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# EVALUATION OF THE THERMAL STABILITIES OF SOME AROMATIC HYDROXY- AND AMINE-TYPE ANTIOXIDANTS

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## ABSTRACT

This paper discusses the evaluation of the thermal stabilities of some additives usually incorporated as antioxidants in mineral oils and lubricating greases. They include aromatic hydroxy and amine type organic compounds. The results of this thermoanalytical investigation, which was performed in a differential scanning calorimeter under ambient atmosphere and thermogravimetrically under an inert atmosphere of nitrogen gas, showed that the hydroxy-derived compounds, which are based on the quinolinic skeleton, to be of the highest thermal stability compared to those of the other additives studied.

## INTRODUCTION

The degradation of lubricants by oxidation is undesirable since it leads to the development of corrosive acids and insoluble resinous matter, and a marked increase in acidity and viscosity, all of which seriously impair the efficiency of the lubricant [1,2].

Oil oxidation is usually inhibited by the incorporation of certain organic additives and a variety of organic chemical compounds have found application as oxidation inhibitors [3]. Aromatic hydroxy and amine compounds have been used extensively as antioxidant additives. They act by interacting with free radicals present in the system, forming a non-radical substrate product and a phenoxy or phenimino radical by donation of a hydrogen atom from the antioxidant to the substrate radical. The resulting radical is well stabilized through resonance or sterically prevented from reacting further [4].

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Since these additives are incorporated in systems in concentrations ranging between 0.25 and 5%, and are subjected to severe temperature conditions, it would be of practical and scientific importance to evaluate the thermal stability of these products. In addition, the data obtained would be useful in suggesting the appropriate additive for a particular application.

Braid [5] investigated the stability of some nitrogen/sulfur containing organic antioxidants at high temperatures using thermogravimetric techniques. The additive is subjected to increasing heat while the rate of weight loss is observed. The temperature at which the rate of weight loss is markedly increased is designated as the inflection temperature, hence, a high inflection temperature indicates high thermal stability. The temperature is increased above the inflection temperature to determine the weight loss above the critical level; the lower the loss of weight, the more stable the additive is considered to be.

Differential scanning calorimetry (DSC) has been used to determine the resistance of petroleum-derived and polymeric products towards oxidative degradation and to study the effect of a range of antioxidants on them [6–8]. On heating a sample of the product in air, using a DSC apparatus, an exothermic effect resulting from oxidative degradation is recorded. The onset temperature of the exotherm can be taken as a measure of the thermal stability of these products. This technique was also used to study the efficiency of a range of organic additives in inhibiting the oxidation of these petroleum-derived and polymeric compounds [9,10]. The higher the onset temperature of the exothermic reaction the more effective the inhibitor, and vice versa.

In the work described in this paper, the thermal stabilities of some aromatic hydroxy- and amine-type antioxidant additives were studied using differential scanning calorimetry under ambient atmosphere and thermogravimetrically under an inert atmosphere.

## EXPERIMENTAL

### *Apparatus*

The DSC, thermogravimetric (TG) and differential thermogravimetric (DTG) measurements were all carried out in a Heraeus TA 500 thermal analyser. In the DSC measurements, samples weighing 5–10 mg were heated at a rate 10°C $\text{min}^{-1}$ in an aluminium crucible under ambient conditions. Pure and dried powdered aluminium oxide were placed in a similar reference crucible. Tin and benzoic acid were used in calibrating the DSC apparatus.

TG and DTG curves were recorded simultaneously by placing a sample weighing 10–15 mg in a platinum crucible and heating at a rate of 20°C $\text{min}^{-1}$ under an atmosphere of nitrogen gas flowing at 100 $\text{cm}^3\ \text{min}^{-1}$. All determinations were performed in duplicate.

### *Materials*

1-Naphthylamine, diphenylamine and *N*-phenyl 1-naphthylamine (all Analar grade) were purchased from BDH Chemicals Ltd. Di-*tert*-butyl para-cresol (DBPC) was obtained from ICI Chemical Co. 1-Naphthol, 5-hydroxyquinoline (both of more than 98% purity) and 5-hydroxyisoquinoline of 90% purity were purchased from Aldrich Chemical Co., Ltd.

## RESULTS AND DISCUSSION

The DSC traces performed between room temperature and 250°C under ambient conditions for the amine- and hydroxy-type antioxidant additives are shown in Figs. 1 and 2, respectively. The onset temperatures of the exothermic effect of oxidative degradation of some of these antioxidants were evaluated from the intersect of the extrapolated tangents of the curves and are shown in the same figures. A sharp major endothermic peak was a typical feature in all the DSC traces of these antioxidants which corresponds to the temperature region of their fusion transitions. A shoulder was also recorded in the DSC trace of 5-hydroxysoquinoline, which is referred to as the "impurity peak" and is attributed to the presence of impurities in this particular additive.

In the DSC traces of the amine-derived antioxidants (Fig. 1), 1-naphthylamine and diphenylamine exhibited onset temperatures of oxidation of 200 and 208°C, respectively. These transitions were preceded by an obvious endothermic offset from the baseline starting at about 150°C in the case of the former additive and at about 140°C for the latter. This behaviour is due

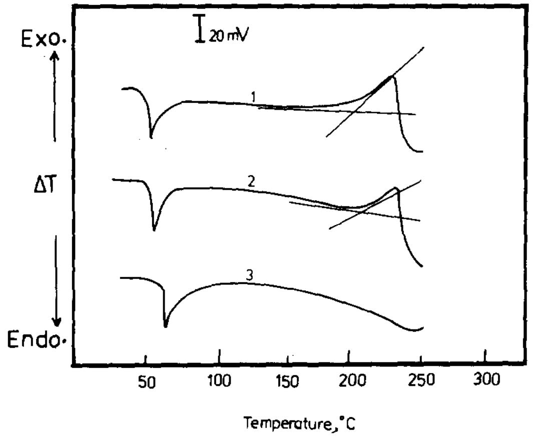

Fig. 1. DSC traces of (1) 1-naphthylamine; (2) diphenylamine; and (3) *N*-phenyl 1-naphthylamine.

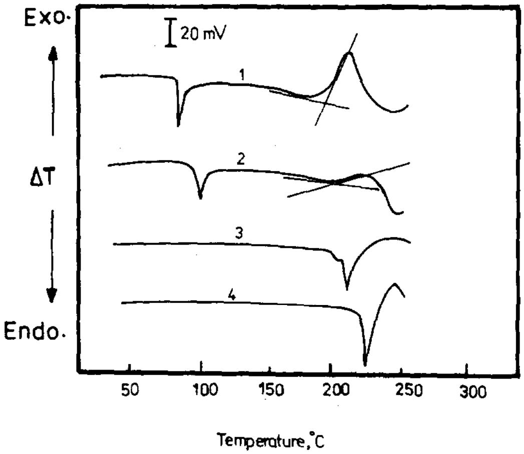

Fig. 2. DSC traces of (1) DBPC; (2) 1-naphthol; (3) 5-hydroxyisoquinoline; and (4) 5-hydroxyquinoline.

to specific heat changes and to the volatilization of the melts of these products. Phenyl 1-naphthylamine also exhibited slight endothermic offset starting at about 135°C, which is again attributed to specific heat changes and volatilization. This offset became more pronounced with increasing temperature. However, no exothermic onset temperature due to oxidative degradation was recorded up to a temperature of 250°C.

It is clear from these results that the order of stability of these amine-type additives towards oxidative degradation is as follows: *N*-phenyl 1-naphthylamine > diphenylamine > 1-naphthylamine. This behaviour may be related to the number of resonating structures of these compounds which follow the same order, i.e., the higher the number of resonating structures of a compound the more stable it is, and vice versa.

In the DSC traces of the hydroxy-derived antioxidants (Fig. 2), DBPC and 1-naphthol exhibited a similar behaviour to that of the amine-derived antioxidants, i.e., an endothermic offset from the baseline starting at about 140°C in the case of DBPC and 150°C for 1-naphthol. The onset temperatures of oxidative degadation were 194°C for the former additive and 200°C for the latter. It is also clear from Fig. 2 that no endothermic offset due to volatilization was recorded prior to the fusion transitions of 5-hydroxyquinoline and 5-hydroxyisoquinoline. However, the rate of oxidation which commenced as soon as the crystal lattice of these compounds collapsed was slower in 5-hydroxyisoquinoline.

From these results, it is clear that the hydroxy-type compounds based on the quinolinic system were more resistant towards oxidative degradation than those based on the phenolic and naphtholic systems. Recently [9], the activity of these quinolinic compounds as additives for lubricating oils was studied and they were found to provide excellent antioxidant protection to mineral oils.

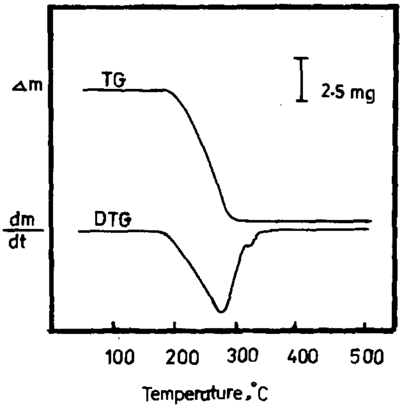

Fig. 3. Typical TG and DTG curves of the antioxidants studied.

Representative TG and DTG thermograms of the amine and hydroxy additives performed between room temperature and 500°C under an inert atmosphere of nitrogen gas are displayed in Fig. 3. The inflection temperatures of these compounds and their relative percentage weight losses at 150, 200 and 250°C are given in Table 1. The weight loss of these compounds corresponds mainly to their volatilization.

It is obvious from Table 1 that 5-hydroxyisoquinoline and 5-hydroxyquinoline had the highest inflection temperatures of transition and the lowest percentage weight losses, while DBPC possessed an inflection temperature of 125°C and the highest weight loss (33% at 150°C and 100% at 200°C).

It can be concluded that the compounds based on the quinolinic system were of the highest thermal stability amongst the additives studied, while the phenolic type compound (DBPC) was the least stable. However, the choice

TABLE 1

The inflection temperatures and the percentage weight losses recorded from the thermograms of the antioxidants studied

| Additive | MP (°C) | Inflection temp. (°C) | Percentage weight loss at | | |
|---|---|---|---|---|---|
| | | | 150°C | 200°C | 250°C |
| 1-Naphthylamine | 49–50 | 140 | 6.7 | 73 | 100 |
| Diphenylamine | 53 | 130 | 5.9 | 59 | 100 |
| *N*-Phenyl 1-naphthylamine | 60–62 | 130 | 6 | 50 | 100 |
| DBPC | 66–68 | 125 | 33 | 100 | – |
| 1-Naphthol | 95–96 | 140 | 15.4 | 98 | 100 |
| 5-Hydroxyisoquinoline | > 200 | 225 | 0 | 5 | 70 |
| 5-Hydroxyquinoline | 223–225 | 225 | 0 | 5.5 | 68 |

of these antioxidants will primarily be dependent on their behaviour and efficiency in a particular lubricant and also on the amount incorporated, which will be influenced by economical factors.

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