Determination of elemental sulfur in phosphorous pentasulfide by temperature modulated differential scanning calorimetry

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Abstract Phosphorous pentasulfide is an important starting material for a number of commercial chemicals. Examples include lubricant additives (Spikes, Trib Lett 17:469–489, 2004), agricultural insecticides (Kirk-Othmer, Encyl Chem Technol 14:549–552, 1995), and mining ore flotation agents. Phosphorous pentasulfide is a mixture of several components, one of which is free elemental sulfur, present at levels of approximately 50 ppm to 20,000 ppm (2 %). The amount of free sulfur present in the phosphorous pentasulfide can impact manufacturing, such as zinc dithiosulfate processing. Therefore, an accurate and fast analytical method to measure elemental sulfur in phosphorous pentasulfide would be of value compared to what is available now.

Keywords Thermal analysis · Modulated differential scanning calorimetry · Sulfur · Crystalline · Amorphous · Phosphorous pentasulfide

Experimental

Instrumentation used for this study was a TA Instruments model Q2000 DSC with Tzero^{TM} heat flow measurement technology and patented sinusoidal temperature modulation (MDSC$^®$), making it possible to separate total heat flow (conventional DSC) into reversing (heat capacity, molecular mobility related) and non-reversing (kinetic related) components [1–6]. It was equipped with a TA Instrument model RCS90 refrigerated cooling system capable of cooling down to −90 °C.

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Multiple instrumental methods were used in this study, the details of which are incorporated into the relevant sections of this document, including sampling and safety precautions.

Introduction

The current method for phosphorous pentasulfide elemental sulfur analysis is labor intensive and not easily reproduced. Suppliers now react ∼10 grams of phosphorous pentasulfide with excess methanol. This is followed by a low temperature precipitation step, collection of sulfur on a filter, and drying to a constant weight. During this procedure, toxic hydrogen sulfide gas must also be trapped. (See Fig. 1a–c).

Our experience with this method gave highly variable and often lower-than-expected results for samples containing less than 2,000 ppm free sulfur. The question arose, "Is there a better method?"

A literature check uncovered no previous work using temperature modulated differential scanning calorimetry (TMDSC) for phosphorous pentasulfide free sulfur measurement. We therefore investigated if this technique could be used, since elemental sulfur-melts quite lower than the major components in phosphorous pentasulfide.

There are several challenges to using differential scanning calorimetry (DSC) for free sulfur analysis in phosphorous pentasulfide. Since it is a trace analysis, matrix effects from the major products present can be significant. This necessitates reference samples from the same manufacturing process as the unknowns, if quantitative results are the goal. Analysis of the data is not always straight forward due to the variability in the forms of free sulfur present, such as amorphous, rhombic, and monoclinic. Sulfur is also very sensitive to applied thermal history,

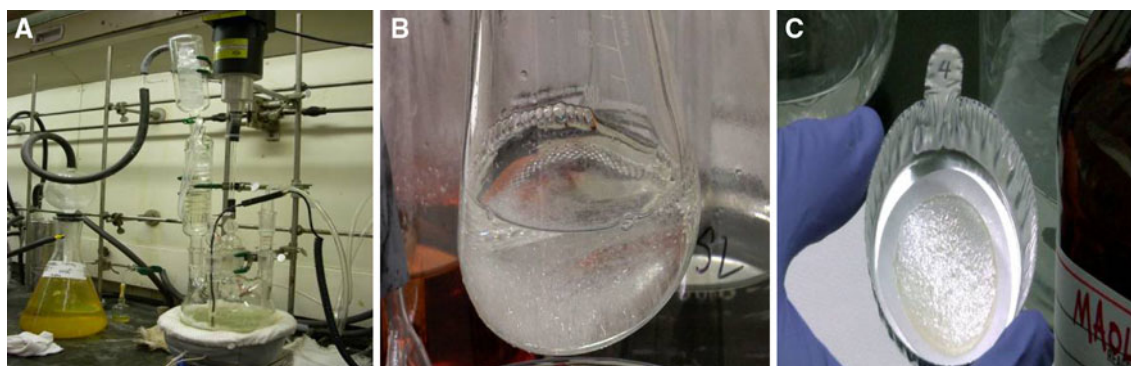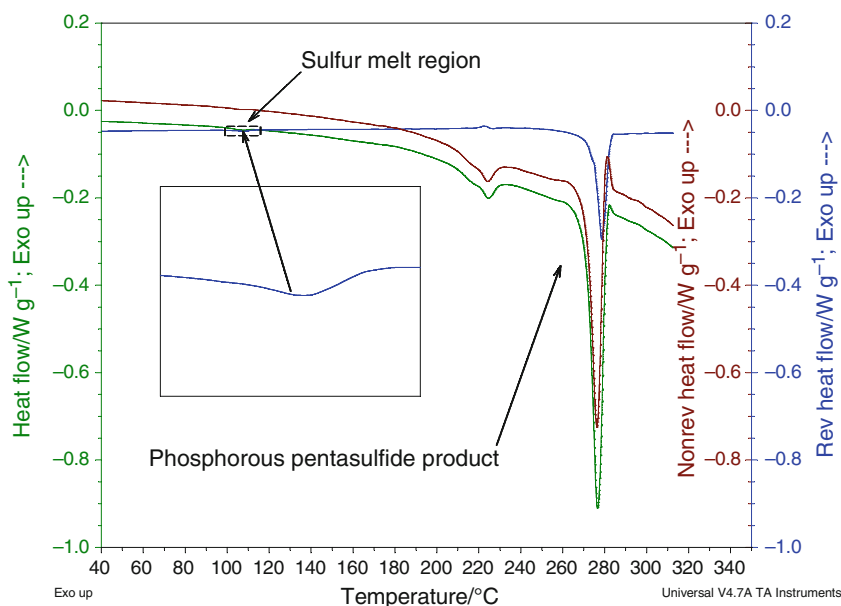**Fig. 1** Visual representation of current, labor-intensive method for phosphorous pentasulfide elemental sulfur analysis

Fig. 2 (Exo up)-Total, reversing, and non-reversing heat flow curves of a single run

especially cooling conditions. And sublimation of sulfur can occur at ∼96 °C while the monoclinic crystals are only stable at temperatures above 95 °C.

Fortunately, some of these same challenges also lead to advantages in using DSC with temperature modulation. Separation of kinetic events from the reversing heat flow thermographs for example gives a more detailed view of the sulfur melts. This provides the sensitivity needed for the phosphorous pentasulfide samples with free sulfur in the lower range (100–1,200 ppm). Batches can be qualitatively evaluated with a heat-only experiment that differentiates samples "as-received" based on overall free sulfur content, sulfur forms, and melting characteristics of the product itself. Responses to controlled heating or cooling conditions can be evaluated with heat-cool-heat experiments and used to determine which batches would be suitable for various production scenarios. Limited quantitative analyses are possible with either approach, if suitable reference samples are available from the manufacturing process being monitored.

There is a very large difference in the melting points (Tm) of the major components in phosphorous pentasulfide and in the various forms of elemental sulfur:

$$P_4S_{10},\ P_4S_9\ =\ Tm \sim 280\,°C$$
$$Sulfur\,(\alpha,\,\beta)\ =\ Tm\ 113,\ 119\,°C$$
$$Sulfur\,(amorphous)\ =\ Tm\ \sim 120\,°C$$

Because of the significant gap in temperature, DSC was chosen for this analysis. To enhance the sensitivity of the melting activity in the DSC, TMDSC was also applied to separate the reversing heat flow activity from the kinetic effects. A literature check uncovered no previous work using TMDSC for phosphorous pentasulfide free sulfur measurement.

Conclusions and discussion

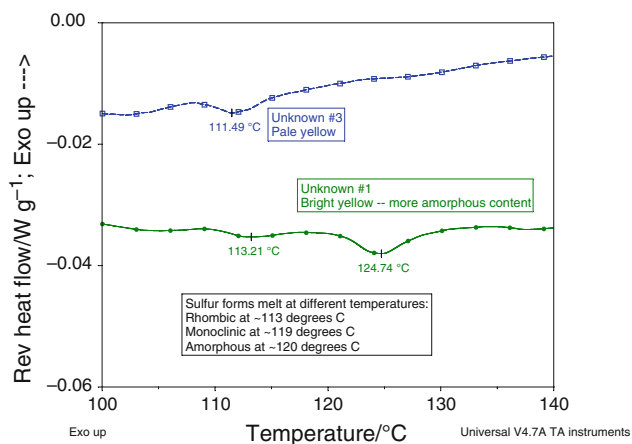The free sulfur content of phosphorous pentasulfide can be detected using TMDSC. Figure 2 displays a full calorimetric

Fig. 3 (Exo up)-Manifestation of different forms of sulfur in the product
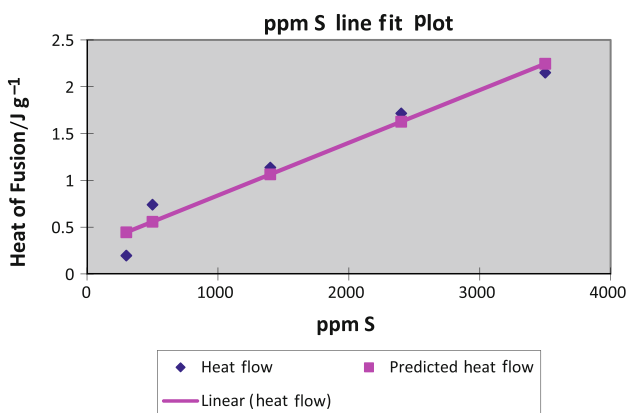

Fig. 4 Quantitative data from two-step method

profile of phosphorous pentasulfide that does contain free sulfur. The sulfur melting region is resolved from the bulk of the product melting region, and the separation of the heat flows by TMDSC provides a measurable peak for analysis. This data can be useful to both manufacturers and consumers of phosphorous pentasulfide.

An additional bonus of using TMDSC is the ability to discern the different forms of sulfur. The examples in Fig. 3 display the melting endotherms in the reversing heat flow curves of a sample with and a sample without amorphous sulfur present.

Two approaches may be taken in choosing a DSC method for analyzing phosphorous pentasulfide. A two-step procedure may be applied to eliminate moisture and to simplify the curve for analysis by melting and cooling the free sulfur into a specific form for analysis. This approach is recommended for quantitative analysis of the free sulfur present. A representation of a series of samples analyzed with the two-step method is displayed in Fig. 4, in which the sulfur melt (expressed as J g^{-1}) is compared to free
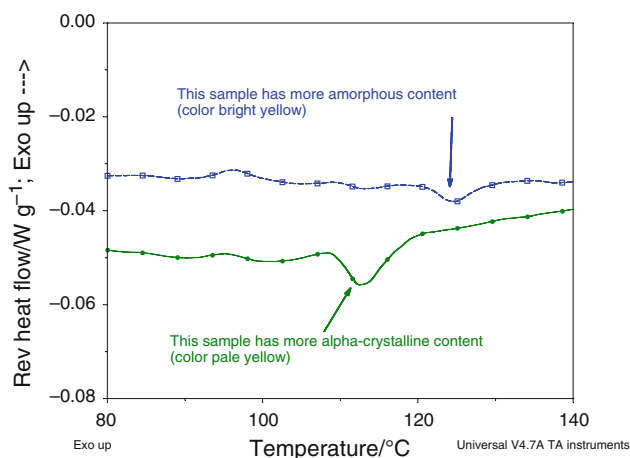

Fig. 5 (Exo up)-Qualitative comparison from one-step method

sulfur results from the wet-chemistry method. A one-step procedure, which is more time-efficient, may be applied if the primary goal of the DSC is to examine the melting point of the phosphorous pentasulfide products, if moisture is not a significant concern, or if qualitative examination of the free sulfur in the material "as-received" is the goal. The one-step procedure can be semi-quantitative depending on moisture content and relative amounts of the sulfur forms present. Figure 5 displays differences in sulfur morphology between two samples with similar quantities of free sulfur present using a one-step procedure.

And finally, samples of phosphorous pentasulfide containing higher amounts of free sulfur (~8000 ppm and above) can be screened out during the initial heating of the sample due to the pronounced exotherm, presumably from the higher tendency for evolution of hydrogen sulfide (H_2S). Figure 6 displays the distinct difference in non-reversing (kinetic) heat flow between a sample with high free sulfur and a sample with lower range free sulfur.

Considerations for choosing method parameters

Both the goal of the application and the behavior of sulfur under various applied thermal conditions must be considered when deciding what experimental parameters should be used to analyze free sulfur in phosphorous pentasulfide. If the goal is to examine the material as-received, for instance in quality-control or raw-material verification applications, then parameters should be chosen that do not change the sulfur morphology. If the goal is to determine how the sample may be treated to obtain a specific form of free sulfur, for instance in production situations where a particular morphology is more conducive to the process, then temperature profiles can be designed to maximize the presence of a particular sulfur form.

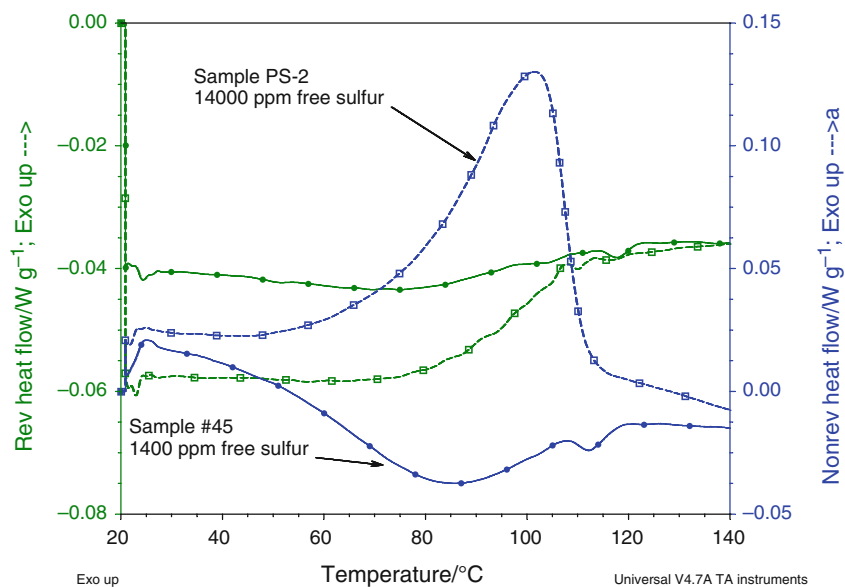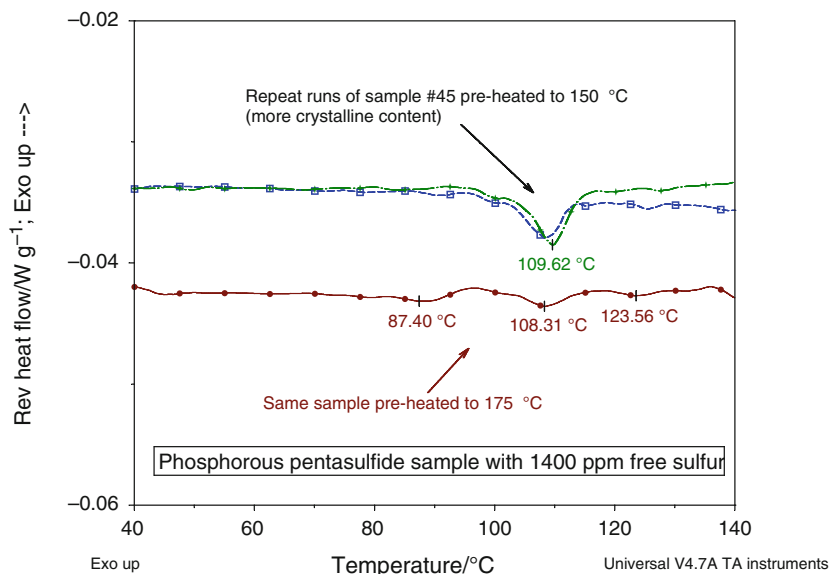**Fig. 6** (Exo up)-Exotherm evident in high free sulfur sample

Fig. 7 (Exo up)-A single sample given different thermal histories

Amorphous sulfur (commonly known as "plastic sulfur") is the quenched product of sulfur-melts above 160 °C. If the goal is to examine the tendency of a sample to form amorphous free sulfur, then the sample should be heated to above 160 °C and can be electronically quench-cooled using a refrigerated cooling system. If the goal is to quantify the free sulfur with minimal perturbation of the sulfur morphology but still drive off the moisture that can confound heat flow measurements, then the sample should be heated to above 150 (but below 160) °C before electronic cooling. Figure 7 illustrates how the same sample can be altered, depending on the applied thermal conditions programed into the DSC method. And if the goal is to view the sulfur content qualitatively for differentiation or to monitor the melting point of the phosphorous pentasulfide

product, then a single heating ramp should be applied. Table 1 illustrates how the melting point of the product can be affected by the presence of free sulfur.

Experimental details

In addition to the safety precautions (ventilation and personal protective equipment) that must be carried out in the laboratory when the possibility of H$_2$S evolution is present, sample handling to reduce the exposure of the sensitive DSC components to the corrosive gas should also be taken. For these studies, Tzero^{TM} aluminum sample pans were hermetically sealed to contain the vapors. Therefore, small sample sizes (target 2.4–3.0 mg) were used to prevent

Table 1 Effects of free sulfur (S) on the melting of the product

Sample ID	S (ppm by wet-chemistry method)	Tm of phosphorous pentasulfide/°C	Comments
# 46	500	276	Anomaly peak between ∼200 and 250 °C also present in samples below ∼750 ppm
# 39	2400	275	
# 43	3500	272	Higher amounts of free S correlate with lower Tm onset of the product
# 2	14,000	272	

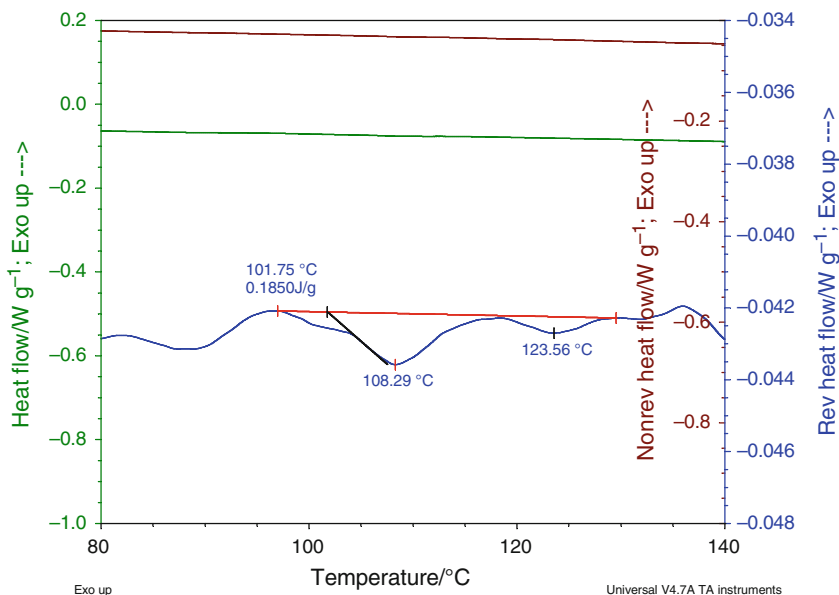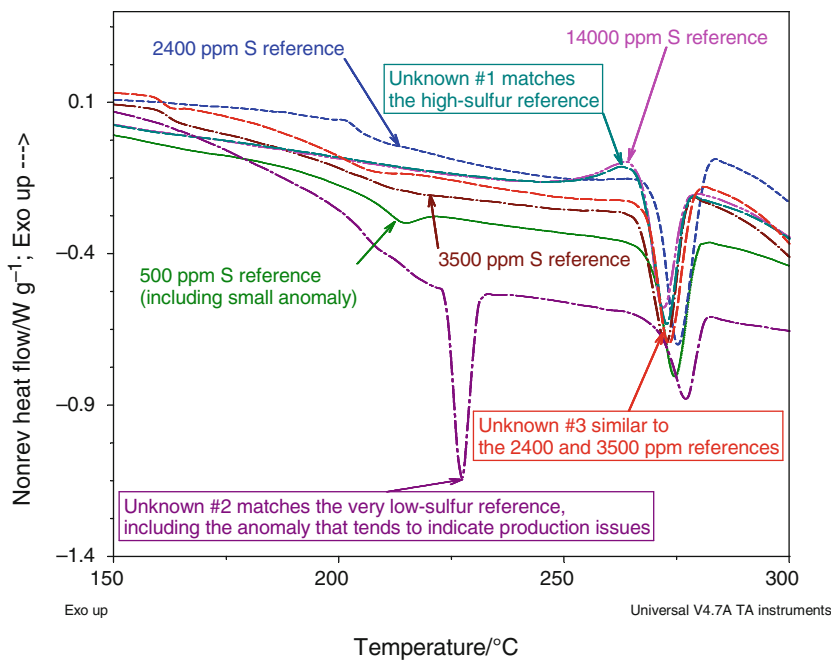**Fig. 8** Example of data processing parameters

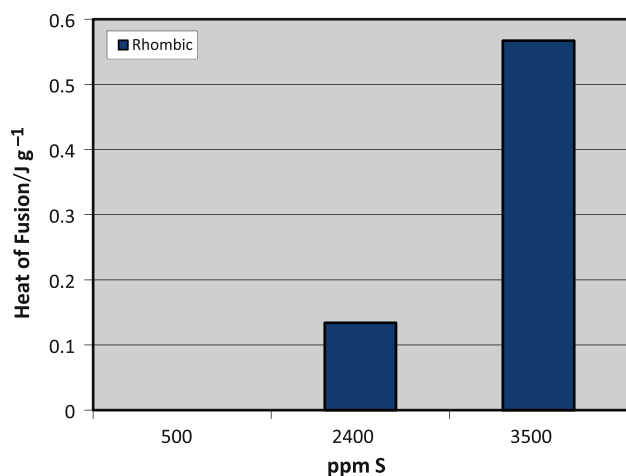**Fig. 9** (Exo up)-Comparing unknowns to analyzed references

Fig. 10 Examination of the rhombic form of sulfur in three samples

overfilling the head space. Aluminum hermetic lids with laser pin-holes may be used in cases where the free sulfur content is greater than ∼8000 ppm to allow for minimal, controlled release of the gas from the head space that may be efficiently swept out of the cell by the gas flow (50 ml/min, dry nitrogen).

The method used for quantitative analysis of free sulfur in phosphorous pentasulfide samples relative to the suppliers' data from the traditional wet-chemistry method began with an equilibration step at 20 °C and an applied temperature modulation of ± 0.53 °C every 40 s (modulation optimized to the melting activity of the phosphorous pentasulfide product). After an isothermal period of 5 min, the temperature was ramped at a rate of 5 °C per minute to 175 °C and held isothermally for 5 min to allow sufficient time for melting of the free sulfur. Next, the sample is electronically quenched and equilibrated at 20 °C before the final temperature ramp of 5 °C per minute to 320 °C.

A series of seven samples ranging in free sulfur content from 300 to 5,800 ppm from multiple suppliers was analyzed for the heat of fusion of the combined sulfur melting endotherms. Figure 8 displays the processing parameters used. If any particular sulfur morphology is of interest, the endotherms could be analyzed separately.

The linear fit to the sulfur values provided by the suppliers resulted in an *R*-value of 0.89 for the initial selection of seven samples. After examination of multiple data files, it became apparent that the matrix effects of the phosphorous

pentasulfide product varied by manufacturer. A more representative calibration curve can be developed using samples from only one manufacturer. The linear fit for a selection of samples from a single supplier over the range of 300–3,500 ppm free sulfur resulted in an R-value of 0.97, as represented in Fig. 4 of the "Conclusions and discussions" section.

The one-step method used for a qualitative assessment of phosphorous pentasulfide samples also began with an equilibration step at 20 °C and an applied temperature modulation of ± 0.53 °C every 40 s. After an isothermal period of 5 min, the temperature was ramped at a rate of 5 °C per minute to 320 °C. Figure 9 displays a comprehensive overlay of how newly received samples can be compared with a selection of reference samples by viewing both the sulfur melting region and the phosphorous pentasulfide product melting region using the non-reversing heat flow curves. This approach gives an understanding of the synergistic effects of the free sulfur content and the overall physical characteristics of the product.

By focusing on the melting region of the free sulfur content, comparisons can be made on that region alone, as depicted in Fig. 5 of the conclusions and discussion section. An example of how this method can be used semi-quantitatively can be found in Fig. 10, in which the heat of fusion of the melting activity of only the rhombic (α crystalline) form of sulfur. The presence of moisture could adversely affect the accuracy of the one-step method to resolve the melting peaks.

References

1. H. Spikes. The History and Mechanisms of ZDDP. Trib Lett. 2004;17(3):469–89.
2. Kirk-Othmer. Encyclopedia of chemical technology, 4th ed. © 1995;14:549–52; and refs. cited therein.
3. Gill P, Sauerbrunn S, Reading M. Modulated differential scanning calorimetry. J Therm Anal Calorim. 1993;40(3):931–9.
4. Reading M, Luget A, Wilson R. Modulated differential scanning calorimetry. Thermochim Acta. 1994;238:295–307.
5. Wunderlich B, et al. Temperature-modulated differential scanning calorimetry of reversible and irreversible first-order transitions. Thermochim Acta. 1999;330(1):21–38.
6. Simon S. Temperature-modulated differential scanning calorimetry: theory and application. Thermochim Acta. 2001;374:55–71.