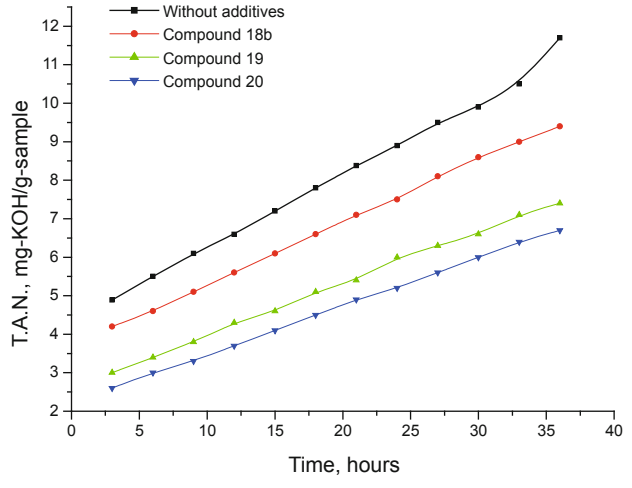


Fig. 6 Variation of the T.A.N. with oxidation time of the tested lubricating oil sample without and with additives (**18b-20**) at 0.1 g/L concentration at 155 ºC up to 36 hours

in this study. Every metal was weighed and immersed in the oxidation system for 36 h under the previous conditions. Then every metal was cleaned and weighed again. The difference in weight was calculated and the efficiency of the used products as corrosion inhibitors was evaluated by using weight loss technique according to ASTMD-130 (Table 3).

Table 3 Effect of additives (0.1 g/L) on the weight loss of metals after 36 hours oxidation at 155 °C at air rate of 5 L/h

Compound No.	Weight loss, 10^{-3} g/cm^2						
	Cu	Cu-Ni	α-brass	Fe	Stainless steel	C-Steel	Al
Oil without additive	11.8	12.6	13.5	14.7	13.1	10.9	9.2
2	2.5	3.4	4.3	7.8	6.1	5.4	1.8
3	2.6	2.9	2.2	5.1	4.5	3.4	1.5
4	3.2	4.1	1.9	1.1	3.9	3.8	2.1
5a	2.7	3.1	3.9	1.9	4.0	2.5	1.3
5b	4.6	3.5	2.8	4.6	4.8	2.3	3.7
5c	3.7	3.8	3.2	6.5	3.8	1.9	5.4
5d	2.2	3.4	2.5	6.2	4.0	2.1	4.3
5e	5.8	3.2	3.4	4.8	3.9	2.5	3.6
6a	4.2	5.5	2.4	6.7	1.9	3.4	4.6
6b	6.1	6.0	3.2	7.7	1.4	2.9	1.3
6c	6.8	5.3	2.6	2.4	2.7	3.0	1.2
7	3.5	1.3	1.3	3.5	3.1	1.2	2.6
8	2.4	2.4	3.4	1.8	3.5	1.9	2.2
9	2.2	1.6	4.3	6.8	2.5	1.5	6.4
10	1.2	2.6	2.5	1	3.4	2.6	1.5
11	2.6	3.7	1.2	2.3	2.0	4.1	1.8
12	1.8	4.5	5.0	1.7	1.6	3.0	1.9
13	1.7	3.6	2.4	1.9	1.4	1.4	1.6
14	1.1	4.1	3.5	1.1	3.1	5.0	1.1
15	1	2.1	2.9	0.8	5.3	4.4	0.9
16	2.3	1.2	2.1	2.4	4.1	3.8	3.6
17a	5.6	1.1	3.5	4.8	4.9	3.0	3.8
17b	4.9	1.7	2.7	3.8	2.4	1.7	2.9
17c	3.8	2.1	1.8	4.1	3.1	1.1	4.4
17d	3.6	2.2	2.5	3.6	1.2	2.3	2.9
18a	3.2	1.7	4.1	1.9	1.7	2.8	5.5
18b	4.2	2.5	1.2	6.9	1.3	4.4	1.2
19	2.6	1.9	1.6	5.5	3.1	3.4	1.1
20	7.1	2.4	2.0	2.9	2.0	1.3	1.1

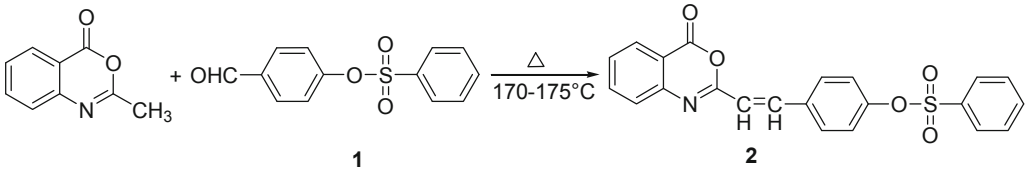
2.2.3 Thermal stability as antioxidant additives

The stability of effective antioxidant and anticorrosive additives towards thermal analysis using thermogravimetric analysis (TGA) and differential thermal gravimetric analysis (DTGA) techniques were conducted by using Shimadzu TGA apparatus.

3 Results and discussion

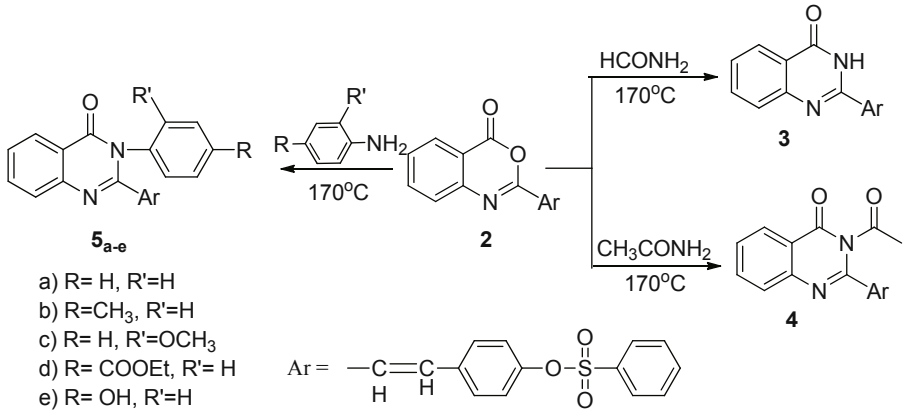
3.1 Chemistry

The required 4-(2-(4-oxo-4*H*-benzo[d][1,3]oxazin-2-yl)vinyl)phenylbenzene sulfonate **2** was prepared by means of the reaction of benzenesulfonylchloride with *p*-hydroxybenzaldehyde and the resulting aldehyde **1** was fused with 2-methyl-4*H*-benzo[d][1,3]oxazin-4-one (Hassan et al, 2011) at 170-175 °C to give **2** (Scheme 1).



Scheme 1 Synthesis of 4-(2-(4-oxo-4*H*-benzo[d][1,3]oxazin-2-yl)vinyl) phenyl benzenesulfonate **2**

Next, because of increased interest in quinazoline derivatives, some new quinazoline derivatives were required for study of their efficiency as oxidation and corrosion inhibitors for local lubricating oils. Benzoxazinone derivative **2** seemed to be a good precursor to fulfill this objective via its reactions with some nucleophilic reagents. Fusion of benzoxazinone **2** with formamide and/or ammonium acetate at 170 °C gave the corresponding quinazolone derivative **3**. In a similar way, fusion of **2** with acetamide under the same experimental conditions afforded the corresponding quinazolone derivative **4**. In a search for some new 4-quinazolones, the present investigation reports on the condensation of the benzoxazinone **2** with some primary aromatic amines. So, fusion of **2** with some primary aromatic amines, namely aniline, *p*-toluidine, *o*-anisidine, ethyl *p*-aminobenzoate and *p*-aminophenol, in an oil bath at 170-175 °C can afford the quinazolone derivatives **5a-e**, respectively (Scheme 2).

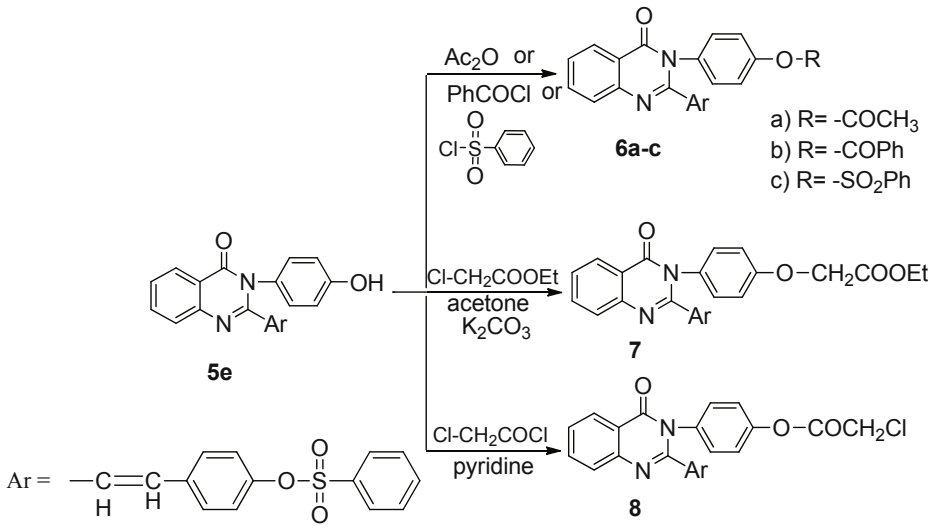


Scheme 2 Reaction of benzoxazinone derivative **2** with aliphatic and aromatic amines

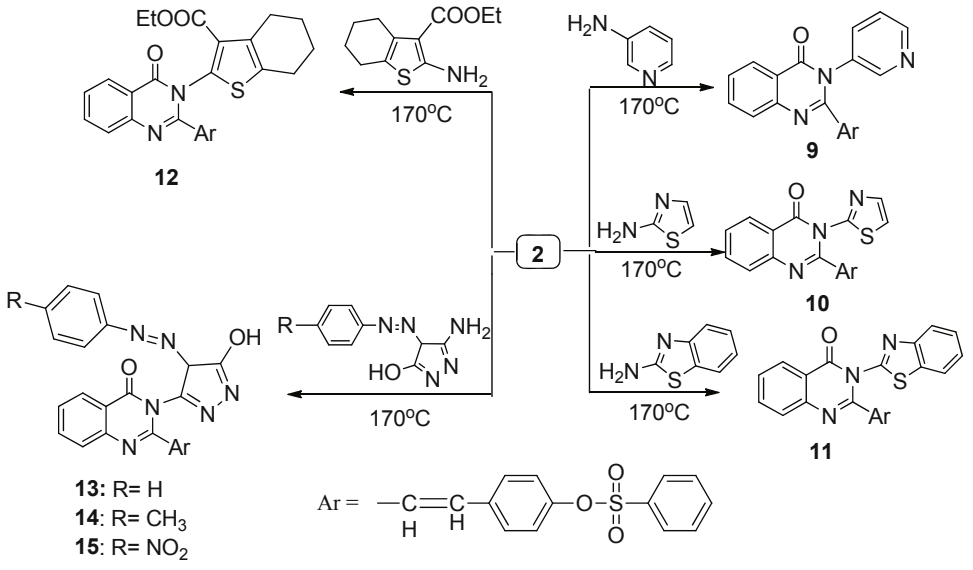
On the other hand, quinazolone derivative **5e** underwent acetylation and benzoylation with acetic anhydride, benzoylchloride and/or benzenesulfonylchloride to afford quinazolone derivatives **6a-c**, respectively. Besides, heating of **5e** with ethylchloroacetate in dry acetone under reflux on a steam bath afforded the corresponding ethyl-2-(4-(4-oxo-2-(4-((phenylsulfonyl)oxy)styryl)quinaz -olin-3(4*H*)-yl)phenoxy)acetate 7. In addition, treatment of **5e** with chloroacetylchloride in dry pyridine gave the corresponding (*E*)-4-(4-oxo-2-(4-(phenylsulfonyloxy) styryl)quinazolin-3 (4*H*)-yl)phenyl 2-chloroacetate **8** (Scheme 3).

Synthesis of quinazolone moiety fused to another heterocyclic ring has attracted wide spread attention (Hassan et al, 2011; Habib et al, 2014) because of their excellent tribological performance. In the present work, fusion of benzoxazinone **2** with some heterocyclic amines, namely 3-aminopyridine, 2-aminothiazole, 2-aminobenzothiazole and ethyl-2-amino-4,5,6,7-tetrahydrobenzo [b]thiophene-3-carboxylate at 170-175 °C, gave the corresponding quinazolone derivatives **9-12**, respectively. Analogously, the appropriate 5-amino-4-(aryldiazenyl)-4*H*-pyrazol-3-ol derivatives reacted with compound **2** under the same experimental conditions to give the corresponding **13-15**, respectively (Scheme 4).

The reactivity of benzoxazinone derivative **2** toward hydrazine hydrate as a nitrogen nucleophile was investigated herein. Treatment of **2** with hydrazine hydrate in ethanol under reflux, obtained only one product (as



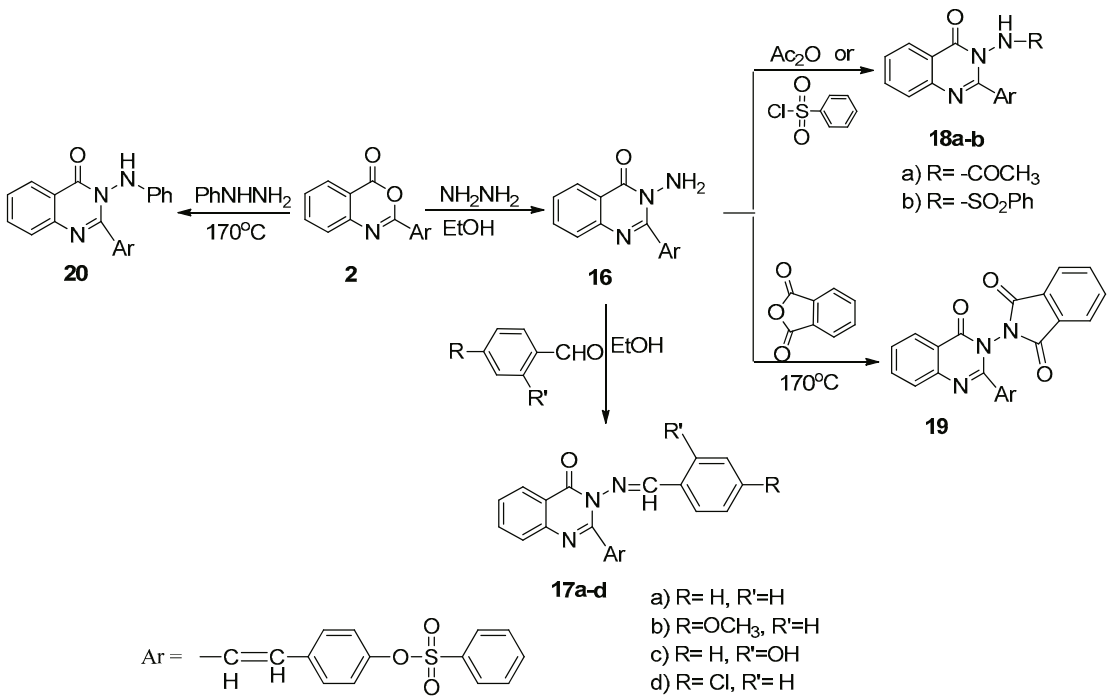
Scheme 3 Reaction of quinazolone derivative **5e** with alkyl halides



Scheme 4 Reaction of benzoxazinone derivative **2** with some heterocyclic amines

tested by thin layer chromatography) that was identified as 4-(2-(3-amino-4-oxo-3, 4-dihydroquinazolin-2-yl) vinyl) phenylbenzene sulfonate **16**. The potential activities of Schiff bases as oxidation and corrosion inhibitors for local lubricating oils are well known (El-Mekabaty et al, 2012). These reports prompted us to synthesis a new series of Schiff bases linked with quinazolone derivatives hoping that these new products might possess excellent tribological performance and enhance the characteristics of lubricating oils to a great extent. So, condensation of compound **16** with some aromatic aldehydes, namely benzaldehyde, p-anisaldehyde, o-hydroxybenzaldehyde and p-chlorobenzaldehyde, in boiling ethanol containing few drops of piperidine afforded the corresponding Schiff bases **17a-d**, respectively. Moreover, quinazolone derivative **16** underwent acetylation and benzoylation with acetic anhydride and/or benzenesulfonylchloride giving **18a-b**, respectively. Fusion of compound 16 with phthalic anhydride at 170 °C gave 4-(2-(3-(1,3-dioxoisoindolin-2-yl)-4-oxo-3,4-di hydroquinazolin-2-yl)vinyl)phenylbenzene sulfonate **19** (Scheme 5).

Finally, we also studied the reactivity of benzoxazinone derivative **2** towards phenyl hydrazine as a nitrogen nucleophile as a possible synthetic route to get new quinazolones. So, heating of **2** with phenyl hydrazine at 170 °C afforded a single product identified as (*E*)-4-(2-(4-oxo-3-(phenylamino)-3,4-dihydroquinazolin-2-yl)vinyl) phenylbenzene sulfonate **20** (Scheme 5).



Scheme 5 Synthesis pathway for compounds **16-20**

3.2 Antioxidant and anticorrosive additives

3.2.1 Evaluation of the prepared compounds as antioxidant additives for the tested lubricating oil

Air oxidation of aliphatic hydrocarbons takes place by a series of free radical reactions as shown by the following scheme:

Initiation:

$$RH + O_2 \rightarrow R^{\bullet} + {}^{\bullet}OOH$$

Propagation:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$

$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH$$

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$$

Termination:

$$RO^{\bullet} + R^{\bullet} \rightarrow ROR$$

$$RO^{\bullet} + RO^{\bullet} \rightarrow ROOR$$

The principle requirement for the majority of antioxidants is the presence of labile hydrogen, or the presence of sulphur, in their chemical structure. It was reported that, the antioxidant molecule reacts with the peroxy radicals which were formed during oxidation, and leads to the formation of inactive products as shown in the following scheme (El-Mekabaty et al, 2012):

$$ROO^{\bullet} + AH \rightarrow ROOAH$$

Followed by:

$$ROOAH + ROO\cdot \rightarrow \text{inactive product}$$

or:

$$ROO^{\bullet} + AH \rightarrow ROOH + A\cdot$$

$$ROO^{\bullet} + A^{-} \rightarrow \text{inactive product}$$

where, AH is the antioxidant molecule and A is an antioxidant radical. Thus, as the labile hydrogen atoms increase, the efficiency of the antioxidant would also be increased.

To verify the effectiveness of the synthesized compounds as antioxidants, different solutions were prepared by adding 0.1 g of the selected compound to 1L of the additive free tested lubricating oil, then the lubricating oil with and without additives was subjected to severe oxidation at 155 °C for 36 h. Samples were taken at regular intervals of 3 h and tested for their oxidation stability in terms of the total acid number (TAN) according to ASTMD 3242. It was found that, in the absence of additives, the oxidation products increased with time. When the prepared additives **2**-**20** were added to the tested oil at a concentration of 0.1 $g \cdot L^{-1}$, the oxidation products also increased with time but at a rate much lower than that without additives. Figs. 1-6 and Table 4 showed that, the TAN of the oil samples containing the prepared compounds after 36 h oxidation showed good oxidation resistant properties compared with additive-free oil. The highest antioxidant activity was observed in the presence of **10**-**15** compounds due to the presence of some antioxidant groups in each of them. We can conclude that, the thiazole, benzothiazole, thiophene moieties, C=C and C=N groups in compounds **10**-**12** may be responsible for its antioxidant activity (acid number= 4.8, 4.9, 5.0 mg-KOH/g-oil respectively). Also, the pyrazole ring, azo, OH and

−C=N groups in compounds **13-1**5 may be responsible for their antioxidant activity (acid number= 4.8, 4.5, 4.1 mg-KOH/g-oil respectively). The data given in Table 4 reveals that quinazolinone derivatives **11** and **12** (acid number =4.9, 5.0 mg-KOH/g-oil respectively) exhibited a lesser antioxidant result than pyrazolo derivatives **14** and **15** (acid number= 4.5, 4.1 mg-KOH/g-oil respectively). This may be attributed to the presence of the pyrazole moiety, OH and azo groups in **14** and **15** which could play a role in increasing the oxidation inhibition of the lubricating oil.

Table 4 Determination of peroxide, carbonyl, ester and hydroxyl values of the tested lubricating oil samples without and with 0.1 g/L of additives **2-20** at 155 °C up to 36 hours

Compound No.	Acid value	Peroxide value	Carbonyl value	Ester value	Hydroxyl value
Oil without additive	11.7	16.5	36.0	60.0	125.0
2	10.3	8.2	30.6	54.4	111.3
3	8.2	11.2	25.6	41.5	63.6
4	7.6	10.8	16.5	42	54
5a	7.1	8.9	10.9	40.3	39.5
5b	8.8	9.5	21.2	51.3	66.7
5c	9.1	10.5	22.8	46.7	71.5
5d	8.8	9.9	15.4	40.5	66.8
5e	9	9.8	14.4	48.4	57.8
6a	7.2	11.2	30.2	44.6	91.5
6b	7.6	10.1	22.2	50.6	86.7
6c	10	13.4	18.7	34.6	74.7
7	10.5	7.8	12.5	49.6	66.7
8	9.5	13	27.6	56.7	84
9	7.8	12.4	28.5	50.4	75
10	4.8	6.8	7.8	33.6	39.5
11	4.9	8.4	6.1	36	23
12	5.0	10.4	27.6	44.5	85.7
13	4.8	7.4	9.7	40.4	46.7
14	4.5	4.5	8.3	34.2	12.9
15	4.1	4.1	7.6	30	9.3
16	5.2	5.2	10.5	40.3	66.8
17a	6.9	6.9	9.9	51	45.5
17b	7.1	7.1	9.4	50	42
17c	7.2	7.2	10.6	33.6	40.4
17d	9.2	9.2	10.2	45	66
18a	10	10	9.9	51.3	57.8
18b	9.4	9.4	11.2	40.5	86.7
19	7.4	7.4	6.8	45.4	37.8
20	6.7	6.7	10.2	44	61

3.2.2 Evaluation of the prepared compounds as corrosion inhibitors for the tested lubricating oil

The prepared compounds were tested as corrosion inhibitors for the corresponding lubricating oil using seven different strips of metals with surface area of 1 cm^2. The results reveal that in oil with additives of all compounds **2-20**, higher corrosion inhibition was observed than in the oil without additives.

Mechanism of corrosion inhibition

In oil, compounds **2-20** exist in general as neutral

molecules, thus adsorption can be considered as a mechanism of corrosion inhibition. The neutral compound may be adsorbed on the metal surface via a chemisorption mechanism, involving the displacement of oil molecules from the metal surface and electron sharing between the N, O and S atoms and the metal. In addition, lone-pair electrons of N and O atoms in the investigated compounds may combine with freshly generated M^{2+} or M^{3+} ions on metal surface forming metal inhibitor complexes.

$$M \rightarrow M^{2+} + 2e \quad (1)$$

$$Inh. + M^{2+} \leftrightarrow [Inh.\text{-}M]^{2+} \quad (2)$$

$$[Inh.]n^{+} + M^{2+} \leftrightarrow [Inh._{n}\text{-}M]^{(2+n)+} \quad (3)$$

M= Fe and Cu

In case of aluminum as metal the equations will be as follows:

$$Al \rightarrow Al^{3+} + 3e \quad (4)$$

$$Inh. + Al^{3+} \leftrightarrow [Inh.\text{-}Al]^{3+} \quad (5)$$

$$[Inh.]n^{+} + Al^{3+} \leftrightarrow [Inh._{n}\text{-}Al]^{(3+n)+} \quad (6)$$

These complexes might get adsorbed onto metal surface by van der Waals forces to form protective films. It can be concluded that the mode of adsorption depends on the affinity of the metal towards the π-electron clouds of the ring system. Metals such as Cu and Fe, which have a greater affinity towards aromatic moieties, were found to adsorb benzene rings in a flat orientation. Thus, it is reasonable to assume that the tested inhibitors are adsorbed in a flat orientation through the N- and O-atoms. It was found that, compounds **2-20** were all good corrosion inhibitors for all the used metals. This might be attributed to the presence of heterocyclic moieties in their structures, and also the presence of NH, C=N groups and sulphur atoms which may react with these metals to form the corresponding sulphides. These results agree with that reported by Gad Allah et al (1989).

3.2.3 Effect of concentration

To study the optimum concentration for the prepared compounds, as additives, that gave the highest antioxidant efficiency, five different concentrations of additives **13-15**, namely 0.01, 0.03, 0.05, 0.07 and 0.1 g, for 1 L oil were used. The results (Figs. 7-9 and Table 5) showed that the increasing additive concentration would lead to a decrease of oxidative products, and the concentration of 0.1g for 1L oil is the most effective concentration of additives **13-15**.

3.2.4 Thermal stability of the prepared antioxidant additives

Some of the highly effective antioxidant additives, namely **10-15**, were subjected to thermal analysis using TGA and DTGA techniques. The data indicated that, the first stage of decomposition for compounds **10-14** begin at 258.8, 155.65, 232.48, 247.89 and 252.96 ºC respectively, and ends at 378.43, 233.32, 487.29, 405.72 and 430.87 ºC with a weight loss of 41.17%, 4.2%, 71.38%, 35.27% and 71.88%, respectively. Whereas, compound **15** exhibited six stages of decomposition in which the first stage begins at 163.64 ºC

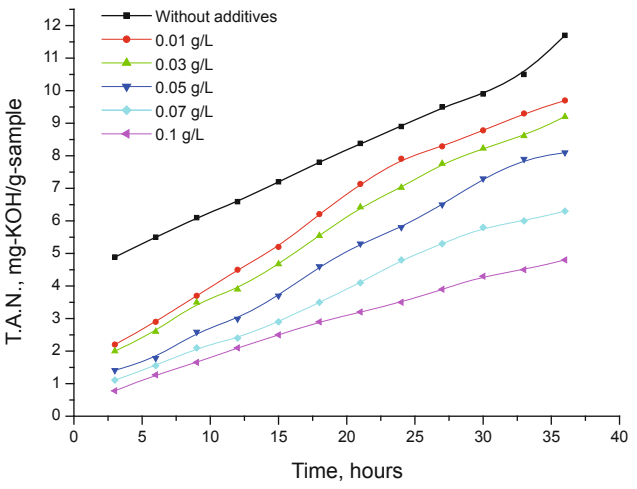


Fig. 7 Variation of the T.A.N. with oxidation time of the tested lubricating oil sample without and with different concentrations of compound **13** at 155 ºC up to 36 hours

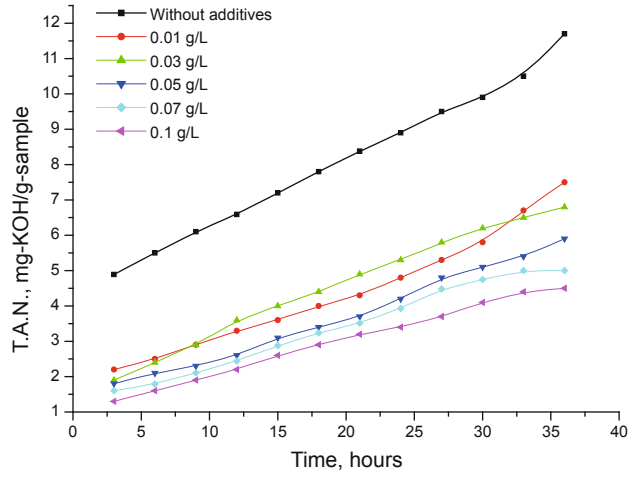


Fig. 8 Variation of the T.A.N. with oxidation time of the tested lubricating oil sample without and with different concentrations of compound **14** at 155 ºC up to 36 hours

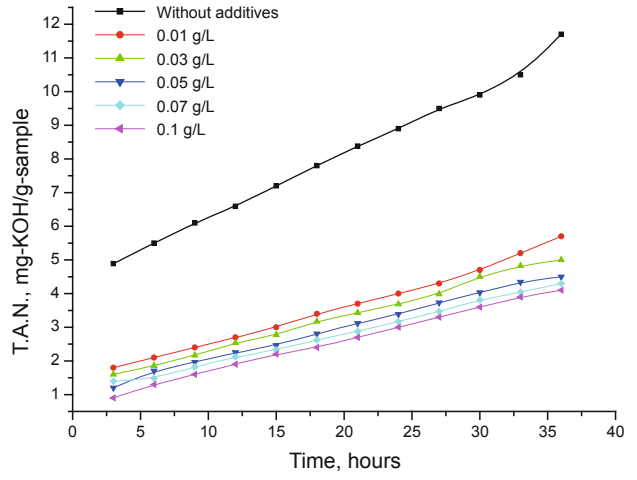


Fig. 9 Variation of the T.A.N. with oxidation time of the tested lubricating oil sample without and with different concentrations of compound **15** at 155 ºC up to 36 hours

Table 5 Variation of TAN with oxidation time of the tested lubricating oil samples without and with different concentrations of compounds **13-15** at 155 °C up to 36 hours

Compound No.	Concentration g/L	Time, hours											
		3	6	9	12	15	18	21	24	27	30	33	36
Without additives	0.1	4.8	5.5	6.1	6.59	7.2	7.8	8.38	8.9	9.5	9.9	10.5	11.7
13	0.01	2.2	2.9	3.7	4.5	5.2	6.2	7.1	7.9	8.2	8.7	9.3	9.7
	0.03	2.0	2.6	3.5	3.9	4.6	5.5	6.4	7.0	7.7	8.2	8.6	9.2
	0.05	1.4	1.7	2.5	2.9	3.7	4.6	5.3	5.8	6.5	7.3	7.9	8.1
	0.07	1.1	1.5	2.1	2.4	2.9	3.5	4.1	4.8	5.3	5.8	6.0	6.3
	0.1	0.7	1.2	1.6	2.1	2.5	2.9	3.2	3.5	3.9	4.3	4.5	4.8
14	0.01	2.2	2.5	2.9	3.3	3.6	4	4.3	4.8	5.3	5.8	6.7	7.5
	0.03	1.9	2.4	2.9	3.6	4.0	4.4	4.9	5.3	5.8	6.2	6.5	6.8
	0.05	1.8	2.1	2.3	2.6	3.1	3.4	3.7	4.2	4.8	5.1	5.4	5.9
	0.07	1.6	1.7	2.1	2.4	2.8	3.2	3.5	3.9	4.4	4.7	5.0	5.0
	0.1	1.3	1.6	1.9	2.2	2.6	2.9	3.2	3.4	3.7	4.1	4.4	4.5
15	0.01	1.8	2.1	2.4	2.7	3	3.4	3.7	4	4.3	4.7	5.2	5.7
	0.03	1.6	1.8	2.1	2.5	2.7	3.1	3.4	3.6	3.9	4.5	4.8	4.9
	0.05	1.2	1.7	1.9	2.2	2.4	2.8	3.1	3.3	3.7	4.0	4.3	4.4
	0.07	1.4	1.5	1.8	2.1	2.3	2.6	2.8	3.1	3.4	3.8	4.1	4.2
	0.1	0.9	1.3	1.6	1.9	2.2	2.4	2.7	3	3.3	3.6	3.9	4.1

and ends 190.07 ºC with a weight loss of 1.864%. The above results indicate that, these compounds are thermally stable and thus, could be used under thermal conditions.

3.2.5 Comparison of the oxidation stability between the tested oil containing the prepared products with lube oil containing a commercial additive

A comparison of the oxidation stability of the tested lubricating oil containing the highly efficient prepared antioxidants (0.1 g·L^{-1}) with a lubricating oil containing a commercial antioxidant additive purchased from the local market (CO-OP Cosf/cc 21 w 151 oil) was made and the results, obtained after 36 h oxidation at 155 °C, are shown in Fig. 10 and Table 6. It can be seen that the lubricating oil containing the compounds **10-15** showed better oxidation stability than that containing commercial antioxidant additive.

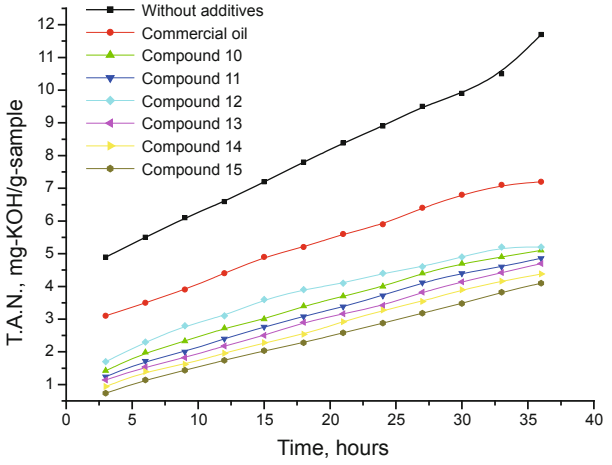


Fig. 10 A comparison between the T.A.N. of the tested lubricating oil samples containing 0.1 g/L of compounds **10-15** with commercial lube oil sample at 155 ºC up to 36 hours oxidation

4 Conclusion

Benzoxazinone derivative **2** was used as a building block for synthesis of some new quinazoline derivatives, and the functionalized quinazoline derivatives were evaluated as oxidation and corrosion inhibitors for local lubricating oils. The highest antioxidant and anticorrosion activities were obtained with compounds **10-15**. The optimum concentration was found to be 0.1g for 1L of oil for these new additives especially for compounds **13-15**. In addition, some of the highly effective antioxidant additives, namely **10-15**, were subjected to thermal analysis and the results indicated that, these compounds are thermally stable and could be used under thermal conditions. Moreover, a comparison of the oxidation stability of the tested lubricating oil containing the prepared products with that containing commercial additives showed that the lubricating oil containing the compounds **10-15** had better oxidation stability than that containing commercial additives. It was found that molecules with aryl sulfonate, benzoxazinone, and quinazolone moieties would possess high antioxidant and anticorrosive characteristics; quinazolone with thiazole, benzothiazole and thiophene ring would possess good antioxidant and anticorrosive performance as in case of compounds **10-12**.

Table 6 A comparison between the T.A.N. of the tested lubricating samples containing 0.1 g/L of compounds **10-15** with the commercial lubricating oil sample at 155 ºC up to 36 hours oxidation

Compound No.	Time, hours											
	3	6	9	12	15	18	21	24	27	30	33	36
Oil without additives	4.89	5.5	6.1	6.59	7.2	7.8	8.38	8.9	9.5	9.9	10.5	11.7
Commercial oil	3.1	3.5	3.9	4.4	4.9	5.2	5.6	5.97	6.4	6.8	7.1	7.2
10	1.1	1.5	2	2.6	3	3.4	3.7	4	4.4	4.7	4.9	4.8
11	1.2	1.6	1.8	2.2	2.6	3	3.3	3.6	4	4.4	4.6	4.9
12	1.7	2.3	2.8	3.1	3.6	3.9	4.1	4.4	4.6	4.9	5.2	5.0
13	0.7	1.2	1.6	2.1	2.5	2.9	3.2	3.5	3.9	4.3	4.5	4.8
14	1.3	1.6	1.9	2.2	2.6	2.9	3.2	3.4	3.7	4.1	4.4	4.5
15	0.9	1.3	1.6	1.9	2.2	2.4	2.7	3	3.3	3.6	3.9	4.1

References

Amer F A, Hassan H M, Moawad E B, et al. Synthesis and evaluation of some new thiazoles as antioxidant additives for Egyptian lubricating oils. Advances in Petroleum Exploration and Development. 2011. 1: 40-49

Branes J R and Bell J C. Laboratory screening of engine lubricants for high temperature performance. Lubrication Engineering. 1989. 45: 549-553

El-Mekabaty A. Improvement of lubricating oils characters using novel additives. International Journal of Modern Organic Chemistry. 2012. 1: 72-95

El-Mekabaty A, Habib O M O, Hassan H M, et al. Synthesis and evaluation of some new oxazolones and imidazolones as antioxidant additives for Egyptian lubricating oils. Petroleum Science. 2012. 9: 389-399

Gad Allah A G, Badawy M W, Rehan H H, et al. Inhibition of corrosion of α-brass (Cu-Zn, 67/33) in acid chloride solutions by some amino pyrazole derivatives. Journal of Applied Electrochemistry. 1989. 19: 928-932

Habib O M O, Hassan H M and El-Mekabaty A. Synthesis and evaluation of some new quinazolones as antioxidant additives for Egyptian lubricating oils. Petroleum Science and Technology. 2014. 2: 125-134

Habib O M O, Hassan H M, Moawad E B, et al. Synthesis of some novel antioxidant and anticorrosive additives for Egyptian lubricating oils. Petroleum Science and Technology. 2012. 30: 2435-2449

Habib O M O, Hassan H M and Moawad E B. Evaluation of some heterocycles as antioxidant additives for lubricating oils. Petroleum Science and Technology. 2010. 28: 1059-1067

Hassan H M, Habib O M O, Moawad E B, et al. Synthesis of some novel antioxidant and anticorrosive additives for Egyptian gasoline motor oils. Lubrication Science. 2011. 23: 119-138

Hassan H M, Amer F A, Moawad E B, et al. Synthesis and applications of some new antioxidant and anticorrosive additives for Egyptian diesel motor oils. Lubrication Science. 2010. 22:163-181

Hassan H M. Utility of bacterial biomass as antioxidant, anticorrosive and antifriction additives for lubricating oils. Petroleum Science and Technology. 2011. 29: 2086-2094

Hassan H M. Utility of some new multifunctional additives to Egyptian gasoline. Indian Journal Technology. 1998. 5: 343-345

Hsu S M. Review of laboratory bench tests in assessing the performance of automotive crankcase oils. Lubrication Engineering, 1981. 37:722-727

Huang J W. Tribological properties of benzothiazole derivatives as additives in rapeseed oil. Tribology International. 2003. 23: 45-48

Huang J W, Dong X J, Li F F, et al. The performance and antiwear mechanism of (2-sulphurone-benzothiazole)-3-methyl esters as additives in synthetic lubricants. Tribology International. 2000. 33: 553-558

Huang J W, Dong X J, Li F F, et al. The tribological study of (2-sulphurone-benzothiazole) -3-methyl-di-butylborate. Lubrication Science. 2001. 14: 73-81

Ren T H, Xue Q J and Wang H Q. The tribological properties of S-(1H-benzotrizole-yl) methyl alkyl xanthates as additives in synthetic lubricants. Lubrication Engineering. 1995. 51: 847-850

Ren T H, Xue Q J and Wang H Q. A study of S-(1H-benzotriazol-1-yl)-methyl N, N-dialkyldithiocarbamates as novel multifunctional oil additives. Wear. 1994. 172: 59-64

Singh T and Chandrasekharan C V. The effect of nitrogen and sulphur compounds as extreme pressure lubricant. Tribology International. 1993. 26: 245-250

Singh T, Singh R, Verma V K, et al. Study of N, O and S heterocyclic compounds as extreme pressure lubricant additives. Tribology International. 1990. 23: 41-46

Singh T, Hattacharga B A and Verma V K. EP activity assessment of certain nitrogen and sulphur heterocyclic compounds as potential additives in four balls test. Lubrication Engineering. 1989. 46: 681-685

Wan Y, Pu Q, Xue Q J, et al. Antiwear and extreme pressure characteristics of 2-mercaptobenzothiazole derivative as the potential lubricating additive. Wear. 1996. 192: 74-77

Wesolowski M. Thermal analysis of petroleum products. Thermochimica Acta. 1981. 46: 21-25

Xu D X, Wan Y and Cao L L. Tribological performance and action mechanism of S-alkyl and S-benzimidazole substituted dialkyldithiocarbamates. Wear. 2000. 241: 41-46

Zhang J Y, Liu W M and Xue Q J. The tribological behaviors of 2-mercaptobenzoxazole derives as additives in liquid paraffin. Wear. 1998. 219: 184-187

Zhang J Y, Liu W M and Xue Q J. The effect of molecular structure of heterocyclic compounds containing N, O and S on their tribological performance. Wear. 1999a. 231: 65-70

Zhang J Y, Liu W M and Xue Q J. A study of 2-(dibutylaminomethyl)-thiobenzimidazole as an oil additive. Wear. 1999b. 231: 279-84

Zeman A. DSC, PDSC—Possible use in the assessment of the thermal oxidative stability of synthetic oils for aircraft turbines. Schmiertecknik and Tribologie. 1982. 29: 55-61

Zeman A, Stuwe R and Koch K. The DSC cell—A versatile tool to study thermal-oxidative degradation of lubricants. Thermochimica Acta. 1984. 80:1-6

(Edited by Zhu Xiuqin)