Talanta 107 (2013) 219–224

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Simulated aging of lubricant oils by chemometric treatment of infrared spectra: Potential antioxidant properties of sulfur structures

Sandrine Amat *, Zeineb Braham [1], Yveline Le Dréau [2], Jacky Kister [3], Nathalie Dupuy [4]

Aix-Marseille Université, LISA, EA 4672 Equipe METICA, Service 451, 13397 Marseille Cedex 20, France

ARTICLE INFO

Article history:
Received 7 September 2012
Received in revised form
7 December 2012
Accepted 13 December 2012
Available online 17 January 2013

Keywords:
Lubricant oil
Sulfur
Infrared
Oxidation
Aging
SIMPLISMA

ABSTRACT

Lubricant oils are complex mixtures of base oils and additives. The evolution of their performance over time strongly depends on its resistance to thermal oxidation. Sulfur compounds revealed interesting antioxidant properties. This study presents a method to evaluate the lubricant oil oxidation. Two samples, a synthetic and a paraffinic base oils, were tested pure and supplemented with seven different sulfur compounds. An aging cell adapted to a Fourier Transform InfraRed (FT-IR) spectrometer allows the continuous and direct analysis of the oxidative aging of base oils. Two approaches were applied to study the oxidation/anti-oxidation phenomena.

The first one leads to define a new oxidative spectroscopic index based on a reduced spectral range where the modifications have been noticed (from 3050 to 2750 cm^{-1}). The second method is based on chemometric treatments of whole spectra (from 4000 to 400 cm^{-1}) to extract underlying information. A SIMPLe-to-use Interactive Self Modeling Analysis (SIMPLISMA) method has been used to identify more precisely the chemical species produced or degraded during the thermal treatment and to follow their evolution. Pure spectra of different species present in oil were obtained without prior information of their existence. The interest of this tool is to supply relative quantitative information reflecting evolution of the relative abundance of the different products over thermal aging. Results obtained by these two ways have been compared to estimate their concordance.

1. Introduction

Among many requirements, car manufacturers aim to space the engine oil drain interval. Lubricating oils are composed of base oils supplemented with 1–30% of additives to improve their quality. They protect against corrosion, reduce damages of moving parts in engine and ease their actuation. To insure the performance and an appropriate lifetime of engines, lubricants have to be protected against aging, which is one of the major causes of oil degradation.

The stability of a lubricant regarding to the thermal and mechanic tension is mainly due to the stability of base oil [1]. Their resistance to oxidation is influenced by the nature of their hydrocarbon constituents and non-hydrocarbon ones [2]. Very small internal and environmental variations may cause major modifications in physicochemical behavior of lubricant. The influence of each component on lubricant stability is fundamental for the formulation of this lubricant. For example, the oxidation of paraffinic compounds begins slowly during the induction period then the oxidation rate increases autocatalytically [3], while aromatics compounds decrease the hydrocarbon oxidation. Their ramifications increase their resistance to oxidation. Burn and Greig [4] have shown that when the aromatic and heterocyclic (A+H) fraction in a lubricant increases a minimum amount of natural sulfur compounds is required to conduce an antioxidant action of the aromatic compounds.

In addition, Ahmad et al. [5] have shown that sulfides (as dialkylsulfides, alkylarylsulfide and diarylsulfide) were better antioxidants than mercaptans, themselves better than thiophenes. Moreover, at 0.5% (w/w) of sulfide, the resistance to oxidation of lubricant increases between 0.5 and 3% the oil inhibition level is constant.

Several researches have highlighted the natural antioxidant character of sulfur compounds naturally present in base oils [6–9]. However, the structures of these antioxidants are not well known.

The aim of this study is to determine the antioxidant behavior of several sulfur compounds on two base oils. This study was

* Corresponding author. Tel.:+33 491289002.
E-mail addresses: sandrine.amat@univ-amu.fr, sandrine.amat@gmail.com (S. Amat), brahamzeineb@gmail.com (Z. Braham), yveline.le-dreau@univ-amu.fr (Y. Le Dréau), jacky.kister@univ-amu.fr (J. Kister), nathalie.dupuy@univ-amu.fr (N. Dupuy).
[1] Tel.: +33 491289034.
[2] Tel.: +33 491282672.
[3] Tel.: +33 491288316.
[4] Tel.: +33 491288551.

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.12.051

achieved with an original Fourier Transform Infrared method using a simulating aging cell. Many kinetics of aging were carried out using different sulfur compounds at several concentrations in order to determine which compounds could be responsible for a natural inhibition of base oils and limits of inhibition with increasing concentration were defined.

A SIMPLe-to-use Interactive Self Modeling Analysis (SIMPLISMA) approach has been used to define chemical species involved during the aging treatment and to follow their evolution [10–12]. Pure spectra of some species were identified without prior information of their existence. The aim of this method is to get relative quantitative information explaining the evolution in time of the relative concentration of the different species during the thermal process.

2. Material and methods

2.1. Sampling

2.1.1. Base oils

Two base oils were chosen among samples available in the laboratory, according to their composition. The first one, oil A, which is synthetic poly-α-olefin base oil containing only paraffinic compounds, was used to study the action of sulfur compounds on paraffins, i.e., long aliphatic chains.

The second one, oil B, is a hydrotreated base oil without aromatic compounds containing paraffinic compounds and about 30% of naphtenic compounds, was selected to reveal the role of naphtenic compounds in the phenomenon of oil inhibition by sulfur compounds. This base oil presents a density of 0.854, a vicosity index (VI) equal to 98 and contains 5 ppm of sulfur.

2.1.2. Sulfur structures

Seven compounds (Sigma-Aldrich) were chosen as sulfur structures susceptible to be present in mineral base oils as following [4]:

- hexadecyl mercaptan (M), with a long aliphatic chain,
- dibutyl sulfide (DBut) with a short aliphatic chain, and didodecyl sulfide (DD), with long chain, were chosen to determine the effect of the chain length on antioxidant effect,
- two aromatic structures: diphenyl sulfide (DPh) and dibenzyl sulfide (DBZ), to study the influence of a methylene group in steric hindrance between aromatic groups.
- thiophene (T) and dibenzothiophene (DBT) chosen to evaluate the effect of the hydrogen in the α position and the influence of the stabilization resonance of aromatic groups.

2.2. Infrared spectroscopy

FTIR spectra were performed on a Nicolet Protégé 460 spectrometer coupled with a Nicolet Nic-Plan infrared microscope fitted with a MCT detector cooled with liquid nitrogen. The standard analytical conditions were, 15× infrared objective, beam size of $100 \times 100\ \mu m^2$. The spectra were acquired using Omnic Nicolet software. 64 scans of symmetrical interferograms were averaged and the spectrum was calculated from 2000 to 850 cm^{-1} at 4 cm^{-1} spectral resolution.

Ageing tests were performed with an ageing cell that had been initially developed in our laboratory to study the structural evolution of liquid fossil organic material [13] during ageing. It allows working in a horizontal geometry decreasing crop of fluids under regulated thermo-oxidizing conditions. To study the resistance to oxidation of base oils of different groups, this cell has been used with some modifications.

The oil sample was "trapped" in a 1 mm deep cavity (diameter 0.5 mm) in a NaCl window (13 mm × 2 mm) machined so that it was possible to collect a background spectrum at any time in a smaller cavity (diameter: 0.5 mm) that did not contain the sample.

6 mg of oil was placed in the 5 mm diameter cavity of the NaCl window and heated from 22 °C up to 170 °C under neutral gas at 11 °C min^{-1}. Then, heating was maintained at 170 °C under oxidant gas (synthetic air) during all the experiment. Spectra were collected every 2 min during the oxidation process.

Aging of samples was followed by calculating a spectroscopic index, from band areas measured from valley to valley [14–17]. The band areas were considered rather than the band heights in order to obtain a finer index.

The following areas were defined (Fig. 1a):

- A1: from 1850 to 1685 cm^{-1} (multiple C=O bands.)
- A2: from 1502 to 1419 cm^{-1} (bands at 1467 and 1450 cm^{-1}.)
- A3: from 1396 to 1369 cm^{-1} (band at 1378 cm^{-1}.)

The carbonyl index is given by the following Eq. (1):

$$I_{C=O} = A1/(A1+A2+A3) \quad (1)$$

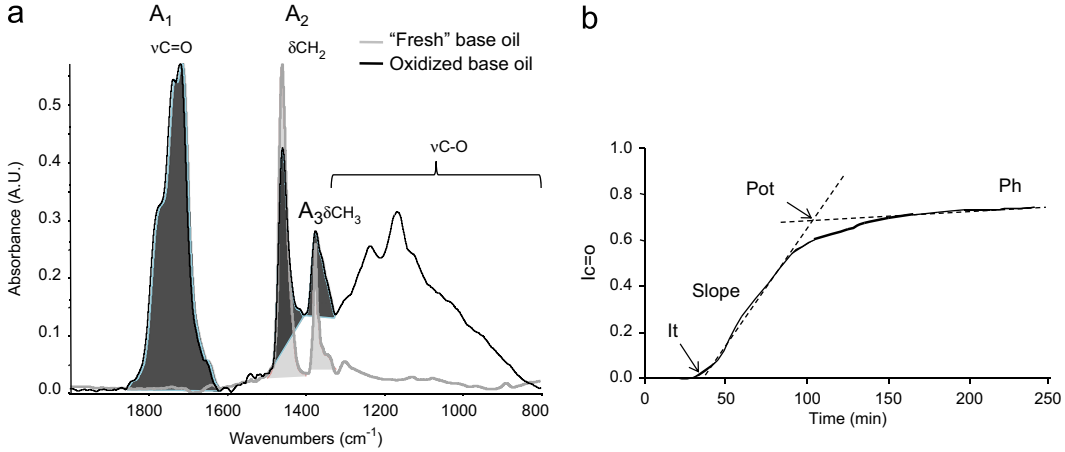

Fig. 1. (a) FTIR spectrum of base oil A before and after oxidation (2000 to 800 cm^{-1}); (b) graphic representation carbonyl index ($I_{C=O}$) versus time of oxidation and the oxidation kinetics parameters. It: induction time; Pot: plateau onset time; Ph: plateau height.