

Oxidative
Behavior
of
Materials
by
Thermal
Analytical
Techniques

*Alan T. Riga and
Gerald H. Patterson, editors*



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Foreword

This publication, *Oxidative Behavior of Materials by Thermal Analytical Techniques*, contains papers presented at the symposium of the same name, held in New Orleans, Louisiana, on 21-22 Nov. 1996. The symposium was sponsored by ASTM Committee E37 on Thermal Methods. Alan Riga and Gerald Patterson served as chairpersons of the symposium and are editors of the resulting publication.

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Overview

This Special Technical Publication represents a compilation of presentations from an international symposium addressing the Oxidative Behavior of Materials by Thermal Analytical Techniques which was held 20-21 Nov. 1996 in New Orleans, Louisiana. The symposium and this subsequent publication examine the new thermal analytical techniques describing the physical properties and oxidative degradative behavior of polymers, lubricants, and petrochemicals. Historical reviews, oxidation mechanisms, new test methods, unique techniques, robotic methods, new reference standards, and bias considerations form the basis of this publication.

It was generally agreed, but certainly highlighted by Roger Blaine, TAI, keynote speaker, that the factors affecting the oxidation induction time (OIT) were: the isothermal temperature; pan type, metallurgy, and shape; and pressure and oxygen flow rate. Polymer oxidation was emphasized in a number of papers. Professor Joseph Perez, Penn State University, keynote speaker, focused on the measurement of oxidation in formulated passenger car and diesel engine oils. Professor Perez discussed the evolution of oxidation systems from the complex Dornite type systems of the 1940s to the current use of microreactors, for example, DSC, TGA, and Klaus Penn State Microreactor (PSMO). He stressed the variables such as: metal surfaces that affect the rate of oxidation or thermal decomposition, temperature effects on the related thermal and oxidative processes, effects of volatility on vapor phase versus liquid phase oxidation, oxygen diffusion rate limitations, and additive effectiveness. Some of the differences in the thermal and oxidative behavior in bulk systems (engine tests) and microsystems (DSC, TGA, PSMO) were discussed.

Alan Riga, Lubrizol, reviewed the recently approved and soon to be published Standard Test Method for Determining OIT of Hydrocarbons by DSC/PDSC. An interlaboratory study using this DSC/PDSC method was reported by Blaine and Riga, with ASTM Reference C, a diluted fully formulated engine oil from Lubrizol and ASTM Reference D, a polyethylene film from TAI.

A successful robotic DSC evaluation by M. Kelsey, Mettler-Toledo, clearly differentiated References C and D at 195°C and one atmosphere of oxygen. This abbreviated OIT method without heating/cooling (from room temperature) or gas switching reduces the experimental time, avoids a nitrogen purge, and gives a slightly better reproducibility. The abbreviated OIT method suggests a possible revision to the DSC ASTM E37 test protocol. A question raised by a number of participants was "Is it possible that some PDSC oxidative testing can be replaced with robotic DSC?"

A modified Arrhenius model was used to predict OIT of polymers. An adaptation of this model for evaluation of the oxidative stability of oils was discussed.

A new scanning DTA/TGA oxidation test was presented. This DTA method is based on air oxidation and defines an oxidation temperature. A good correlation was observed between the isothermal PDSC OIT in oxygen of eight readily available olefin reference polymers and the oxidation temperature. The DTA air oxidation method as well as the PDSC oxygen method use the melting temperatures and heat of fusion of polyethylenes and polypropylenes to verify the temperature and heat calibrations.

A unique approach to the oxidation process was presented by Rick Seyler (Kodak). This paper considered oxidation as a negative factor in the determination of vapor pressure by

DSC in nitrogen. The observed exotherms in DSC measurements were associated with partial oxidation of the chemical specimen from residual air in the DSC specimen container. An application of this method is to study vapor phase oxidation of organics.

Other applications of DSC or PDSC oxidation tests included: radiation-damaged polyethylene, cellulose, thin film oxidation, medical polymers, and asphalts.

The attendees agreed that this symposium was rewarding and much knowledge was gained. They commented that the presentations focused on areas that have not been previously discussed. Symposium cochairman, Alan Riga, suggested that another meeting be organized in two years at a future NATAS conference. The speakers and attendees agreed.

Rick Seyler, Kodak, summarized the symposium in the form of the following poem:

OIT BLUES A SYMPOSIUM REVIEW

By R. J. Seyler

Don't you know its not thermodynamic?
Rather, OIT is really quite kinetic!

So when you do your OIT
It most likely won't be like me!

With so many ways to do the test
Precision within-lab will be the best.

When finally on a protocol we agreed
Exact control of temperature we'll need.

So now proceed as best we can
Just make sure its an aluminum pan.

Beware when other metal is present
Copper catalysis is a serious contaminant.

Other conditions like area, weight, and flow
Their influence we will need to know.

To switch the purge gas it was shown
One need not, for the BIAS is now known.

A last condition we yet must know
What point in time do we declare zero?

When all our tests we run one way
Which value of OIT do we report today?

Extrapolated onset, threshold, or the peak
'Tis a single number of value that we seek.

We need to realize that induction time
May have different significance for yours and mine.

Unless our sample is without formulation
OIT will address the type of stabilization!

We have tried our best to listen well
To learn all the messages you had to tell.

But when all is said and done
We should yet be troubled by just this one.

That from accelerated aging over which we toiled
The egg we hatched may have been Hard Boiled!

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