

Thermal Analysis Application Brief

High Resolution TGA / Mass Spectroscopy Characteristics of Fuel Oil Transport Additives

Number TA-141

SUMMARY

An understanding of the thermal and oxidative stability of fuel oil additives is essential when formulating blends for higher temperature applications. High Resolution TGA combined with mass spectroscopy provides information about the volatilization and decomposition processes in those materials, thereby improving that understanding.

INTRODUCTION

Oil additives are designed to improve the properties (e.g., flow, and oxidative stability) of the base fuel oil with which they are blended. Clearly, it is important to ensure that these additives continue to provide their intended benefit throughout the temperature range of use. However, many of these additives volatilize and/or decompose as temperature increases. Nevertheless, by better understanding when and how these undesirable processes occur, the oil chemist can tailor the additives to specific situations.

Thermogravimetric analysis (TGA), which measures weight changes in materials as the temperature is increased, provides an excellent way of characterizing fuel oil systems. However, while TGA readily provides quantitative weight change information about decomposition and volatilization, it does not generally provide information about the identity of specific off-gas materials. Obviously, the latter information is valuable in understanding decomposition mechanisms. Hence, TGA is often coupled with other analytical techniques (e.g., mass spectroscopy and FTIR) in order to obtain this qualitative data. Furthermore, with the recent advent of commercially available high resolution TGA capability, the ability to obtain this qualitative information is improved.

EXPERIMENTAL

A TA Instruments' High Resolution (Hi-Res™) Thermogravimetric Analyzer TGA 2950, with autosampler accessory and Thermal Analyst 2100 Controller, were used to measure the weight loss profiles of several common fuel additives. The TGA 2950 was used in both the conventional constant heating rate mode and in the high resolution mode. In the high resolution mode, the TGA heating rate is adjusted in response to changes in the rate of weight loss, resulting in faster experiments as well

as improved resolution of overlapping weight losses. The instrumentation has been described in detail elsewhere (1). The evolved degradation products were passed into a VG (Fisons) quadruple mass spectrometer, Model 300. Commercial and “in-house” software was used to analyze the thermogravimetric and mass spectrometric data.

Samples of approximately 5-10mg were heated in platinum TGA pans at constant or dynamic rates from ambient to 700°C in a flowing (50 ml/min) air or nitrogen atmosphere. For combined TGA/ mass spectrometric analyses a purge gas mixture of 20% oxygen in argon was used to minimize background signals.

RESULTS

Figure 1 shows the TGA weight loss derivative curves for a commercially available polyether additive (Oxilube 500) heated at 50°C/min in both oxidizing and inert atmospheres. Under the inert atmosphere (nitrogen), the polyether volatilizes over a broad temperature range (200-350°C) with a maximum rate of weight loss (1.1%/°C) at 220°C. In oxygen, on the other hand, the rate of weight loss is nearly 20 times faster than in nitrogen and occurs at a temperature about 30°C lower. These two curves show that the behavior in oxygen is different and indicates that

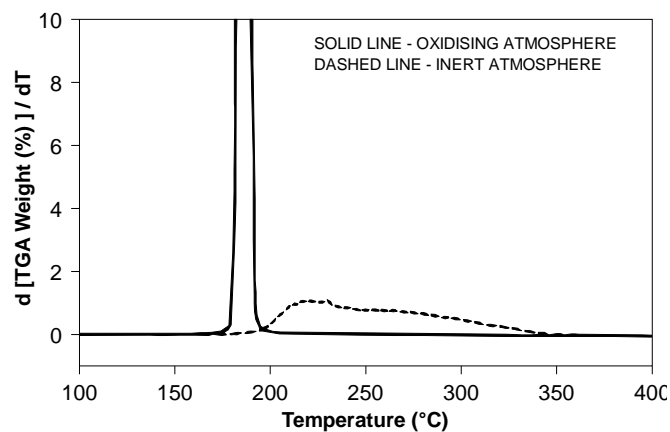


Figure 1

decomposition (oxidation) is probably occurring. However, without identification of the evolved gases, absolute verification is difficult.

Figure 2 illustrates that coupling to a mass spectrometer helps to provide that verification. In this case, the behavior of phenylchlorofomate (MW 156.6), another oil additive, is characterized while heating at 15°C/min in air (oxidizing environment). The TGA curve shows immediate onset of weight loss with heating, and by 100°C the entire sample weight is lost. Evaluation of the mass spectrometer m/e plot at the point of maximum loss (6.42 minutes), Figure 2, indicates that the only off-gas product is the base material, thereby verifying the fact that volatilization, not oxidation, is occurring.

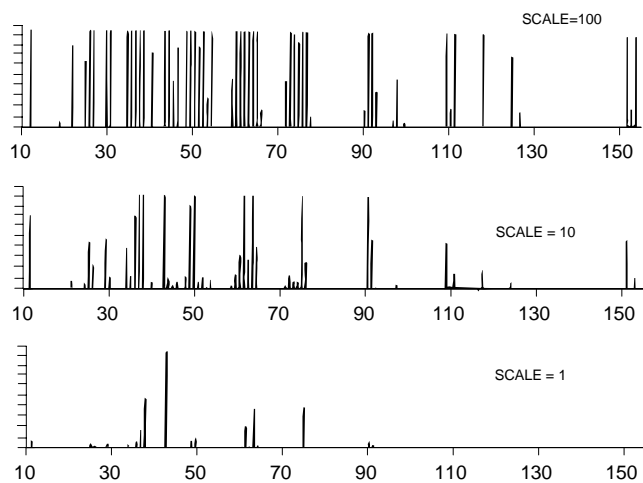


Figure 2

Figures 3 and 4 show the comparative conventional TGA and High Resolution TGA results for two polymer derivatives used with fuel oils. These materials are more complex than the two earlier organic liquid additives and generally consist of a polymer backbone to impart solubility and thermal stability, a coupling agent, and a “property enhancing” group. The overall aim for these polymer derivatives is wide temperature stability with low residue breakdown. The later is important since carbonaceous residue could affect engine performance. The TGA derivative profiles are compared in this case because fine detail “fingerprint” information is more easily seen.

For Polymer Derivative A (Figure 3) conventional TGA yields a broad, non-descript derivative profile. It is difficult to determine if multiple weight losses are present. Hence, projecting the breakdown mechanism and quantifying the associated weight changes is impossible. Hi-Res™ TGA, on the other hand, yields a sense of separate weight loss peaks which mass spectroscopy shows to be toluene (the solvent used during preparation of the material) and several polymer fragments typical of hydrocarbon backbone. The more complete information provides direction when researching ways to improve the thermal stability of the material. Table 1 summarizes weight losses associated with the degradation steps. The weight at 160°C, after the loss of solvent,

has been ratioed to 100% to allow all calculations to be made on a “dried” basis.

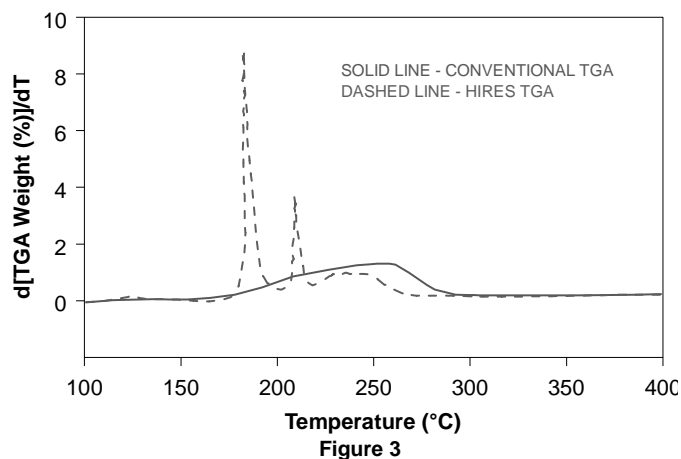


Figure 3

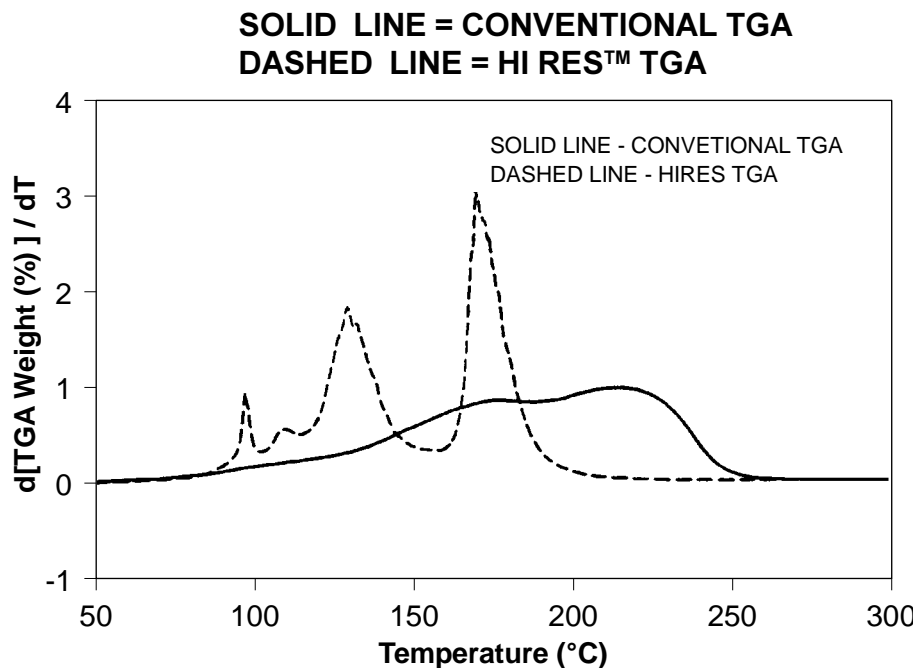
Table 1

Weight Loss Step	Temperature of Maximum Rate of Weight Loss (°/°C)	Weight Loss (%). Calculated on the "Dried" Weight at 160°C.
1	184	44.75
2	212	15.45
3	237	38.34

Table 2

Weight Loss Step	Temperature of Maximum Rate of Weight Loss (°/°C)	Weight Loss (%). Calculated on the Dried Weight at 160°C.
1	99	6.29
2	111	5.48
3	132	39.1
4	174	49.1

The results for Polymer Derivative B (Figure 4) are similar. Conventional TGA indicates at least two weight losses are present, based on the weak inflection at about 200°C. Hi-Res™ TGA not only separates those two major weight losses for further identification, but also indicates that two additional smaller weight losses are present. Table 2 summarizes the weight losses observed.



References

I. P.S. Gill, S.R. Sauerbrunn & B.S. Crowe, *JThermalAnal*, **38**, 255-266 (1992)

Acknowledgments

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