

Evaluation Study of Inhibition and regeneration characters for Substituted Anilines extracted from Crude oil

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Abstract

An aniline derivative was extracted from crude oil received from Al- Dora refinery . The crude oil was dissolved in toluene (1:3) and extracted through a column containing activated cationic resin type Amberlyte (15), then eluted by absolute ethanol and identified by infra red spectroscopy.

FT-IR spectroscopy for the lubricant oil was performed before employing in an internal combustion engine and 15 working hours daily for seven days after. It was seen that the FT-IR of the oxidized oil contains a new peak in the region $1800-1700\text{ cm}^{-1}$, which is generated due to the oxidation process of the used oil which belongs to carbonyl group. The FT-IR specter for the formulated crude oil with a specific concentration of the extracted substituted aniline after applying the same conditions of oxidation showed minimum peak intensity at $1710-1770\text{ cm}^{-1}$ than that observed in FT-IR done in absence of extracted compound .

The extracted sample was examined as antioxidant for lubricant oil stock 50 by manometric oxidation apparatus. The values of induction periods in presence of (0.20 and 0.30) mol/l of the sample at 393 K were: (766 sec. 1630 sec.), while it was (55 sec.) in their absence .

The maximum rate of oxidation for clean lubricant oil was $(3.5 \times 10^{-4})\text{ mol./l.sec.}$ while they were: $(3.0 \times 10^{-4}$ and $2.0 \times 10^{-4})\text{ mol./l. sec.}$ after blending with extracted sample. These values were still not arrived the value of maximum rate of oxidation of the clean oil.

The same study was applied on the universal antioxidant inhibitor Unol (phenolic type) which his value of stoichiometric factor for inhibition (f) is equal to (2) under the same conditions, the obtained induction periods were (150, 290 sec.) respectively .

Introduction

Engine oils are composed of base stocks and various chemical additives . These additives are necessary to enhance the performance of these oils and to restore constituent compounds which may have been lost during the refinement process [1] . While the final application determines the exact nature of the formulation, these oils typically contain around 10% w/w of additives. These formulated lubricants tend to serve different functions in an engine. Some of the important functions include controlling friction and wear, cooling the surfaces, removing debris and contaminants, and redistributing stresses over various operating surfaces. The two major classes of base stocks used in formulating engine oils are (a) petroleum or mineral-oil derived; and (b) specially synthesized oils known as synthetic base stock. The latter exhibit greater thermal and oxidative stability than the former, but are much more expensive. On the other hand, since most liquid lubricants derived from inexpensive mineral oil basestocks are hydrocarbons, they tend to oxidize, thermally decompose, and polymerize relatively quickly [2, 3] . Lubricating oils are usually used in presence of air whereby oxidative chemical reactions can take place. The rate of these oxidative processes varies greatly with the nature of oils, the extent of processing in refining, the temperature , and the presence of metallic catalyst [4]. Such oxidations have a drawback on the oil, thus leading to failures in lubrication that accompanied by damage of machines .

Large degree of damage is due to the formation of viscous, solid bodies, or jelly-like emulsions which interferer with the regular distribution of the lubricant

Consequently, antioxidant additives became highly required to decrease oil oxidation, with a secondary effect of reducing corrosion of certain types of sensitive bearing materials .[5]

Antioxidants play an important role in protecting the lubricant against injurious chemical transformations during the life of its operation. The suitability of antioxidants in engine oils depends on its oil solubility [3] .Antioxidants act in two different ways : (1) by radical scavenging and (2) By decomposition of hydroperoxides .

Radical scavengers react with peroxy radicals (ROO^\bullet), preventing further propagation of the free radical chain [1] and are referred to as primary antioxidants, as they operate by breaking the propagation chain [6]. Peroxide decomposers react with the hydroperoxides (ROOH) molecule, preventing the formation of peroxy radicals. Antioxidants can generally be considered as free radical inhibitors of peroxide decomposition, and may vary in their chemical structures . The important classes of antioxidants used in engine oils include hindered phenols, amines, sulphur and phosphorus compounds [3] . The two types of primary antioxidants are hindered phenol and aromatic amines .

Both function by donating a hydrogen atom to a peroxy radical. Examples of hindered phenols include 2, 6-di-tert-butyl-4-methylphenol phenols, in which the hydroxyl group is strictly blocked or hindered. Aromatic amines act as peroxide radical traps to interrupt the oxidation chain reaction. Examples of aromatic amines include N-phenyl- naphthylamine

and alkylated diphenyl amine . All these types are chemically synthesized prior use .

In the present work N-alkyl aniline derivative was extracted from crude oil received from Al- Dora refinery and examined as antioxidant for liquid phase oxidation of lubricant engine oil [7] .

Materials & Method

The lubricant oil used in this research was of stock (50) its specifications are listed in table (1):

Table (1): Specifications of the used Lubricant Oil

| Specifications | Values |
|------------------|-------------|
| Viscosity (cSt) | |
| At 40°C | 60 – 90 |
| At 120°C | 8 - 10 |
| Pour point (°C) | -6 maximum |
| Color | 1.5 |
| Flash point (°C) | 250 minimum |

Chemicals used for the target as solvents and as eluents were reagent grade and used without further purification .The resin was washed with distilled water, dried, and then soaked by 1N hydrochloric acid for 24 hrs. rinsed with distilled water, and then dried till the final three weight readings were constant A solution of crude oil (10 ml.) dissolved in (30 ml.) toluene was passed through glass column (15mm.id x 200mm.length) contained reactivated cationic amberlyte 15 with a rate of 1 ml./ min . The captured materials were eluted by 30 ml. absolute ethanol. The later was distilled under vacuum .

Infra red examination for the extracted sample was carried out by Burker IFS 113V with KBr cells, and CHCl_3 solvent with 1% maximum concentration at ambient temperature .

Fourier Transform Infra red (FTIR) Spectroscopy for lubricant oil before and after exposure to oxidation process in absence and with presence of extracted aniline .

5ml of lubricant oil was used in manometric oxidation instillation in presence of (0.20 and 0.30) mol/l of the extracted sample at 393K in presence of calculated amount of oxygen gas and 0.05% of benzoyl peroxide as free radical initiator .

Results & Discussion

Infrared examination for the extracted sample showed absorption band regions at $2750\text{-}3000\text{ cm}^{-1}$, $1200\text{-}1300\text{ cm}^{-1}$ and $1400\text{-}1500\text{ cm}^{-1}$ assigned to heteroatom in the extracted sample which argued by the peak appeared in the region $3350\text{-}3550\text{ cm}^{-1}$. It is clear that the intensity at 3465 cm^{-1} was belonging to amino group in the sample .

Automotive lubricants contain hydrocarbon base stock as carrier fluid along with other additives that serve specific purposes. The exposure of these lubricants to high temperatures, light and/or metal catalysts result in their decomposition and subsequent generation of alkyl free radicals [2, 3, 6, 8] .

The first step in the oxidation process involves the conversion of alkyl radical to hydroperoxide. At high

temperatures, hydroperoxide decomposes to form an alkoxy radical and hydroxyl radical . The generated alkoxy radical can degrade by two different pathways . It can either abstract a hydrogen radical from an oil molecule to form an alcohol, or the alkoxy radical can undergo chain scission reaction to produce low molecular weight carbonyl-containing compounds such as aldehydes and ketones and subsequently carboxylic acids .

The aldehydes, ketones and carboxylic acids have carbonyl groups which produce a peak in the same region ($1800\text{-}1700\text{ cm}^{-1}$) of the FT-IR spectrum and hence changes in the intensity of this peak may be used to monitor the oxidation. Many authors have extensively employed FT-IR to study such oxidation products [9, 10, 11, 12, and 13] .

Figure (1) and Figure (2) showing the FT-IR spectrum of base oil before and after it is subjected to oxidation at elevated temperatures respectively. The FT-IR spectrum of the lubricant oil at (0) hr (prior to baking) contains mainly CH peaks from base oil. On the other hand, the FT-IR spectrum of lubricant oil subjected to oxidation for 15 working hours daily for seven days contains a new peak in the region $1800\text{-}1700\text{ cm}^{-1}$, which is generated due to the process of oxidation for the oil which belongs to carbonyl groups .

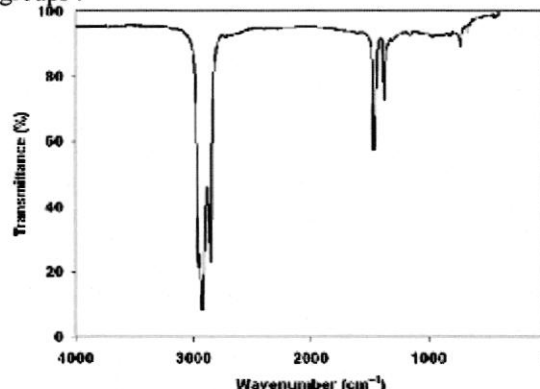


Figure 1: FT-IR spectrum of lubricant oil at 0hr

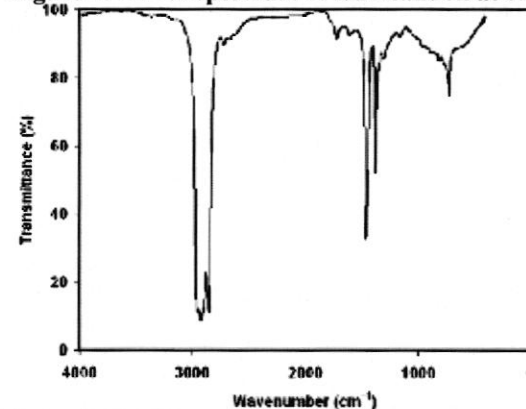


Figure 2: FT-IR spectrum of lubricant oil after 15 working hours daily for seven days of oxidizing time at 120°C. A new peak corresponding to the presence of carbonyl groups at ($1700\text{-}1800\text{ cm}^{-1}$) is observed

The peaks in these spectra corresponding to specific wave numbers are assigned to the respective

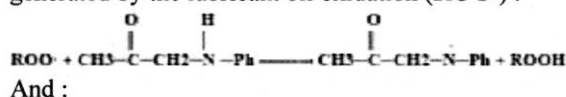
functional groups (bonds) as described in Table (2) :

Table (2): Assignment of peaks to wave number

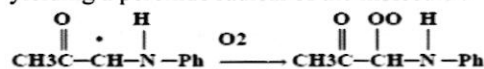
| Wave number (cm ⁻¹) | Assigned peaks |
|---------------------------------|---|
| 3000-2000 | Saturated CH stretching |
| 1400- 1200 | C-H bending |
| 3480- 3380 | N-H of aminic antioxidant |
| 1770-1710 | Carbonyl of carboxylic acid, aldehydes, ketones, esters |

The aromatic amines antioxidants functioned by donating a hydrogen atom to a peroxy radical [8]. We had seen that the reaction mechanism of these antioxidants for the specific cases of substituted aniline isolated from Iraqi crude oil is proceeding in the following steps at elevated temperature :

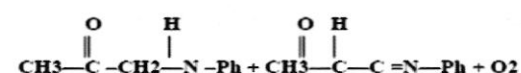
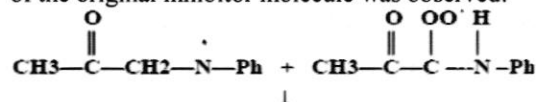
A. The process at which the effective inhibitor molecule in the extracted sample behaves as deactivating agent i.e. deactivates the free radical generated by the lubricant oil oxidation (ROO·).



B. The process at which the effective inhibitor molecule in the extracted sample was auto oxidized yielding a peroxide radical of the molecule .



By proceeding the two mechanisms (A&B) at the same time, and by the reaction of the generated free radicals in the medium of the reaction, regeneration of the original inhibitor molecule was observed:



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Inhibitor molecule

This result was proved by calculations of induction periods according to [14] for this inhibitor by using different concentrations with the lubricant oil . The values of induction periods in presence of (0.20 and 0.30) mol/l of extracted sample, and with out their presence at 393 K were: (766 sec. 1630 sec.) and (55 sec.) respectively, while the maximum rates of oxidation were:

(3.0×10^{-4} and 2.0×10^{-4}) mol/l.sec. These values were still not qualified the value of maximum rate of oxidation for the lubricant oil alone (3.5×10^{-4}) mol/l.sec.

From FT-IR spectra for the lubricant oil, it was observed that the specter of the blended oil with the extracted antioxidant, some amount of carbonyl group was already present in the original material. The observed carbonyl group in this formulation is combination of the quantities of the carbonyl group present before and after oxidation .

Conclusions

From the results obtained in this research it can be concluded that :

1. The mechanism of the extracted anilines depends upon the operating temperature .
2. The ability of extracted anilines antioxidants was (14) times stronger to terminate the free radical chain reactions than do the phenolic type (Unol) .
3. The extracted anilines antioxidants having the ability to regenerate their structure during the time of oxidation process .

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دراسة تقييمية للخاصية التثبيطية واعادة التكوين للاتلين المعوض المستخلص من النفط الخام

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الملخص

تم استخدام جزيئة الاتلين المعوض و المستخلص من عينة النفط الخام لمصفى الدورة كمثبط لعملية اكسدة زيت المحركات في حاله السائله حيث تم اذابة النفط الخام في التولوين بنسبة (1:3) بعدها تم امراره خلال عمود يحتوي على راتنج موجب نوع أمبرلايت (15) المنشط .
 تم استخلاص المركب من على سطح الراتنج بواسطة الكحول الأنتيلي المطلق والذي تم تقطيره بعد انتهاء عملية الاستخلاص تحت الضغط المتخلخل حيث اجري عليه فحص الأشعه تحت الحمراء لتشخيص المجاميع الفعالة .

أجري فحص طيف اشعة (FT-IR) لزيت المحركات نوع (SAE- 50) قبل استخدامه في محرك ذات الاحتراق الداخلي وبعد استخدامه بواقع (15) ساعة عمل لمدة سبعة ايام حيث اثبتت النتائج وجود قمه في الموقع (1700 – 1800 سم⁻¹) التي تدل على وجود مجموعة الكاربونيل بعد عملية الأكسدة .

أما طيف اشعة (FT-IR) للزيت بعد اضافة تركيز معين من الأتلين المعوض المستخلص من النفط الخام وبعد اخضاعه لنفس ظروف الأكسدة فقد اعطى قمه ذات شدة واطئه في المجال (1710 - 1770 سم⁻¹) عن ذلك النموذج الذي لا يحتوي على اي تركيز من المركب المستخلص .
 أن قيم زمن الاحتجاز التي تم الحصول عليها باستخدام جهاز الأكسدة المنومترية وبوجود (0,20 و 0,30) مول/لتر من المركب المستخلص مع الزيت بدرجة حراره 393 كلفن كانت (766 و 1630) ثانيه بينما كانت (55) ثانيه بدون اضافة المستخلص وبنفس درجة الحراره اما معدل سرعة الأكسدة القصوى للزيت بدون اضافة أي تركيز من المستخلص فكانت (3,5 × 10⁻⁴) مول/لتر. ثانيه بينما اصبحت (3,0 × 10⁻⁴) و (2,0 × 10⁻⁴) مول/لتر. ثانيه .

اجريت دراسة مقارنة للنتائج التي تم الحصول عليها من المستخلص مع النتائج التي تم الحصول عليها باستخدام مثبط الأكسدة النوع الفينولي (يونول) ذات معامل التثبيط (2) وتحت نفس الظروف حيث سجل زمن احتجاز (150 و 290) ثانيه لنفس التراكيز المستخدمة مع المستخلص .
 في هذا البحث تم اقتراح ميكانيكه توضح عملية اعادة تكوين جزيئة المثبط المستخلصه من النفط الخام اثناء عملية الأكسدة .