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Synthesis of Petroleum Derived Aromatic Amines and Their Evaluation as Antioxidants

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ABSTRACT. Two aromatic extracts separated from light (grade 40) and heavy (grade 60) petroleum oil distillates by a selective solvent (furfural) were subjected to nitration followed by catalytic reduction to their corresponding amine derivatives. Only the polyaromatic consituents of the extracts underwent these reactions. The effectiveness of various concentrations of the products obtained in inhibiting oxidation of a mineral oil sample under oxidizing conditions was studied statically by differential scanning calorimetery (DSC) and dynamically by a catalytic oxidation test procedure. The results obtained from these two methods of evaluation, indicated that, the petroleum derived aromatic amine compounds imparted good antioxidant protection to the mineral oil.

A variety of organic compounds have been used as oxidation inhibitors in mineral oils. The most popular type of these compounds are the aromatic amine derivatives (Braithwaite 1967) which include the naphthyl- and phenyl-naphthylamines. They usually function by interacting with the free radicals present in the system forming a non-radical substrate product, thus increasing the life-time of the oils (Ranney 1979).

Recently, Al-Sammerrai and Ahmed (1981) reported the preparation of amine type antioxidants by the direct nitration of mineral oils of average molecular weights of at least 350 followed by catalytic reduction to their corresponding amine derivatives. Only the polyaromatic constituents of the oils underwent these reactions (Al-Sammerrai *et al.* 1983).

Addition of these aminated oils in concentrations ranging between 0.2 to 0.6% by weight (based on the aromatic constituents only) imparted good properties as

oxidation inhibitors for different types of lubricating oils (Al-Sammerrai and Ahmed 1981).

Since petroleum extracts are readily available from the solvent extraction processes performed on lubricating oil distillates, and usually possess a rich content of polyaromatic compounds (Nejak 1975), it would be of scientific and economical importance to evaluate the products obtained from their nitration-catalytic reduction as oxidation inhibitors in lubricating oils employing a DSC technique as one of the main methods in addition to a dynamic procedure of evaluation.

The effectiveness of the aminated extracts in inhibiting oxidation was compared with that of the untreated extracts.

Experimental

Materials

The grade 40 and 60 aromatic extracts (separated from furfural) were obtained from a local refinery. Specifications of these products are given in Table 1.

A technical grade white mineral oil having a viscosity of 10.5 cSt at 40°C supplied by the same refinery was used as the test oil.

Table 1. Specifications of the untreated and aminated aromatic extracts

Specifications*	Grade 40	Grade 60	Aminated 40	Aminated 60
Specific gravity at 15.5°C	0.8864	1.0256	0.9636	1.0511
Refractive index at 20°C	1.4822	1.5697	1.5325	1.5970
Viscosity, cSt at 100°C	5.2	28.5	6.6	33.5
Flash point, °C	162	245	–	–
S, % wt	0.44	4.31	0.42	4.3
Saturates, % wt	26	20.5	25.5	20
Aromatics, % wt	73	77.5	73	77
N, % wt	0.7	0.8	1.5	1.55

* Measured according to ASTM standard methods

Procedure: Preparation of the Aminated Extracts

a) *Nitration of the extracts:* The nitration process was performed on a 50% by weight solutions of the extracts in normal hexane, since direct nitration of the extracts led to the formation of very thick and gummy products which proved to be very difficult to handle. The method of nitration consisted of treating a sample of

the solution with aqueous nitric acid (50% sol.) at 40°C for 4 hours with continuous stirring. The organic layer was separated from the aqueous layer, washed several times with water. This was followed by neutralization with calcium hydroxide at 40°C, cooling, filtering and then drying the dark-red solution over anhydrous sodium sulfate.

b) *Reduction of the solution containing the nitrated extract:* Catalytic hydrogenation of the hexane solution containing the nitrated extracts was performed at room temperature under four atmospheres of pressure over 10% palladium/charcoal until no more hydrogen gas was consumed. The solution was then filtered off, dried over anhydrous sodium sulfate, filtered again and hexane removed in a vacuum evaporator leaving a dark-yellow highly viscous liquid. The physico-chemical properties of the aminated extracts are presented in Table 1. Various concentrations of the aromatic extracts and aminated products in the white mineral oil were prepared at room temperature by thorough mixing of these products.

c) *Evaluation of the products as antioxidants:* Differential scanning calorimetric measurements were carried out on a Heraeus TA 500 thermal analyser. Oil samples weighing 5-10 mg were heated at a rate of 10°C min^{-1} in an aluminium crucible under static air atmosphere. The reference cell was left empty. The dynamic oxidation test method for evaluating the effectiveness of the aminated aromatic extracts and untreated extracts as antioxidants was conducted as follows. In a 200×20-mm test tube is placed a 25 gram sample of the test oil having immersed therein $2cm^2$ of polished copper wire. The oil sample is heated to a temperature of 120°C and maintained at this temperature while dry air is passed through at a rate of 3L/h for a period of five days (120h). The changes in acid number and viscosity were recorded before and at the end of the 120 hours oxidation period. All measurements were carried out in duplicate. Infrared and p.m.r spectra of the extracts were recorded using a Phy-Unicam SP 3-30 and a Varian-390 (90 mHz) instruments respectively.

Results and Discussion

Under the conditions of the reaction described in the experimental section, nitration proceeds predominantly with the polyaromatic constituents of the extracts. This confirms the results recorded earlier (Al-Sammerrai, *et al.* 1983) on nitration of oils.

Formation of the nitronium ions followed by an electrophilic attack on polyaromatic molecules yields the nitrated products. Furthermore, upon catalytic reduction of the nitrated products, only the nitro groups are reduced to the

corresponding amino derivatives. The percentage yield of the final products ranged between 70 and 80% by weight.

Proof of the chemical composition of the nitrated and reduced products was obtained from nitrogen analysis (Table 1), ir and p.m.r spectra. The ir spectra of the nitrated extracts showed strong absorbances at 1530 and 1320 cm^{-1} due to NO_2 stretching vibrations. These absorptions disappeared with the appearance of a strong broad peak at about 3400 cm^{-1} upon catalytic reduction of the nitrated products corresponding to NH_2 stretching vibration. Further confirmation was obtained from the p.m.r spectra in deutriated benzene with the appearance of a strong peak at τ 3.8 attributed to the protons of the NH_2 group without any alterations in the other features of the spectra.

Evaluation of the Aromatic Aminated and Untreated Extracts

Differential scanning calorimetery

Recently (Noel 1972), differential scanning calorimetery has been applied successfully as a tool in estimating the thermal stability of oils and studying the efficiency of a range of oxidation inhibitors. On heating a sample of oil in air, a DSC apparatus was used to record an exothermic effect resulting from oxidative degradation of the oil. The onset temperature of the exotherm can be taken as a measure of the thermal stability of the oil. This technique was used to study the effect of a range of oxidation inhibitors on lubricating oils (Barbooti and Al-Sammerrai 1984, Al-Sammerrai 1985, and Al-Sammerrai and Salih 1985). The higher the recorded onset temperature of the exothermic reaction, the more effective is the inhibitor, and the converse also holds. The onset temperature of the exothermic effect of the lubricating oil oxidation is usually evaluated by extrapolating the tangents of the DSC trace.

The DSC signals of the test oil in the presence of various concentrations of aromatic amines and untreated extracts are shown in Figs. 1 and 2 respectively. The onset temperature of oxidation of the test oil on its own was 180°C.

When the test oil was treated with the grade 40 aminated extract, the improvement in the oil stability was appreciable at an additive concentration of 1%. At 1.5% additive concentration, the onset temperature increased markedly to 223°C, *i.e.* 43°C higher than the oxidation onset temperature of the untreated oil (Fig. 1a). Meanwhile, the oxidation stability of the test oil was only slightly improved by the addition of the untreated grade 40 extract and reaching 195°C at 1.5% additive concentration (Fig. 2a).

The DSC signals of the test oil in the presence of various concentrations of the grade 60 aminated extract (Fig. 1b) indicated a significant improvement of the

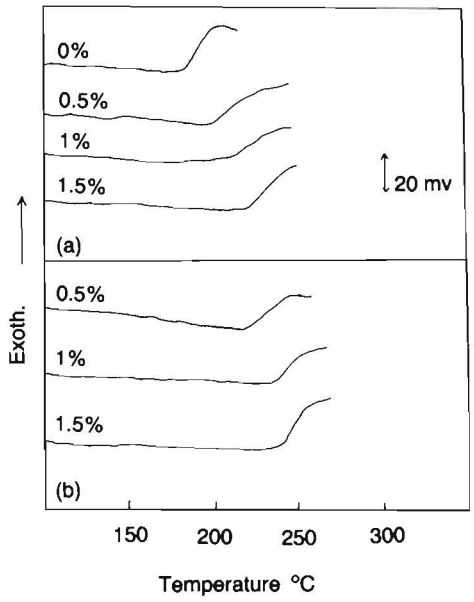

Fig. 1. DSC traces of various concentrations of aminated extract in test oil: a) grade 40 and b) grade 60.

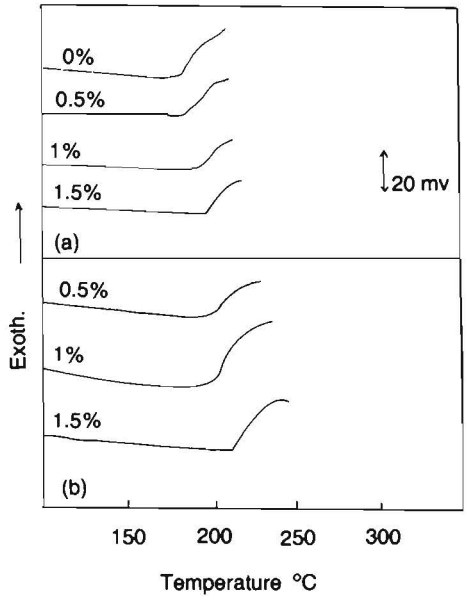

Fig. 2. DSC traces of various concentrations of untreated extract in test oil a) grade 40, and b) grade 60.

oxidation stability of the oil with increase of the additive concentration. The working temperature of the oil can be expanded up to 235°C which is 55°C higher than that of the untreated oil by the addition of 1% aminated extracts. An increase in additive concentration from 1% to 1.5% lead to an improvement of 4°C over the value recorded at the 1% dose.

The oxidation stability of the test oil could not be appreciably improved with the addition of the untreated grade 60 extract at concentrations lower than 1%. Meanwhile, the onset temperature of the oil increased noticeably up to 215°C at an additive concentration of 1.5% (Fig. 2b). This behaviour could be related to the presence of polyaromatic compounds in the untreated extracts which are well known to act as natural oxidation inhibitors (Al-Sammerrai *et al.* 1987).

Antioxidants dynamically

Evaluation of aromatic aminated and untreated extracts dynamically was performed according to the oxidation stability test method described in the experimental section.

Acidity and viscosity changes of the oil samples containing various concentrations of these products were recorded before and at the end of five days (120 hr).

The value of the acid number depends on the formation of carboxylic acids after prolonged oxidation. The acid number increases with the increase in carboxyl formation and usually decreases upon increasing the concentration of an effective oxidation inhibitor.

Figures 3a and 3b are plots of acidity expressed in milligram of potassium hydroxide per gramme of sample at the end of 120 hr against various concentrations of the aromatic aminated and untreated extracts in the test oil respectively. The acid number was measured according to ASTM Method D-974. The acid number value of the untreated oil at the end of oxidation time (120 hr) was 4.8.

A steady decrease in the acid number values of the test oil was recorded upon increasing the concentration of the aminated extracts. The acid number values at the end of oxidation time of the oil treated with 1.5% grade 40 and grade 60 aminated extracts were 2.2 and 1.8 respectively (Fig. 3a), while the acid numbers of the same oil containing 1.5% of untreated grade 40 and 60 aromatic extracts were 2.85 and 2.7 respectively and as shown in Figure 3b.)

Another important criterion in studying the stability of oils is viscosity changes that occur during oxidation. Viscosity of an oil usually increases with the time of

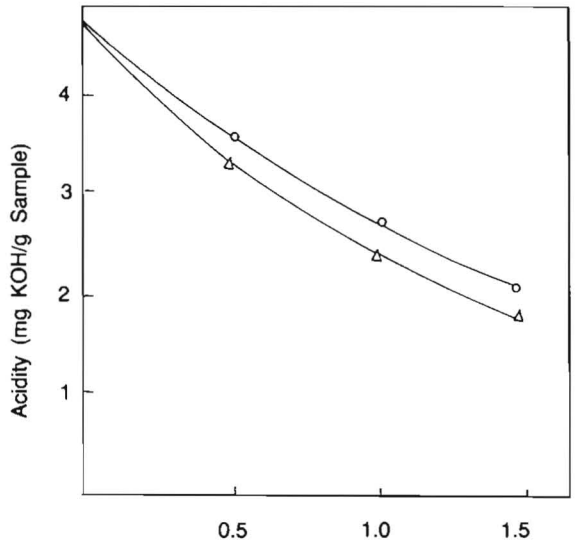

Fig. 3a.

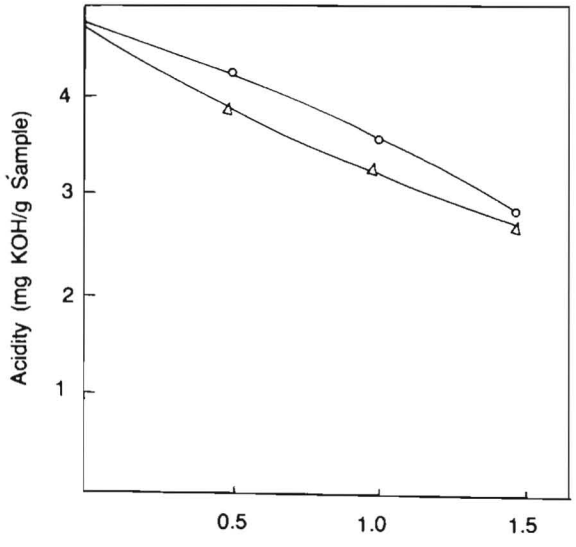

Fig. 3b.

Fig. 3. Plot of acidity at the end of oxidation time expressed in mg KOH/g of sample against concentration in weight % for the test oil containing various added concentrations of a) ○, grade 40 aminated extract and △, grade 60 aminated extract, and b) ○, untreated grade 40 extract and △, untreated grade 60 extract.

oxidation. However, with higher dosages of an oxidation inhibitor, changes of viscosity with time become less pronounced.

Figures 4a and 4b are plots of viscosity expressed in cSt at 40°C at the end of 120 hr against various concentrations of the aromatic amine extracts and untreated extracts in the test oil respectively. Viscosity measurements were performed according to ASTM Method D-445. The viscosity value at the end of oxidation time of the untreated oil was 77 cSt.

A lower increase in viscosity of the test oil sample was recorded at the end of oxidation time (120 hr) upon addition of increasing concentrations of the grade 40 and 60 aminated extracts when compared to that of the corresponding untreated extracts. For example, at 1.5% dose of aminated extracts, viscosity values were 35.5 and 31.5 respectively (Fig. 4a) while at the same level of concentration of the untreated grade 40 and 60 extracts, viscosity values at the end of oxidation time were 44 and 42.5 respectively (Fig. 4b).

It can be concluded that upon evaluation of the aminated and untreated extracts, the former products imparted good anti-oxidation protection to the test oil while the latter products were of lesser activity in inhibiting oxidation at the same level of concentrations.

Finally, the data presented in this work demonstrated an excellent correlation of the results obtained from the two methods of evaluation, *i.e.* static (DSC) and dynamic (oxidation stability test) methods. The former method proved to be reliable and simple with the added advantages of using only very small sample sizes and being less time consuming.

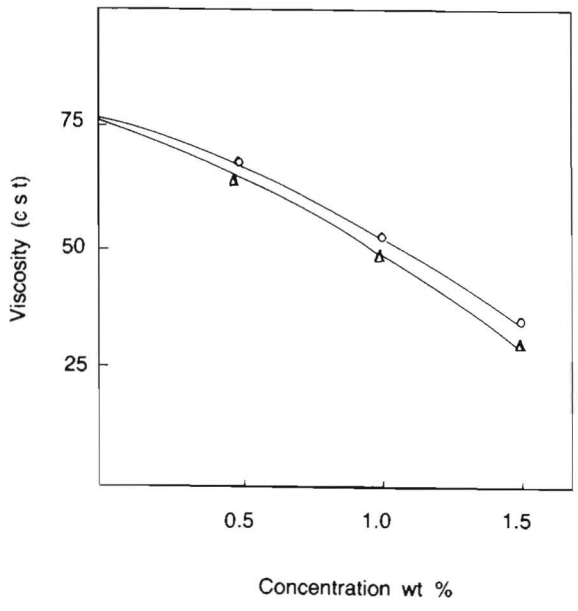

Fig. 4a.

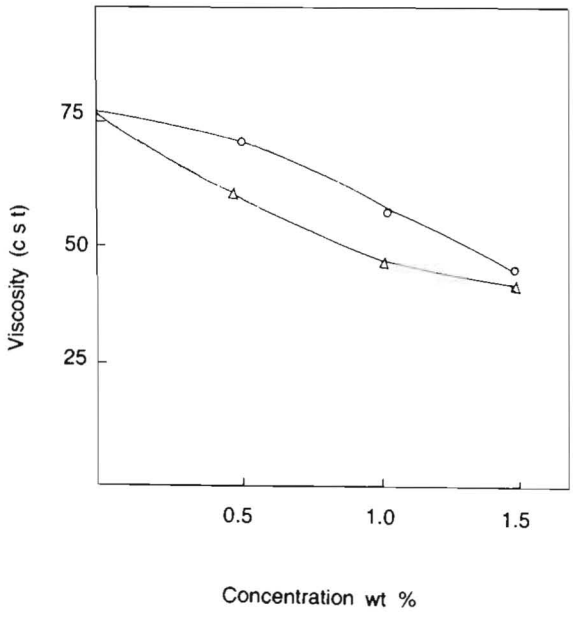

Fig. 4b.

Fig. 4. Plot of viscosity at the end of oxidation time expressed in cST at 40°C against concentration in weight % for the test oil containing various added concentrations of a) ○, grade 40 aminated extract and △, grade 60 aminated extract, and b) ○, untreated grade 40 extract and △, untreated grade 60 extract.

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تحضير أمينات عطرية نفطية الاشتقاق وتقييمها كاضافات مانعة للأكسدة

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تم تعريض نوعين من المستخلصات العطرية المفصولة بواسطة المذيب فورفورال من مقطرين زيتيين نفطيين بنوعي ٤٠ و ٦٠ إلى عملية النترتة ومن ثم إلى الاختزال بالعامل المساعد للحصول على المشتقات الأمينية المناظرة. أثرت التفاعلات أعلاه فقط على المكونات العطرية المتعددة الحلقات المتواجدة في هذه المستخلصات.

لقد تم دراسة فاعلية تراكيز مختلفة من النواتج المستحصلة في تثبيط أكسدة نموذج من زيت معدني تحت ظروف أكسدة ثابتة (ستاتيكية) باستعمال التحليل المسعري الحراري وبصورة متحركة (ديناميكية) بطريقة اختبار التأكسد بالعامل المساعد.

النتائج المستحصلة بواسطة هاتين الطريقتين بينت بأن المركبات الأمينية نفطية الاشتقاق تضفي حماية جيدة ضد التأكسد للزيت النفطي.