Synthesis and Evaluation of Some Thiazolidinone Derivatives as Antioxidants for Local Base Stock

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ABSTRACT
In this work, the three-thiazolidinone derivatives namely (301, 302 and 303) are prepared. The structures of the prepared compounds are confirmed and characterized using elemental analysis, Fourier transform infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance (1H-NMR). The prepared compounds are tested as anti-oxidants for Egyptian base stock through the change in Total Acid Number (TAN) at fixed temperature and different intervals of time with different concentrations. The oxidation stability is monitored and the efficiency of the antioxidants is ranked as follows, 303 > 302 > 301.

KEYWORDS: Base stock, Oxidation stability, Total acid number, Thiazolidinones

INTRODUCTION
A lubricant is a substance introduced to reduce friction between moving surfaces. It may also have the function of transporting foreign particles. The property of reducing friction is known as lubricity. Some oils have greater oxidation resistance than others; this is attributed to the presence of naturally occurring antioxidants. These naturally occurring products varied, depending on crude source or refining techniques. Some of these natural antioxidants were found to contain sulfur, nitrogen or oxygen bearing functional groups. Therefore, it is not surprising that, certain additives that are used to impart special properties to the oil, such as sulfur-bearing chemicals, were found to provide additional antioxidant stability. The fundamental aspects of oil performance are: achieving the required level of friction, wear rates, and maintaining these standards in spite of continuous degradation of the oil. Chemical reaction of the lubricant with atmospheric oxygen and water is inevitable because the lubricant is mainly hydrocarbons.

A lubricant is a mixture – a blend – of two key components, base oil and additives. Internal combustion engine components are dependent on the engine oil for the necessary cooling which represents about of the required engine cooling[1]. These parts have definite temperature limits that must not be exceed. Most previous studies on engine oils focused on the development of additives to accomplish desirable tribological properties of these oils [2]. Considerable attention is given to the development of oil properties such as super alkalinity [3], lower acidity [4], thermal stability and viscosity improvers [5,6], dispersants [7], antioxidants and antiwear agents [8,9]. High oil temperatures develop thermo-oxidative stresses, which leads to deterioration of the physical and chemical properties of the oil in the lubrication system of the engine and render it ineffective over a
period of time. It leads to not only excessive wear and corrosion, but may also cause catastrophic failure of lubricated components [10].

The self-accelerating oxidation of hydrocarbons is called autoxidation. Its initial stage is characterized by a slow reaction with oxygen followed by a phase of increased conversion until the process comes to a standstill. The degradation is driven by an autocatalytic reaction described by the well-established free radical mechanism which consisting of four distinct stages [11,12]. Firstly, initiation of the radical chain reaction, propagation of the radical chain reaction, chain branching and finally termination of the radical chain reaction. Conventional liquid lubricants show poor oxidative and thermal stability at high temperature ranges. In order to avoid these problems, lubricants need to possess superior oxidative stability. Therefore, antioxidants are the key additive that protects the lubricant from oxidation degradation, allowing the oil to meet the demanding requirements for use in industrial applications [13].

The development of modern engine and transmission technologies would be impossible without lubricant additives. From its conception in the early 1900s, the lubricant additives industry had worked in partnership with the oil and the automotive industries to enhance durability and performance of engine and drive line systems through lubricant design. Vehicle design advances are the starting point for the development of the new performance requirements, which in turn stimulate the development of the new lubricant and additives technologies [14]. A lot of basic studies have been engaged in the antiwear and antioxidants mechanisms of organosulfur compounds as additives in lubricants mainly in the form of sulfurized sperm oil, sulfurized terpenes, sulfurized olefins, biphenyl disulfide and di-n-butyl disulfide, etc. [15-17]. Heterocyclic compounds have been reported as antiwear (AW) and extreme pressure (EP) additives such as thiazoles and benzotriazoles [18-21]. Doaa et al [22] studied the oxidation stability of local base stock in the presence of two prepared azo compounds namely 2-sec-butyl-4-[(4-methoxyphenyl)-diazenyl] phenol (I) and 2-sec-butyl-4-[(4-nitrophenyl)-diazenyl] phenol (II).

Otherwise, Ashraf et al studied the effect of some liquid crystals as antioxidants for base oil [23]. The prepared liquid crystals (Azo-phenol liquid crystals) studied as antioxidants for base stock [24,25].

Experimental:
Materials and Reagents:
All chemicals were used without further purification. N-Hexyl bromide 98 %, n-dodecyl bromide 97 %, Toluene 99 %, anhydrous Aluminum chloride, Carbon disulfide 99 %, Maleic anhydride 98 %, Phenol 98.5 % and Ammonia solution were purchased from Aldrich, Fluka and Merck. Absolute ethanol was supplied by Acros Chemical Company.

Preparation of compounds (301, 302 and 303):
To a solution (0.01 mol.) of β-arylacrylic acids, (101, 102 and 103), in ethanol (50 ml.), a freshly prepared (0.01 mol.) ammonium p-tolylicarbamodithioate (26) is added portion wise and the whole mixture is stirred at room temperature for one hour. The solid precipitated (201, 202 and 203) is filtered off and acidified with dilute hydrochloric acid and the solid produced is filtered off and recrystallized from absolute ethanol to yield (301, 302 and 303), Scheme 1. The synthesized compounds are confirmed using the traditional tools of analysis as Elemental analysis, FT-IR and 1H-NMR spectroscopy. Elemental analysis were carried out by Elementary Viro El Microanalysis. Infrared spectra were recorded via FTIR spectrophotometer (Model 960 Mooog, ATI Mattson Infinity Series, USA). 1H-NMR spectra recorded on a Varian 300 MHz (Germany 1999) using TMS as internal standard.

![Scheme 1: Where, (301), R = Me, 5-(2-Oxo-2-[p-toly]ethyl)-2-thioxo-3-(p-toly)thiazolidin-4-one. (302), R = -OC6H411, 5-(2-[4-{Hexyloxy}phenyl]-2-oxoethyl)-2-thioxo-3-(p-toly)thiazolidin-4-one.](image-url)
(303), R = -OC12H25, 5-(2-[4- [Dodecyloxy]phenyl]-2-oxoethyl)-2-thioxo-3-(p-tolyl)thiazolidin-4-one.

RESULTS AND DISCUSSION

Physicochemical properties of the base stock:

The physicochemical characteristics of the delivered base stock were carried out according to ASTM standard test methods. The results were shown in Table 1.

Table 1: physicochemical characteristics of the base stock

<table>
<thead>
<tr>
<th>Test</th>
<th>Result</th>
<th>Standard Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15.56 °C, (g/cm³)</td>
<td>0.8817</td>
<td>ASTM D – 1298</td>
</tr>
<tr>
<td>Pour Point, (°C)</td>
<td>0</td>
<td>ASTM D – 97</td>
</tr>
<tr>
<td>Viscosity at 40 °C, (mm²/s)</td>
<td>52.34, 7.41</td>
<td>ASTM D – 445</td>
</tr>
<tr>
<td>@ 100 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>92</td>
<td>ASTM D – 2270</td>
</tr>
<tr>
<td>Total Acid Number, (mg KOH/g)</td>
<td>0.067</td>
<td>ASTM D – 664</td>
</tr>
<tr>
<td>Sulfur Content, (wt.%)</td>
<td>0.34</td>
<td>ASTM D – 4294</td>
</tr>
<tr>
<td>Color</td>
<td>2.5</td>
<td>ASTM D – 1500</td>
</tr>
<tr>
<td>Ash Content, (wt.%)</td>
<td>0.003</td>
<td>ASTM D – 482</td>
</tr>
<tr>
<td>Copper Corrosion</td>
<td>1 a</td>
<td>ASTM D – 130</td>
</tr>
<tr>
<td>Flash Point, (°C)</td>
<td>220</td>
<td>ASTM D – 92</td>
</tr>
<tr>
<td>Aniline Point, (°C)</td>
<td>100.5</td>
<td>ASTM D – 611</td>
</tr>
<tr>
<td>Molecular Weight (g/mol.)</td>
<td>468.9</td>
<td></td>
</tr>
</tbody>
</table>

The prepared compounds (301, 302 and 303) were characterized via the following:

3.2. Elemental Analysis:

Table 2: Elemental analysis of compounds 301, 302 and 303

<table>
<thead>
<tr>
<th>Compound</th>
<th>Element</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>S%</th>
</tr>
</thead>
<tbody>
<tr>
<td>301</td>
<td></td>
<td>64.20</td>
<td>64.42</td>
<td>4.82</td>
<td>4.68</td>
</tr>
<tr>
<td>302</td>
<td></td>
<td>65.28</td>
<td>64.85</td>
<td>6.16</td>
<td>5.89</td>
</tr>
<tr>
<td>303</td>
<td></td>
<td>68.53</td>
<td>68.70</td>
<td>7.48</td>
<td>7.44</td>
</tr>
</tbody>
</table>

Table (2) illustrates that the observed results were in good agreement with the calculated ones.

3.3. 1H-NMR:

From the data obtained in table (3), we observed that:

- The aromatic proton (a) has high chemical shift, (7.891 to 8.21 ppm), because of the deshielding effect of carbonyl group.
The (d) proton possesses the lowest (2) value, due to the electron donating alkoxy group to the aromatic ring.
Proton (e) has the value (4.747 to 4.888 ppm) which is an indication to the effect of the withdrawal C = O group in the thiazolidinone ring.
The methylene protons (f) of compounds (302 and 303) have the values of 4.096 and 4.208 ppm respectively; this is due to the effect of the electronegative ether Oxygen.
In case of protons (f, g in 301 and g, h in 302 and 303), they have different (2) values because of the asymmetry of the two carbene protons, therefore they have the triplet multiplicity.
The (h) protons in (301) and (i) protons in (301, 302 and 303), methyl group attached directly to aromatic ring, have the value of ranged from 2.393 – 2.406 ppm.
In case of protons (k), (6 protons in 302 and 18 protons in 303), have the same (2) values (1.301 and 1.282 respectively) this is interpreted to the same environment.
Methyl protons (l) in 302 and 303 possess the expected values, (0.875 and 0.802 ppm respectively).

**FT-IR:**

**Table 4: Infrared spectra (\(\text{cm}^{-1}\)) of compounds (301, 302 and 303)**

<table>
<thead>
<tr>
<th>Cpd.</th>
<th>Aliphatic CH</th>
<th>Aromatic CH</th>
<th>C = S</th>
<th>C - S</th>
<th>C = O</th>
<th>R – O – R</th>
<th>Keto form</th>
<th>Enol form</th>
</tr>
</thead>
<tbody>
<tr>
<td>301</td>
<td>2852</td>
<td>2922</td>
<td>1510</td>
<td>721 - 692</td>
<td>1758</td>
<td>-</td>
<td>1705</td>
<td>3427</td>
</tr>
<tr>
<td>302</td>
<td>2865</td>
<td>2954</td>
<td>1508</td>
<td>715 - 684</td>
<td>1756</td>
<td>1240</td>
<td>1712</td>
<td>3457</td>
</tr>
<tr>
<td>303</td>
<td>2856</td>
<td>2987</td>
<td>1511</td>
<td>718 - 678</td>
<td>1762</td>
<td>1235</td>
<td>1708</td>
<td>3445</td>
</tr>
</tbody>
</table>

The data obtained in table (4), illustrate the functional groups of compound 301, 302 and 303.

**Table 5: Variation of total acid number, TAN with and without additives**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc./ppm</th>
<th>24</th>
<th>48</th>
<th>72</th>
<th>96</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-</td>
<td>0.8042</td>
<td>0.9874</td>
<td>1.2451</td>
<td>1.5683</td>
</tr>
<tr>
<td>301</td>
<td>100</td>
<td>0.1312</td>
<td>0.3574</td>
<td>0.5353</td>
<td>0.8243</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.1122</td>
<td>0.3012</td>
<td>0.4247</td>
<td>0.7315</td>
</tr>
<tr>
<td>302</td>
<td>100</td>
<td>0.0985</td>
<td>0.1254</td>
<td>0.1532</td>
<td>0.2854</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.0823</td>
<td>0.0954</td>
<td>0.1352</td>
<td>0.1454</td>
</tr>
<tr>
<td>303</td>
<td>100</td>
<td>0.0552</td>
<td>0.0625</td>
<td>0.0785</td>
<td>0.0851</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.0445</td>
<td>0.0518</td>
<td>0.0584</td>
<td>0.0628</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.0322</td>
<td>0.0389</td>
<td>0.0457</td>
<td>0.0513</td>
</tr>
</tbody>
</table>

The study of the data tabulated in table 5 debated as the following:

**Oxidation of blank sample, (the delivered base stock):**

Oxidation of the blank sample, (base stock without additives table 5), clarified very poor results. The values of the total acid number increases from 0.067 mg KOH/g, (at zero time, Table 1), during the time interval up to 1.5683 mg KOH/g, (after 96 h) Figure 1.

**Fig. 1:** Variation of TAN values of blank sample with time

This result is attributed to the formation of the acidic groups (Scheme 2).
Scheme 2: Oxidation of the base stock oil

Effect of additives concentrations:

Effect of concentration of antioxidant 301 on blank sample:

The data shown in table 5 revealed that, after thermal oxidation of the base oil up to 96 hours in presence of antioxidant 301, the values of the TAN gave efficient results which ranged from 0.1312 up to 0.8243 mg KOH/g (100 ppm), 0.1122 to 0.7315 mg KOH/g (200 ppm), and from 0.0988 to 0.6998 mg KOH/g (300 ppm) respectively (Figure 2).

Fig. 2: TAN variation of the base oil with and without antioxidant 301 of concentrations 100, 200, and 300 ppm

Effect of concentration of antioxidant 302 on blank sample:

As obtained from table 5, by adding the antioxidant 302 to the blank sample, the values of the TAN showed improved results after thermal oxidation of the base oil up to 96 hours. The values ranged from 0.0985 to 0.2854 mg KOH/g (100 ppm), 0.0823 up to 0.1454 mg KOH/g (200 ppm) and from 0.0787 up to 0.1384 mg KOH/g (300 ppm) respectively (Figure 3).

Fig. 3: TAN variation of the base oil with and without antioxidant 302 of concentration: 100, 200, and 300 ppm
Effect of concentration of antioxidant 303 on blank sample:
In presence of antioxidant (303), the results that have been obtained from table 5 affirmed that the TAN values showed perfect results at the interval time of oxidation, (24 up to 96 h). The values ranged from 0.0552 to 0.0851 mg KOH/g (100 ppm), 0.0445 up to 0.0628 mg KOH/g (200 ppm) and from 0.0322 uphill to 0.0513 mg KOH/g (300 ppm) respectively (Figure 4).

Effect of substituted alkyl chain length:
Results of the TAN in presence of the antioxidants, (301, 302 and 303), with different alkyl chain lengths varied from methyl-, hexyloxy- and dodecyloxy- groups respectively, after the previous thermal oxidation period (24, 48, 72 and 96 h) are given in table 5.

Effect of substitute alkyl chain length with 100 ppm antioxidants:
After oxidation time intervals demonstrated in table 5 the TAN values of the blank sample after adding the three antioxidants (301, 302 and 303), with concentration of 100 ppm, we noticed that the values ranged from 0.1312, 0.0988 down to 0.0552 at 24 h and from 0.3574, 0.1254 to 0.0625, at 48 h respectively. Whereas at 72 h, the values ranged from 0.5353, 0.1532 to 0.0785 and consequently the values ranged from 0.8243, 0.2854 down to 0.0851 respectively at 96 h. From the previous results, the efficiency of these antioxidants at a concentration of 100 ppm is ranked as follows: 303 > 302 > 301, (Figure 5).

Effect of substituted alkyl chain length with 200 ppm antioxidants:
At a concentration of 200 ppm of (301, 302 and 303), the results obtained in table 5 revealed that the order of increasing efficiency is also as follows 303 > 302 > 301, (Figure 6).
3.5.3.2 Effect of substituted alkyl chain length with 300 ppm antioxidants:
Consequently, at a concentration of 300 ppm of (301, 302 and 303), the results obtained in table 5 illustrated that the order of increasing efficiency with the oxidation time intervals is ranked as follows 303 > 302 > 301, Figure 7.

From the previous data we concluded that, as the chain length increased the efficiency of the antioxidants prepared increased. This may be attributed to the higher chain length of the hydrophobic part of 303 rather than 302 and 301 respectively.
**Fig. 8**: (a, b, c, and d): Antioxidants efficiency with different time intervals

Figure 8 (a, b, c, and d) demonstrates the antioxidants efficiency on the base stock with the four oxidation time intervals separately, which emphasized the previous results.

**Conclusion**:

From the previous data we concluded the following:

1. The prepared compounds (301, 302 and 303) are characterized precisely through the conventional tools of analysis.
2. Increasing the oxidation time, always increase the total acid number of the base stock.
3. The prepared antioxidants (301, 302 and 303) proved to be successful in controlling the oxidation stability of the base stock.
4. Compound (303), with the long hydrophobic part, is the most efficient one as antioxidant rather than Compounds (302) and (301) respectively.
5. The data reveals that the most effective concentration of (303) is (300 ppm).

**REFERENCES**


