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Synthesis and Evaluation of Some New Thiazoles as Antioxidant Additives for Egyptian Lubricating Oils

F. A. Amer[1]**;**
H. M. Hassan[1,*]**;**
E. B. Moawad[1]**;**
Noha Shaker[1]

[1] Chemistry Department, Faculty of Science, Mansoura University, Mansoura, 35516, Egypt

* Corresponding author. Email: prof.drhussain@yahoo.com

Abstract: 4-(2-Aminothiazol-4-yl)-phenol (1) reacted with 2-(4-methoxy-benzylidene)-malononitrile or 1,3-diphenyl-1H-pyrazole-4-carbaldehyde to afford enaminonitrile, pyrazolo derivatives 2 and 3, respectively. On the other hand, methylation of 1 afforded the acetyl derivative 4 which reacted with phenyl isothiocyanate, diazonium salt, acetic anhydride, cyclic anhydride, ethyl acetoacetate, benzaldehyde or phosphorous oxychloride to afford compounds 5-9, 11 and 12, respectively. Moreover, the compound 12 reacted with ethyl cyanoacetate to afford compound 13. A one-pot reaction of compound 1 with ethyl acetoacetate and benzaldehyde afforded compound 10. The synthesized compounds were evaluated as antioxidant additives for lube oil.

Key words: Aminothiazole; Condensation; Antioxidant Additives

1. INTRODUCTION

Organic species in mineral oils and lubricants are subjected to deterioration by oxidation, especially at high temperatures and in the presence of air and metal (Ohgake *et al*., 1989). The lube oils suffer from auto-oxidation as a result of contact with air at elevated temperatures for long periods and in contact with metals, to form oxygenated compounds which increase the oil viscosity and motor metal corrosions. Thiazole derivatives were reported in the literature to be used as antioxidant additives (Singh *et al.*, 1990; Huang *et al*., 2004; Wei *et al*., 1989; Jones Jr *et al*., 2000; Weijiu *et al*., 2001; Wei & Song, 1992). Lubricating oils produced by solvent refining of high boiling petroleum distillates consist mainly of long chain hydrocarbon molecules.

In the internal combustion engines, lube oils suffer from autoxidation as a result of contact at elevated temperatures with air rate for long periods and metals, *e.g.* iron, copper, aluminum, etc. were used in the manufacture of the engine. These metals act as catalyst for oxidation and resulting in the formation of oxygenated oil soluble and insoluble products which exert an adverse effect on the performance of the lube oils (Hassan *et. al*., 1985; Hassan *et. al*., 1998; Hassan *et. al*., 2000; Fa çanha *et. al*., 2007; Aucelio *et. al*., 2007; Suzuki *et al*., 2009).

2. RESULTS AND DISCUSSION

Many types of organic heterocyclic compounds were used as antioxidant additives for lubricating oils. In continuation to our previous studies in this field (Hassan & Habib *et. al*., 2010; Hassan & Amer *et. al*., 2010; Hassan, 2010), some new heterocyclic compounds **1-13** were prepared and their antioxidant activities for some Egyptian gasoline motor oils were evaluated. These compounds were characterized by elemental analyses and spectral data as shown in Tables 1 and 2.

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Tab. 1: Characterization Data of Newly Prepared Compounds

Cpd. No.	m.p. (℃), Crystallization Solvent	Yield (%)	Mol. Formula (Wt.)	Elemental analysis Calc. (Found)		
				C%	H%	N%
1	140, EtOH	79	$C_9H_8N_2OS$ (192.24)	56.23 (56.34)	4.19 (4.23)	14.57 (14.64)
2	210, aq. EtOH	61	$C_{20}H_{16}N_4O_2S$ (376.43)	63.81 (63.85)	4.28 (4.31)	14.88 (14.92)
3	156, AcOH	65	$C_{25}H_{18}N_4OS$ (422.50)	71.07 (71.11)	4.29 (4.34)	13.26 (13.35)
4	195, EtOH	73	$C_{10}H_{10}N_2OS$ (206.26)	58.23 (58.35)	4.89 (4.97)	13.58 (13.64)
5	210, Benzene	52	$C_{17}H_{15}N_3OS_2$ (341.45)	59.80 (59.88)	4.43 (4.47)	12.31 (12.39)
6	245, MeOH	65	$C_{22}H_{21}N_7O_3S_2$ (495.58)	53.32 (53.37)	4.27 (4.30)	19.78 (19.86)
7	200, DMF-EtOH	73	$C_{12}H_{12}N_2O_2S$ (248.30)	58.05 (58.14)	4.87 (4.93)	11.28 (11.36)
8	139-141, AcOH	65	$C_{18}H_{12}N_2O_3S$ (336.36)	64.27 (64.32)	3.60 (3.68)	8.33 (8.42)
9	125, Xylene	80	$C_{14}H_{14}N_2O_3S$ (290.34)	57.92 (57.86)	4.86 (4.79)	9.65 (9.61)
10	265, Acetone	53	$C_{20}H_{16}N_2O_3S$ (364.42)	65.92 (65.99)	4.43 (4.50)	7.69 (7.78)
11	246, EtOH	74	$C_{17}H_{14}N_2OS$ (294.37)	69.36 (69.47)	4.79 (4.87)	9.52 (9.56)
12	> 300, DMF-Ethylacetate	68	$C_{11}H_{10}N_2O_2S$ (234.27)	56.39 (56.45)	4.30 (4.37)	11.96 (12.03)
13	> 300, DMF-EtOH	79	$C_{16}H_{15}N_3O_3S$ (329.37)	58.34 (58.38)	4.59 (4.62)	12.76 (12.83)

Tab. 2: Spectral Data of the Newly Prepared Compounds

Compound No.	Spectral data
1	IR (KBr)$\nu_{max.}$ cm^{-1}: 3484 (OH), 3376, 3124 (NH_2), 1508 (C=N). MS: *m/z* (%), 193 (M^++1, 22.1), 176 (M^+, 33), 100 (35.2), 76 (100.0), 85 (68.1). ^{1}H NMR (DMSO) (δ, ppm), 6.70-6.75 (m, 4H, Ar-H), 6.94 (s, 1H, CH, thiazole), 7.60 (s, 2H, NH_2), 9.42 (s, 1H, OH).
2	IR (KBr)$\nu_{max.}$ cm^{-1}: 3419 (OH), 3342, 3261 (NH_2), 2200 (CN), 1608 (C=N). MS: m/z (%), 377 (M^++1, 15.7), 376 (M^+, 19.1), 341 (64.5), 268 (100.0), 222 (31.0), 192 (30.5), 148 (42.8), 108 (11.0). ^{1}H NMR ($CDCl_3$) (δ, ppm), 1.21 (s, 1H, CH), 2.25 (s, 2H, NH_2), 3.33 (s, 1H, OH), 3.73 (s, 3H, OCH_3), 6.93-7.47 (m, 8H, Ar-H).
3	IR (KBr)$\nu_{max.}$ cm^{-1}: 3461 (OH), 3338, 3272 (NH_2), 3099 (=C-H, stretching). MS: m/z (%), 421 (M^+-1, 32.4), 342 (29.0), 318 (33.4), 271 (100.0), 245 (63.3), 197 (38.0), 168 (41.7), 123 (45.2), 69 (15.0). ^{1}H NMR (DMSO) (δ, ppm), 5.56 (s, 1H, OH), 7.12-7.98 (m, 14H, Ar-H), 8.56 (s, 1H, CH, pyrazole), 9.32 (s, 1H, CH, thiazole), 10.0 (s, 1H, CH, aliphatic).
4	IR (KBr)$\nu_{max.}$ cm^{-1}: 3268, 3114 (NH_2), 1623 (C=N). MS: m/z (%), 207 (M^++H, 13.15), 206 (M^+, 69.1), 191 (59.0), 163 (27.1), 149 (100.0), 121 (46.3), 93 (16.2), 77 (37.3), 63 (15.9), 60 (10.8). ^{1}H NMR (DMSO) (δ, ppm), 3.76 (s, 3H, OCH_3), 6.81 (s, 1H, CH, thiazole), 7.73 (s, 2H, NH_2), 6.90-6.96 (m, 4H, Ar-H).

To be continued

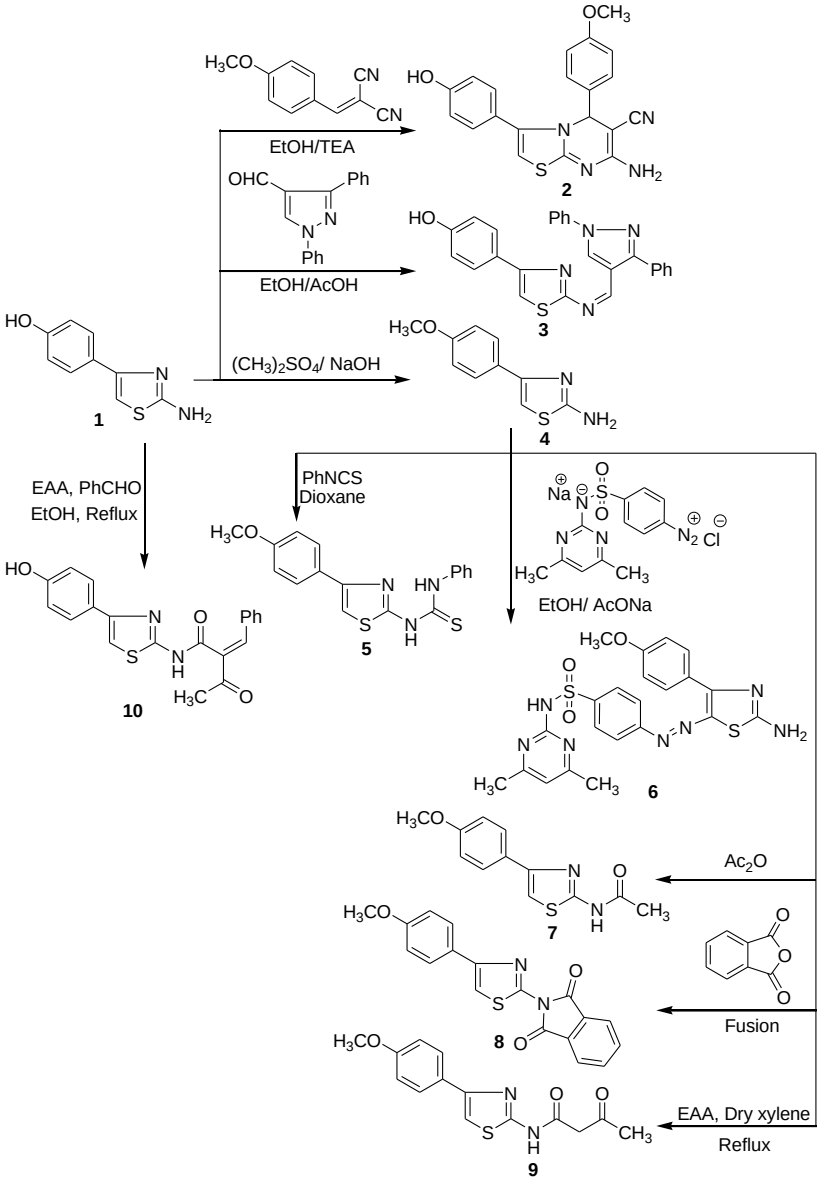
Continued

Compound No.	Spectral data
5	IR (KBr)$\nu_{max.}$ cm^{-1}: 3183, 3045 (2NH). MS: m/z (%), 341 (M^+, 25.0), 206 (100.0), 151 (70.0), 77 (55.0), 63 (40.0). ^{1}H NMR (DMSO) (δ, ppm), 3.3 (s, 2H, 2NH), 3.8 (s, 3H, OCH_3), 7.36 (s, 1H, CH, thiazole), 7.38-7.51 (m, 9H, Ar-H).
6	IR (KBr)$\nu_{max.}$ cm^{-1}: 3311, 3205 (NH_2), 3025 (NH), 1538 (N=N). MS: m/z (%), 495 (M^+, 34.6), 478 (40.6), 447 (39.9), 430 (68.8), 402 (42.9), 340 (96.3), 279 (55.5), 261 (45.2), 248 (46.0), 223 (55.2), 194 (71.8), 138 (67.9), 107 (63.6), 70 (100.0). ^{1}H NMR (DMSO) (δ, ppm), 3.89, 3.92 (s, 6H, $2CH_3$), 3.92 (s, 3H, OCH_3), 6.74 (s, 2H, NH_2), 7.02-8.03 (m, 8H, Ar-H), 8.04 (s, 1H, CH, thiazole), 11.8 (s, 1H, NH).
7	IR (KBr)$\nu_{max.}$ cm^{-1}: 3168, 3065 (NH), 2835 (CH, aliphatic), 1697 (C=O). MS: m/z (%), 248 (M^+, 4.65), 192 (100.0), 150 (41.5), 121 (76.6), 105 (16.9), 93 (22.7), 77 (35.4), 63 (45.9). ^{1}H NMR (DMSO) (δ, ppm), 3.79 (s, 3H, $COCH_3$), 4.05 (s, 3H, OCH_3), 6.96 (s, 1H, CH, thiazole), 6.97-7.83 (m, 4H, Ar-H), 12.2 (br, s, 1H, NH).
8	IR (KBr)$\nu_{max.}$ cm^{-1}: 1668 (2C=O). MS: m/z (%), 337 (M^++1, 26.7), 336 (M^+, 66.7), 250 (26.7), 191 (33.3), 164 (86.7), 104 (66.7), 76 (100.0). ^{1}H NMR (DMSO) (δ, ppm), 3.81 (s, 3H, OCH_3), 6.93 (s, 1H, CH, thiazole), 6.96-7.83 (m, 8H, Ar-H).
9	IR (KBr)$\nu_{max.}$ cm^{-1}: 3147, 3112 (NH), 2840 (CH, aliphatic), 1735, 1675 (2C=O). MS: m/z (%), 290 (M^+, 20.9), 289 (M^+-1, 100.0), 268 (47.6), 248 (16.2), 232 (30.2), 202 (23.9), 185 (24.5), 159 (16.1), 129 (18.2), 85 (33.6). ^{1}H NMR (DMSO) (δ, ppm), 2.21 (s, 3H, $COCH_3$), 3.76 (s, 2H, CH_2), 3.79 (s, 3H, OCH_3), 6.81 (s, 1H, CH, thiazole), 6.9-7.84 (m, 4H, Ar-H), 12.25 (s, 1H, NH).
10	IR (KBr)$\nu_{max.}$ cm^{-1}: 3407 (OH), 3133, 3054 (NH), 1702, 1633 (2C=O). MS: m/z (%), 365 (M^++1, 22.0), 364 (M^+, 25.7), 338 (20.2), 303 (19.7), 285 (24.6), 262 (25.3), 236 (37.9), 206 (100.0), 191 (48.4), 149 (49.6), 118 (33.1), 77 (19.8). ^{1}H NMR (DMSO) (δ, ppm), 3.76 (s, 3H, $COCH_3$), 3.8 (s, 3H, OCH_3), 4.58 (s, 1H, CH), 6.81 (s, 1H, CH, thiazole), 6.93-7.82 (m, 9H, Ar-H), 13.62 (s, 1H, NH), 14.6 (s, 1H, OH).
11	IR (KBr)$\nu_{max.}$ cm^{-1}: 1623 (C=N). MS: m/z (%), 296 (M^++2, 11.6), 295 (M^++1, 18.6), 294 (M^+, 41.9), 293 (M^+-1, 25.6), 206 (79.1), 149 (83.7), 64 (100.0). ^{1}H NMR (DMSO) (δ, ppm), 3.83 (s, 3H, OCH_3), 5.65 (s, 1H, N=CH), 6.72 (s, 1H, CH, thiazole), 6.75-7.72 (m, 9H, Ar-H).
12	IR (KBr)$\nu_{max.}$ cm^{-1}: 3259, 3193 (NH_2), 1671 (C=O). MS: m/z (%), 234 (M^+, 29.0), 232 (M^+-2, 49.0), 207 (34.1), 192 (42.2), 165 (30.3), 146 (30.8), 133 (50.1), 120 (100.0), 98 (71.3), 77 (75.7), 64 (76.5). ^{1}H NMR (DMSO) (δ, ppm), 3.82 (s, 3H, OCH_3), 7.02-7.05, 7.65-7.68 (m, 3H, Ar-H), 8.35 (s, 2H, NH_2), 8.51 (s, 1H, CH, thiazole), 9.58 (s, 1H, CHO).
13	IR (KBr)$\nu_{max.}$ cm^{-1}: 3419 (OH), 3376, 3203 (NH_2), 2225 (CN), 1735 (CO, ester). MS: m/z (%), 326 (M^+-3, 19.5), 318 (19.8), 305 (20.96), 257 (23.3), 243 (38.0), 220 (100.0), 199 (20.8), 174 (29.0), 153 (84.6), 133 (55.6), 103 (60.5), 89 (36.8). ^{1}H NMR (DMSO) (δ, ppm), 1.21 (t, 3H, $CH_2\underline{CH_3}$), 3.81 (s, 3H, OCH_3), 3.84 (s, 2H, NH_2), 4.18 (q, 2H, $\underline{CH_2}CH_3$), 7.02-7.10 (m, 3H, Ar-H), 8.01 (s, 1H, CH, thiazole), 9.58 (s, 1H, CH).

2.1 Synthesis Results

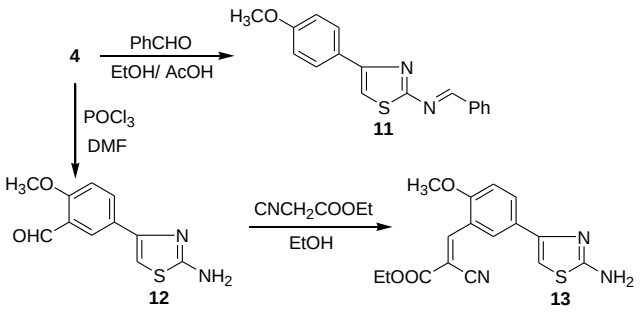
The synthetic procedures adopted to obtain the target compounds are depicted in Schemes 1 and 2. The starting 4-(2-amino-thiazol-4-yl)-phenol (1) was reacted with 2-(4-methoxy-benzylidene)-malononitrile in ethanol catalyzed by triethylamine to afford the enaminonitrile derivative 2 through the addition of amino group to the cyano group followed by cyclization. Moreover, the condensation reaction of aminothiazole 1 with 1,3-diphenyl-1H-pyrazole-4-carbaldehyde catalyzed by few drops of glacial acetic acid afforded the pyrazolo derivative 3. Methylation of the hydroxyl group in compound 1 was carried out using dimethyl sulfate to yield the acetyl derivative 4. Once more, compound 4 reacted with phenyl isothiocyanate in dioxane to afford a cyclic

product 5. Diazotizing of 4-amino-N-(4,6-dimethyl-pyrimidin-2-yl)-benzenesulfonamide and coupling with 4 in ethanolic sodium acetate solution at 0-5°C afforded 4-[5-(2-amino-thiazol-4-yl)-2-methoxy-phenylazo]-N-(4,6-dimethyl-pyrimidin-2-yl)-benzenesulfonamide (6). Monoacetylation of compound 4 in acetic anhydride led to the formation of N-acetyl derivative 7 in which the IR and ^{1}H NMR spectra revealed the absence of the amino group, also, the mass spectrum showed the molecular ion peak at m/z 248 (M^+, 4.65) which is equivalent to the molecular formula $C_{12}H_{12}N_2O_2S$. The amonolysis reaction of 4 with phthalic anhydride was carried out through the fusion in oil bath at 160°C to afford additive 8. Moreover, the reaction of 4 with ethyl acetoacetate in dry xylene afforded the amide derivative 9 through the elimination of ethanol molecule. On the other hand, aminothiazole 1 followed a one-pot reaction with ethyl acetoacetate and benzaldehyde in refluxing ethanol to afford the compound 10.



Scheme 1

Furthermore, Condensation of **4** with benzaldehyde in ethanol catalyzed by glacial acetic acid afforded compound **11** in which the IR and ^{1}H NMR spectra revealed the absence of the amino group. Vilsmeier formylation of **4** with phosphorus oxychloride in DMF led to the formyl derivative **12**, which reacted with ethyl cyanoacetate in refluxing ethanol to furnish compound **13**.



Scheme 2

Newly synthesized compounds were established on the basis of elemental analyses and spectral data (*e.g.;* IR, ^{1}H NMR, mass spectra; *C.f.* Exp. Part and Tables 1, 2).

The compounds were evaluated as antioxidant additives for local lubricating oil by heating 1 liter the lubricating oil without and with 0.1 g/liter concentration of the compounds **1-13** at 155^{o}C for 36 h and a rate of air 5 liter/ h. On the other hand, the peroxide, carbonyl, ester, hydroxyl values were estimated after 36 h oxidation under the previous condition. The results revealed that, the acid value was 11.7 mg KOH/g oil; the hydroxyl value was 125 mg KOH/g oil; the saponification value was 60 mg KOH/g oil; the carbonyl value was 36 mg (O)/g oil and the peroxide value was 16.5 mg (KI)/g oil.

3. EXPERIMENTAL

All melting points are recorded on Gallenkamp electric melting point apparatus. The IR spectra υ cm^{-1} (KBr) were recorded on Perkin Elmer Infrared Spectrophotometer Model 157, Grating. The ^{1}H NMR spectra were obtained on a Varian Spectrophotometer at 200 MHz. using TMS as an internal reference, $CHCl_3$ and DMSO-d_6 were used as solvent. The mass spectra (EI) were recorded on 70 eV with Kratos MS equipment and/or a Varian MAT 311 A Spectrometer. Elemental analyses were carried out at the Micro Analytical Center of Cairo Univ., Giza, Egypt. The starting 4-(2-amino-thiazol-4-yl)-phenol (**1**) was purchased from Aldrich company. Antioxidant application was carried out in the laboratory of Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt.

3.1 Preparation of Antioxidant Additives

7-Amino-3-(4-hydroxy-phenyl)-5-(4-methoxy-phenyl)-5*H*-thiazolo[3,2-*a*]pyrimidine-6-carbonitrile (2)

A mixture of 4-(2-amino-thiazol-4-yl)-phenol (**1**) (0.01 mol) and 2-(4-methoxy-benzylidene)-malononitrile (0.01 mol) in ethanol (20 mL) containing a catalytic amount of triethylamine (4 drops) was refluxed for 10 h. The reaction mixture was poured into ice-cold water, acidified by dilute HCl, the precipitated solid was filtered off, dried and recrystallized to afford **2** (*C.f.* Tables 1 and 2).

4-{2-[(1,3-Diphenyl-1*H*-pyrazol-4-ylmethylene)-amino]-thiazol-4-yl}-phenol (3)

A mixture of **1** (0.01 mol) and 1,3-diphenyl-1*H*-pyrazole-4-carbaldehyde (0.01 mol) in ethanol (25 mL) containing catalytic amount of glacial acetic acid (5 drops) was refluxed for 2 h. The reaction mixture was poured into ice-cold water; the precipitated solid was filtered off, dried and recrystallized to afford **3** (*C.f.* Tables 1 and 2).

4-(4-Methoxy-phenyl)-thiazol-2-ylamine (4)

A solution of **1** (5 g, 0.03 mol) in sodium hydroxide solution (1.5 g/ 250 mL H_2O), dimethyl sulfate (5 mL) was added. The reaction mixture was stirred for 15 min in ice bath; dimethyl sulfate (2.4 mL) and sodium hydroxide (1 g) were added. Continuing stirring, repeating the previous step and the reaction mixture was stirred until the precipitate was formed. The formed precipitated was filtered, dried and crystallized to afford **4** (*C.f.* Tables 1 and 2).

1-[4-(4-Methoxy-phenyl)-thiazol-2-yl]-3-phenyl-thiourea (5)

A mixture of **1** (0.01 mol) and phenyl isothiocyanate (0.01 mol) in dioxane (25 mL) was refluxed for 3 h. The reaction mixture was poured into ice-cold water; the precipitated solid was filtered off, dried and recrystallized to afford **5** (*C.f.* Tables 1 and 2).

4-[5-(2-Amino-thiazol-4-yl)-2-methoxy-phenylazo]-*N*-(4,6-dimethyl-pyrimidin-2-yl)-benzenesulfonamide (6)

To a well stirred cooled solution of 4-amino-*N*-(4,6-dimethyl-pyrimidin-2-yl)-benzenesulfonamide (1.11 g, 4 mmol) in (1.5 mL) conc. HCl and (2 mL), a solution of $NaNO_2$ (0.28 g, 4.1 mmol in 5 mL H_2O) was added drop wise. The above cooled diazonium solution was added slowly to a well stirred solution of **4** (0.83 g, 4 mmol) in ethanol (10 mL) and sodium acetate (5 mmol). The reaction mixture was stirred for 2 h. The crude product was filtered off, dried well and recrystallized to give **6** (*C.f.* Tables 1 and 2).

***N*-[4-(4-Methoxy-phenyl)-thiazol-2-yl]-acetamide (7)**

A solution of **4** (2.06 g, 0.01 mol) in acetic anhydride (20 mL) was refluxed for 2 h. the reaction mixture was poured into ice-cold water with continuous stirring the formed solid precipitate was filtered, dried and crystallized to afford **7** (*C.f.* Tables 1 and 2).

2-[4-(4-Methoxy-phenyl)-thiazol-2-yl]-isoindole-1,3-dione (8)

A mixture of **4** (2.06 g, 0.01 mol) and phthalic anhydride (1.48 g, 0.01 mol) were fused in an oil bath at 160^{o}C for 2 h. the formed solid was washed with dilute HCl, dried and crystallized to furnish **8** (*C.f.* Tables 1 and 2).

***N*-[4-(4-Methoxy-phenyl)-thiazol-2-yl]-3-oxo-butyramide (9)**

A mixture of **4** (2.06 g, 0.01 mol) and ethyl acetoacetate (1.27 mL, 0.01 mol) in dry xylene (20 mL) was refluxed for 5 h. The reaction mixture was poured into ice-cold water; the precipitated solid was filtered off, dried and recrystallized to afford **9** (*C.f.* Tables 1 and 2).

2-Benzylidene-*N*-[4-(4-hydroxy-phenyl)-thiazol-2-yl]-3-oxo-butyramide (10)

A mixture of **4** (2.06 g, 0.01 mol), ethyl acetoacetate (1.27 mL, 0.01 mol) and benzaldehyde (1.02 mL, 0.01 mol) in ethanol (25 mL) was refluxed for 3 h. The reaction mixture was poured into ice-cold water; the precipitated solid was filtered off, dried and recrystallized to afford **10** (*C.f.* Tables 1 and 2).

Benzylidene-[4-(4-methoxy-phenyl)-thiazol-2-yl]-amine (11)

A mixture of **4** (2.06 g, 0.01 mol), and benzaldehyde (1.02 mL, 0.01 mol) in ethanol (15 mL) in the presence of catalytic amount of glacial acetic acid was refluxed for 5 h. The reaction mixture was poured into ice-cold water; the precipitated solid was filtered off, dried and recrystallized to afford **11** (*C.f.* Tables 1 and 2).

5-(2-Amino-thiazol-4-yl)-2-methoxy-benzaldehyde (12)

To a solution of **4** (2.06 g, 0.01 mol) in DMF (10 mL) was stirred in an ice bath for 5 min. in another flask, phosphorous oxychloride (0.93 mL, 0.01 mol) in DMF (10 mL) was stirred in an ice bath for 5 min. the second flask was added to the first flask with continuous stirring. The reaction mixture was refluxed on water bath for 4 h. The reaction mixture was poured into ice-cold water; the precipitated solid was filtered off, dried and recrystallized to afford the formyl derivative **12** (*C.f.* Tables 1 and 2).

3-[5-(2-Amino-thiazol-4-yl)-2-methoxy-phenyl]-2-cyano-acrylic acid ethyl ester (13)

A mixture of **12** (2.34 g, 0.01 mol) and ethyl cyanoacetate (1.06 mL, 0.01 mol) in ethanol (15 mL) was refluxed for 4 h. The reaction mixture was poured into ice-cold water; the precipitated solid was filtered off, dried and recrystallized to afford **13** (*C.f.* Tables 1 and 2).

3.2 Evaluation of the Prepared Compounds

3.2.1 Evaluation of the Prepared Compounds as Antioxidant Additives for Lube Oil

The tested lube oil was supplied by "Misr petroleum company" Egypt in which the density at 15^{o}C is 0.8973, viscosity by a saybolt apparatus at 37.8^{o}C / sec. is 159, viscosity index is 95, flash point by Bensky Martenz (closed cup) is 195^{o}C, carbon residue wt. % is 0.05%, Pour point is -4.50^{o}C. The lube oil free from additives as well as different blends of the oil containing different concentrations of the prepared products have been subjected to a severe oxidation with air at a rate of 5 liter/ hr at 155 ℃ for 36 h. Samples were taken at regular intervals of three up to 36 h of oxidation and the oxidation stability were evaluated in terms of the total acid value (T.A.N.), hydroxyl value, carbonyl value, ester value and peroxide value (Siggia *et. al*., 1963). The results are shown in Table 3 and Figures (1-4).

Tab. 3: Comparison of Oxidation Products Obtained Using Additives 1-13

Compound No.	Acid Value gm KOH/ g oil	Peroxide Value gm (KI)/ g oil	Carbonyl Value gm (O)/ g oil	Ester Value gm (KOH)/ g oil	Hydroxyl Value gm (KOH)/ g oil
without additives	11.70	16.50	360.00	60.00	125.00
1	7.48	9.25	20.5	34.80	86.93
2	8.10	11.00	23.9	31.24	80.72
3	8.80	12.34	24.2	34.33	94.33
4	9.78	13.80	30.65	49.99	106.99
5	7.10	9.00	20.09	24.05	85.75
6	7.12	9.01	20.00	33.50	70.07
7	8.60	11.50	25.20	26.60	90.66
8	8.84	12.39	23.40	33.09	95.06
9	7.90	10.83	21.00	24.99	74.60
10	8.50	12.15	23.50	35.70	70.56
11	10.12	13.33	29.00	50.90	99.00
12	9.30	10.34	29.00	45.00	88.70
13	7.96	8.99	21.50	35.50	79.01

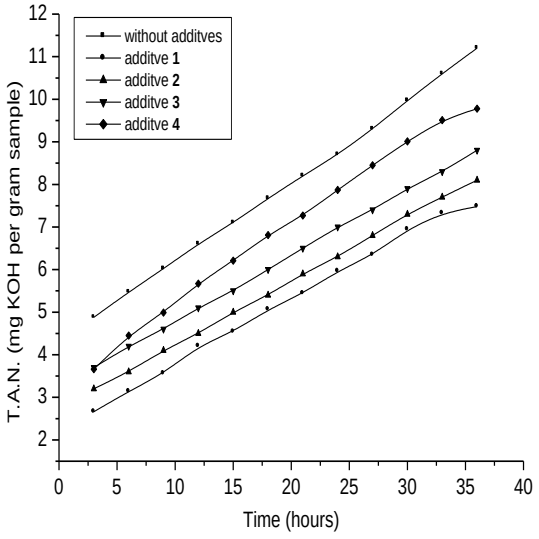


Fig. 1: Variation of the T.A.N. with Oxidation Time of the Tested Lube Oil Sample without and with Additives 1-4 at 0.1 g/liter Concentration at 155°C up to 36 Hours

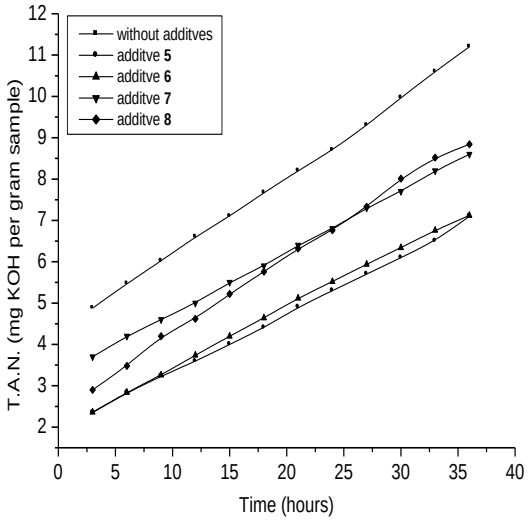


Fig. 2: Variation of the T.A.N. with Oxidation Time of the Tested Lube Oil Sample without and with Additives 5-8 at 0.1 g/liter Concentration at 155°C up to 36 Hours

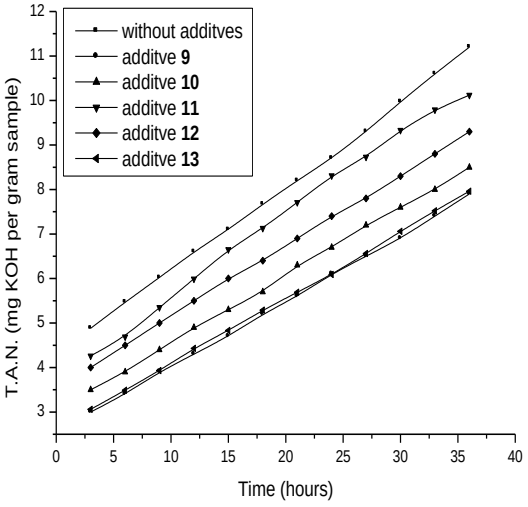


Fig. 3: Variation of the T.A.N. with Oxidation Time of the Tested Lube Oil Sample without and with Additives 9-13 at 0.1 g/liter Concentration at 155 C up to 36 Hours

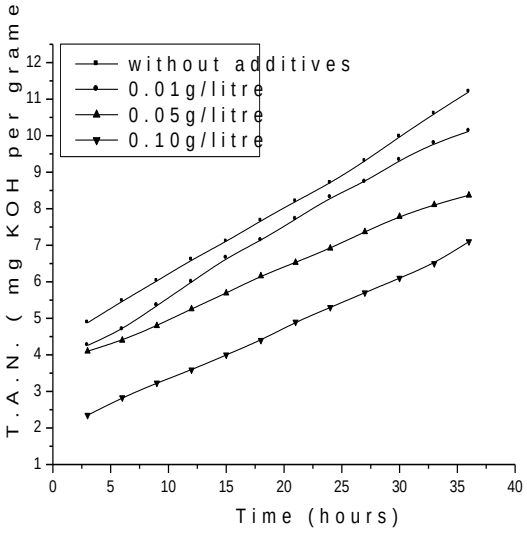


Fig. 4: Variation of the Acid Value with Oxidation Time of the Tested Lube Oil Samples without and with Different Concentrations of Additive 5 at 155 ℃ up to 36 Hours

4. DISCUSSION

a. Evaluation of the Prepared Compounds as Antioxidant Additives for Lube Oil

It is obvious from the obtained results that in the absence of additives, the oxidation products increased with time. When the prepared compounds were added to the tested oil, the oxidation products also increase with time but at a rate much less than those without additives. Figures (1-4) reveal that, the prepared compounds exhibited good oxidation resistances compared with the used lube oil. Compound 1 exhibited the highest antioxidant stability. On the other hand, it is obvious from Figures (1-3) that both the hydroxyl, carbonyl and saponification values of the oxidation of lube oil with and without the tested additives increases with time. This means that the oxidation of the oil may lead to the formation of carboxylic acids, in addition to alcohols, ketones, esters and hydroxyl acids.

b. Effect of Concentration

It was interesting to study the effect of concentration of the most effect antioxidant, in order to obtain the optimum concentration recommended to be used. Thus, three different concentrations of additive 5 namely; 0.01, 0.05 and 0.1 g/ liter were used and the total acid numbers of the oil were determined, Figure 4. The obtained results illustrated that increasing the additive concentration led to a decrease of the oxidative products and the concentration 0.1 g/liter is the most effective concentration to be used.

It was also of interest to compare the oxidation stability of the used lube oil containing the highly efficient antioxidants 1, 5 and 6 (0.1 g/ liter) with a commercial lube oil (Misr super 7500, 20w/50 h) purchased from the local market after 36 hour oxidation, Figure 5 which illustrates that the lube oil containing these compounds showed the higher oxidation stabilities compared with the used commercial lubricating oil.

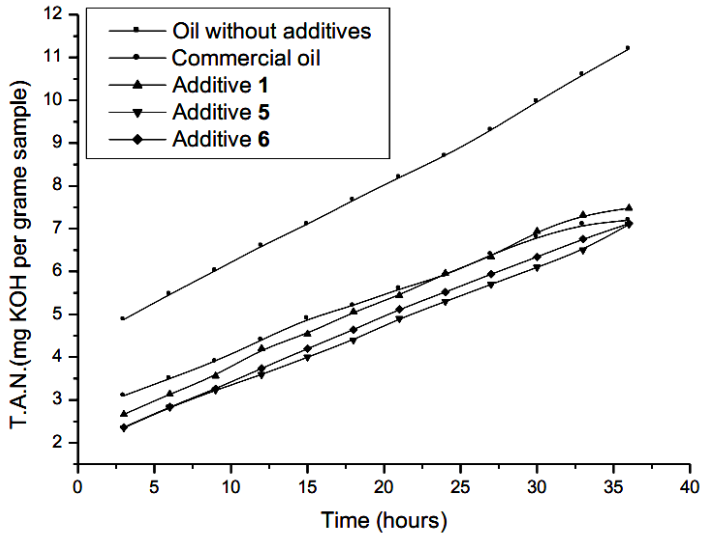


Fig. 5: Evaluation of the Tested Lube Oil Additives 1, 5 and 6 Comparison with Commercial Lube Oil Sample

c. A Comparison between the Oxidation Stability of the Tested Oil Containing the Compounds and with Lube Oil Containing a Commercial Additive

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