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# EVALUATION OF 1-AMINO AND 1-HYDROXYNAPHTHALENES AS ANTIOXIDANTS FOR MINERAL OILS BY DIFFERENTIAL SCANNING CALORIMETERY

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## ABSTRACT

1-Amino and 1-hydroxynaphthalenes were evaluated as oxidation inhibitors for mineral oil using differential scanning calorimetry. The former compound imparted good antioxidant protection even at low additive concentration, while significant improvement in the oxidation stability of the oil was recorded upon increasing the concentration of the latter compound. These results correlated well with those obtained from a dynamic method of evaluation based on a catalytic oxidation test procedure.

## INTRODUCTION

Aromatic amine and hydroxy compounds have found wide application [1] as antioxidants in organic materials. They usually function by interaction with free radicals formed, yielding a non-radical substrate product and an oxy or imino radical [2]. The resulting antioxidant radical is well stabilized through resonance with the aromatic system such as in naphthols or amines.

Substituted naphthalenes have been used extensively as additives in the prevention of oxidation of mineral oils and greases [3], thus increasing the useful lifetime of these materials.

Stability of mineral and lubricating oils towards oxidation is usually evaluated by static, bomb and dynamic standard methods [4].

Recently however [5], thermoanalytical techniques, such as differential scanning calorimetery (DSC), have been used to determine the oxidation stability of mineral oils and to study the effects of a range of oxidation inhibitors on lubricating oils [6–10].

The aim of this paper is to study and compare the efficiency of 1-amino and 1-hydroxynaphthalenes as antioxidants for mineral oil using differential scanning calorimetry. The results recorded were correlated with those ob-

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tained from a dynamic method of evaluation based on a catalytic oxidation test procedure.

## EXPERIMENTAL

### *Apparatus*

The DSC measurements were carried out in 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 ambient conditions. The reference cell was left empty. The DSC apparatus was standardized with pure tin prior to the start of the determinations. The dynamic oxidation test method for evaluating the effectiveness of the naphthalene derivatives as antioxidants was conducted as follows. In a 200 × 20 mm test tube is placed 25 g of the test oil which has 2 $cm^2$ of polished copper wire immersed in it. The oil sample is heated to a temperature of 120°C and maintained at this temperature while dry air is passed through it at a rate of 3 l $h^{-1}$ for a period of 120 h. The changes in acid number and viscosity were recorded before and at the end of the experimental run according to ASTM methods D-974 and D-445, respectively. All measurements were carried out in duplicate.

### *Materials*

1-Amino and 1-hydroxynaphthalenes of more than 98% purity were purchased from Aldrich Chemical Co. Ltd. The mineral oil used in this investigation was a white oil of technical grade having a viscosity of 10.5 cSt at 40°C.

### *Procedure*

Solutions of the naphthalene derivatives at concentrations ranging from 0.1 to 0.4% by weight were prepared by dissolving them with heating in the mineral oil at 60°C.

## RESULTS AND DISCUSSION

### *Evaluation of the naphthalene derivatives by DSC*

The onset temperature of the exothermic effect of oil oxidation was evaluated from the intersect of the extrapolated tangents of the DSC trace. The DSC signals of oil oxidation with and without 1-amino and 1-hydroxynaphthalenes are shown in Figs. 1 and 2, respectively. The numerical

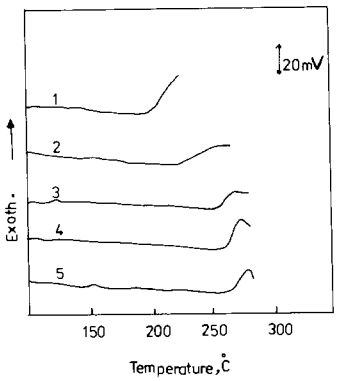


Fig. 1. DSC signals of the oxidation of the oil in the presence of 1-aminonaphthalene: (1) 0%; (2) 0.1%; (3) 0.2%; (4) 0.3%; (5) 0.4%.

evaluation of the DSC curves of the oxidation of oil in the presence of different concentrations of the additives is given in Table 1. The onset temperature of oxidation of the oil on its own is 195°C.

The antioxidation effect of these compounds is closely related to the stability of their phenoxy and phenimino radicals which are formed by the donation of a hydrogen atom from the antioxidant to the substrate radical and are stabilized through conjugation with the aromatic system.

When the oil was treated with 1-aminonaphthalene, the improvement in its stability was appreciable at an additive concentration of 0.2%. The onset temperature of oxidation recorded at this concentration was 255°C which is 60°C higher than that of the untreated oil. Only a slight increase in the onset temperature of 5°C was recorded upon increasing the concentration of 1-aminonaphthalene to 0.4%.

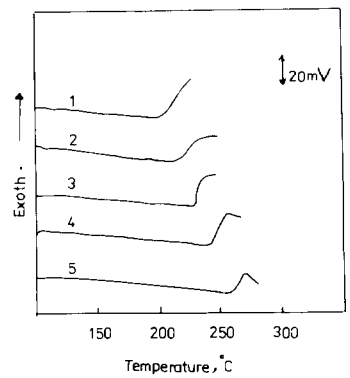


Fig. 2. DSC signals of the oxidation of the oil in the presence of 1-hydroxynaphthalene: (1) 0%; (2) 0.1%; (3) 0.2%; (4) 0.3%; (5) 0.4%.

TABLE 1

The onset temperature of oxidation of the oil in the presence of different concentrations of the additives (results are the average of two determinations)

| Antioxidant | 0% | 0.1% | 0.2% | 0.3% | 0.4% |
|---|---|---|---|---|---|
| 1-Aminonaphthalene | 195 | 225 | 255 | 258 | 260 |
| 1-Hydroxynaphthalene | 195 | 220 | 235 | 240 | 257 |

When the same oil was treated with 1-hydroxynaphthalene, a gradual improvement of its oxidation stability was recorded with increase in additive concentration. The working temperature of the oil at 0.4% concentration is increased to 257°C, which is 62°C higher than that of the untreated oil. The onset temperature at this level of concentration is almost identical to that of the oil treated with 0.2% of 1-aminonaphthalene.

*Evaluation of the naphthalene derivatives as antioxidants dynamically*

Evaluation of the naphthalene compounds was performed according to the oxidation stability test described in the experimental section. Acidity and viscosity changes of the oil samples containing various concentrations of these compounds were recorded before and at the end of oxidation (120 h).

The value of the acid number (AN) depends on the formation of carboxylic acids after prolonged oxidation. The AN increases with increasing carboxy formation and usually decreases upon increasing concentration of an effective oxidation inhibitor.

Figure 3 shows plots of acidity expressed in mg KOH per gram of sample at the end of oxidation time for various concentrations of the additives in

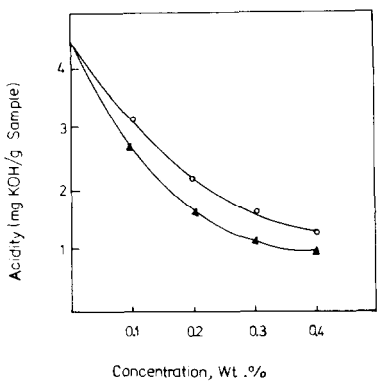


Fig. 3. Plot of acidity at the end of oxidation time expressed in mg KOH/g of sample against concentration in wt.% for the oil containing various added concentration of (▲) 1-aminonaphthalene and (○) 1-hydroxynaphthalene.

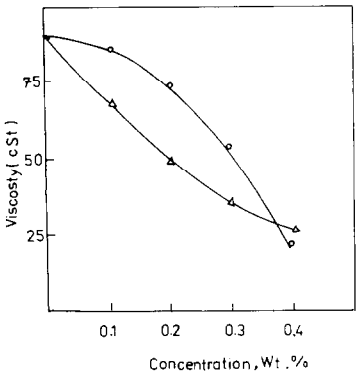


Fig. 4. Plot of viscosity at the end of oxidation time expressed in cSt at 40°C against concentration in wt.% for the oil containing various added concentrations of (△) 1-aminonaphthalene and (○) 1-hydroxynaphthalene.

the mineral oil, against concentration in wt.%. The AN value at the end of oxidation time of the untreated oil was 4.5. A marked decrease in AN values was observed upon increasing the concentration of 1-aminonaphthalene to 0.2%. The AN value at this level of concentration was 1.6. Only a small decrease in AN was recorded upon increasing the concentration of 1-aminonaphthalene from 0.2 to 0.4%. Meanwhile, a steady decrease in AN values of the oil was observed upon increasing the concentration of 1-hydroxynaphthalene, reaching a value of 1.45 at 0.4%. This value is very similar to that (1.6) of the same oil containing 0.2% 1-aminonaphthalene.

Another important criterion in studying the stability of oils is viscosity changes that occur during oxidation. The viscosity of an oil usually increases with oxidation time. However, with a higher dosage of an oxidation inhibitor, changes of viscosity with time becomes less pronounced.

Figure 4 shows plots of viscosity expressed in centistokes (cSt) at 40°C at the end of oxidation for various concentrations of additives in the mineral oil against concentration in wt.%. Viscosity values for the untreated oil before and after oxidation were 10.5 and 89 cSt, respectively. A steady decrease in viscosity of oil samples was recorded at the end of oxidation upon addition of increasing concentrations of 1-amino and 1-hydroxynaphthalenes. At 0.4% dose of additive, viscosity values were 26 and 24 cSt, respectively.

It can be concluded that upon evaluation of 1-aminonaphthalene and 1-hydroxynaphthalene as antioxidants, the former compound imparted good antioxidation protection to the mineral oil at a comparatively lower additive concentration than the latter. The data presented in this work demonstrate an excellent correlation of the results obtained from the two methods of evaluation, i.e., DSC and dynamic oxidation stability tests. The former method proved to be simple and reliable with the added advantage of using

only very small sample sizes and being less time consuming. The potential of the DSC technique is to be expanded further to include other types of antioxidants and mineral oils.

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