

Thermal Analytical Characterization of Lube Oils and Greases

By: R. L. Blaine, E. I. du Pont de Nemours & Co.

Presented at the NLGI 43rd Annual Meeting in St. Louis, Missouri, October 1975

THE LUBRICANT chemist is often faced with the problem of determining a wide variety of chemical and physical properties of materials that are mixtures and blends. These properties must be measured on crude starting materials and spent waste materials, as well as refined products. In order to accomplish this rather formidable task, the lubricant industry has developed a large set of sometimes complex, almost always empirical, analytical methods. The equipment and procedures used for a specific test can seldom be used for other tests, necessitating a large investment in equipment and skilled operators.

The analytical laboratory that is equipped with thermal analysis equipment, however, finds that it has an extremely useful tool to apply to lubricant products. Thermal analytical techniques, particularly differential scanning calorimetry (DSC), are capable of providing a large number of quality and stability parameters useful in evaluating a number of lubricant products and parameters. The data gathered by DSC often can be correlated with standard ASTM methods, permitting comparison with samples run by conventional methods. In addition, thermal analysis often presents marked advantages over conventional methods when applied to lubrication products.

Thermal analysis methods are: 1) faster — most thermal analysis procedures are easily accomplished within an hour; 2) more reproducible — thermal analysis accurately measures thermodynamic properties with an objective nonhuman detector; 3) more sensitive — milligram quantities of sample are required; 4) suitable for multiple use — the basic equipment can be used for a wide variety of tests without modification; 5) more fundamental — thermal methods are low on empiricism making the data gathered in the quality control laboratory useful to the research laboratory; 6) more versatile — thermal methods often provide multiple information in a single experiment.

The basic principles of thermal analysis and their application to a wide variety of materials have been reviewed in popular laboratory literature and in monographs¹⁻⁹. In addition, several comprehensive articles on thermal analysis applied to petroleum products have appeared in the recent literature^{2,3,4,5}.

While some of the pioneering work on lubricants was carried out by workers using modified equipment, all of the techniques discussed here can be accomplished on commercially available equipment.

DSC is the most widely used thermal analysis technique in the lubricant laboratory. In DSC, the environment of a sample is either heated or cooled at a linear rate (i.e., the "scanning" part of DSC). During this scan, the energy uptake or release by the sample is compared quantitatively (i.e., calorimetrically) with an inert material (i.e., differentially). This measurement (and its display by a recording device) of the sample's basic thermodynamic properties is related to quality assurance parameters.

Discussion

Many lubricating oils, the base for many lubricants, contain paraffinic (waxy) hydrocarbons, which crystallize upon cooling. The crystallization of a portion of a lube oil affects its viscosity and, of course, its lubricating ability. In order to lower the useful temperature of a lubricating oil, this crystallizable portion must be removed. There are two common ways of doing this. The first is to take a lower boiling fraction. Although this will improve the lower temperature performance of the oil, it does so at the expense of high temperature performance. A second procedure is to remove by filtration those products that crystallize upon cooling. This extends the useful temperature range of the product by lowering its crystallization temperature while maintaining a high boiling point. Clearly, then, the crystallization temperature and wax content of a particular oil are important quality control parameters.

DSC can be used to determine quickly both crystallization temperature and wax content of oils in the same scan. Figure 1 illustrates some DSC scans obtained by cooling samples from room temperatures to near -100 C. Since these are cooling curves the scans run from right to left, and crystallization (an exothermic process) is indicated by an upward deflection. Three important parameters can be measured: 1) crystallization onset temperature, 2) crystallization peak temperature, and 3) heat of crystallization.

ANALYSIS OF LUBRICATING OILS

Paraffin Crystallization

[F. Noel in *J. Inst. Petrol.* 57, 354 (1971)]

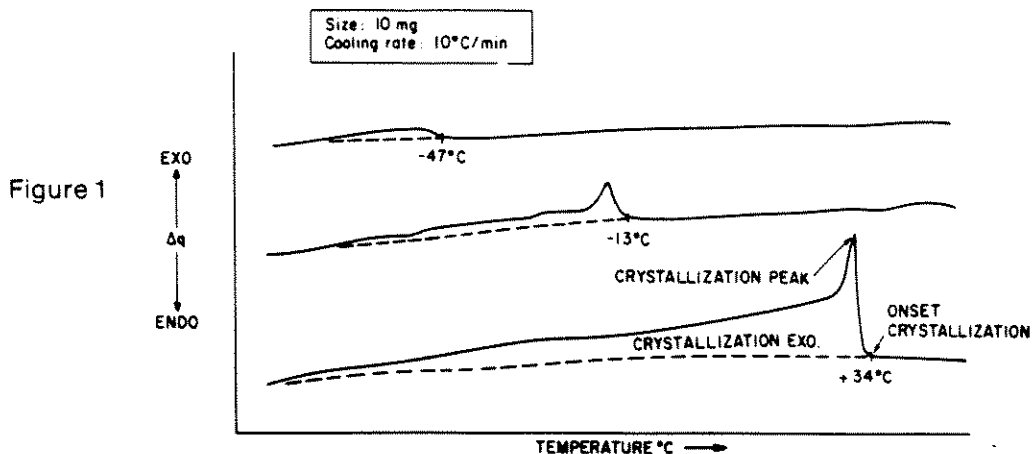


Figure 1

Noel has correlated the crystallization onset and peak temperature with the ASTM cloud point (D-2500) and pour point (D-97) determinations, respectively^{2,6}. His correlations are shown in Figures 2 and 3. For cloud point, a linear relationship exists over the temperature range from -60 to +60 C, even though the actual temperature value is about 5 degrees lower as determined by DSC. For pour point, which is considered to define the lower useful limit of the oil, the relationship is not as linear nor as closely correlated as is the case for cloud point. However, a useful linear portion exists between ambient temperature and -40 C, in which temperature range many lube oil samples lay.

Figure 4 illustrates the wax crystallization peak for a

lubricant made up to have a specific wax content. By integrating over time the area under the exothermic crystallization peak, one obtains the heat of crystallization. By ratioing this value to that for a 100% wax sample, the wax content can be determined.

The shape and area of the endothermic melt peak produced by first completely freezing the sample, then heating it, are often slightly different from those produced by this crystal fusion technique. Our experience indicates that comparable values for wax composition are obtained if the standard material is run in the same manner as the sample. Both methods are used in the literature^{2,3,6,7}.

ANALYSIS OF LUBRICATING OILS

Crystallization Onset Temperature vs. Cloud Point

[F. Noel in *Thermochim. Acta* 4, 377 (1972)]

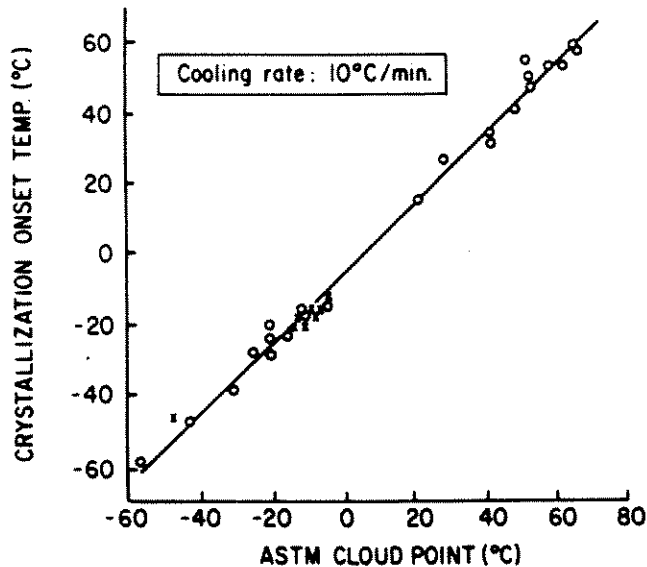


Figure 2

ANALYSIS OF LUBRICATING OILS

Crystallization Peak Temperature vs. Pour Point

[F. Noel in *Thermochim. Acta* 4, 377 (1972)]

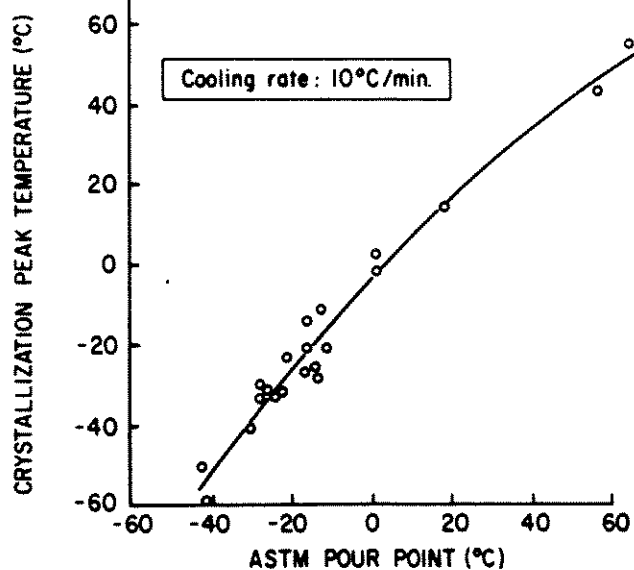
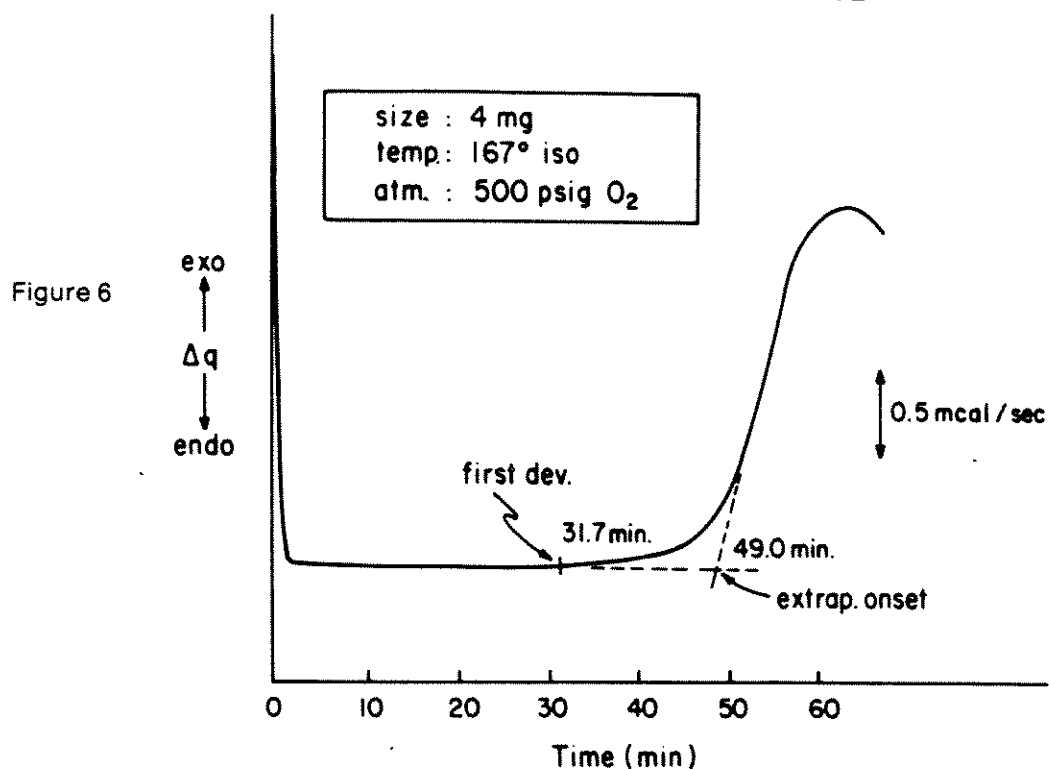


Figure 3

OXIDATIVE STABILITY 1.5% ANTIOXIDANT IN GREASE



here, can be correlated with antioxidant level. A straight line correlation exists between 0.5 and 2.5 weight percent.

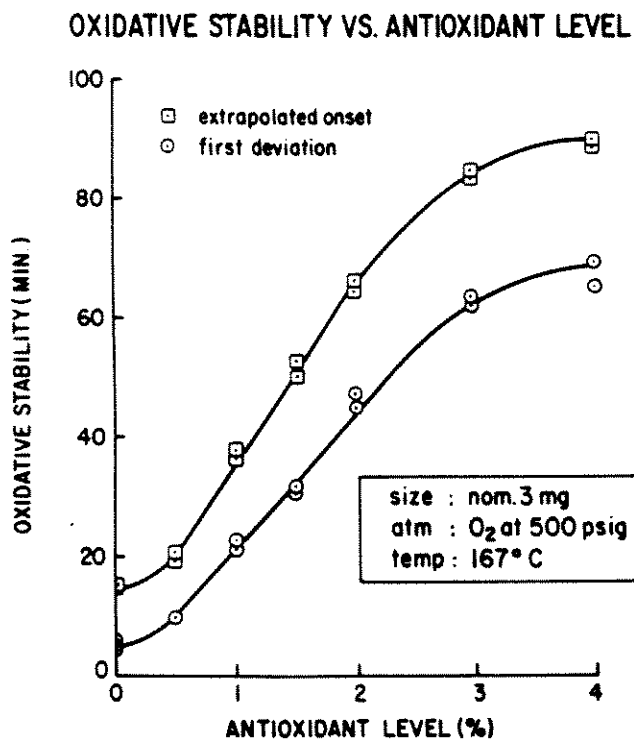


Figure 7

Noel, using a similar temperature programming technique, has correlated the oxidative stability as determined by DSC with that determined by the ASTM rotary bomb test (D-2272). A semilogarithmic correlation resulted, as shown in Figure 8, with oils inhibited with antioxidants having a different correlation than uninhibited oils.

One of the major advantages of DSC is its ability to determine a number of parameters in a single experiment. This is illustrated in Figure 9, an experiment in which a lube oil is heated from -120 C to above its oxidative decomposition point. An air atmosphere at ambient pressure is used. Three important features can be observed: the glass transition, the wax dissolution temperature, and the onset of oxidative decomposition. The oxidative decomposition and waxy dissolution (opposite of crystallization) have been discussed already. Since the curve is a heating curve, the wax portion of the sample will melt and dissolve (an endothermic reaction), whereas in cooling curves, the wax crystallization is an exothermic reaction.

The glass transition is something not yet discussed. For lubricants that have been dewaxed, the lower useful temperature is defined by a physical transition in which the amorphous material undergoes an abrupt and marked increase in viscosity. The temperature at which this occurs is called the glass transition temperature (T_g), and is accompanied by a sharp change in the

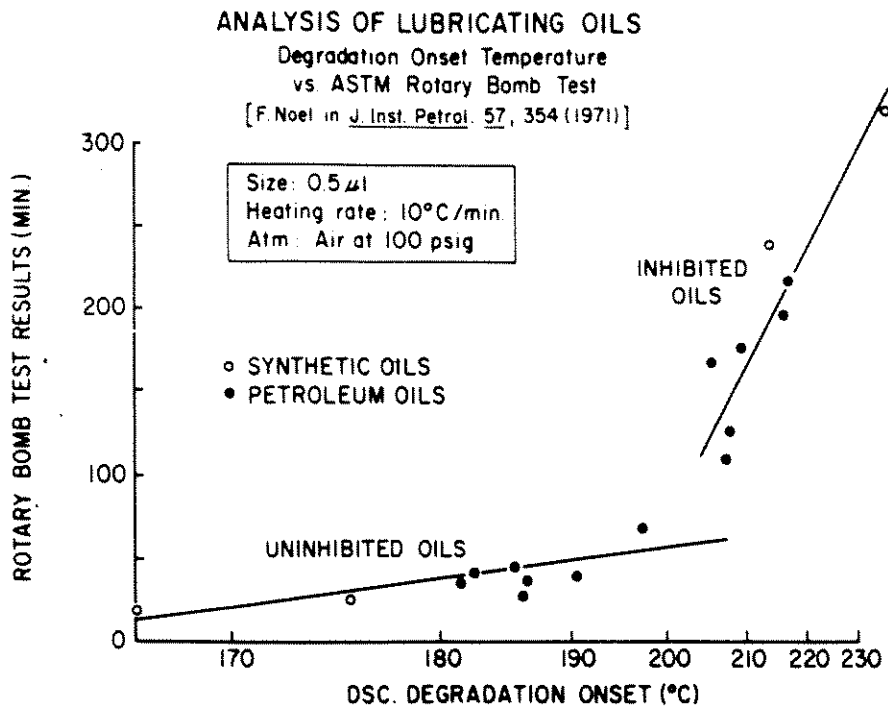


Figure 8

specific heat of the material. This change in specific heat is easily detected by use of DSC. The glass transition temperature has been correlated empirically with a number of other properties. Stearns and co-workers⁶ used the glass transition (which normally occurs between -100 and -60 C) to predict the viscosity/temperature relationship of lubricants within the temperature range of 50 to 100 C⁹. Noel has correlated the glass transition with oil boiling point range⁶.

Perhaps nowhere can the utility of thermal analysis to the lubricant chemist be more graphically demonstrated

than in the case of greases. Greases are often 80 to 90% lubricating oils, to which are added a gelling agent, such as a metal soap (e.g., lithium stearate), and sometimes a high-temperature thickener, such as polyethylene. The ASTM methods of analysis of greases are similar to those for lube oils, except that even longer times are required for parameters such as oxidative stabilities.

A typical grease DSC scan, showing the now familiar glass transition, wax dissolution, and oxidative decomposition, is shown in Figure 10. In addition, we see two new high-temperature endotherms corresponding to

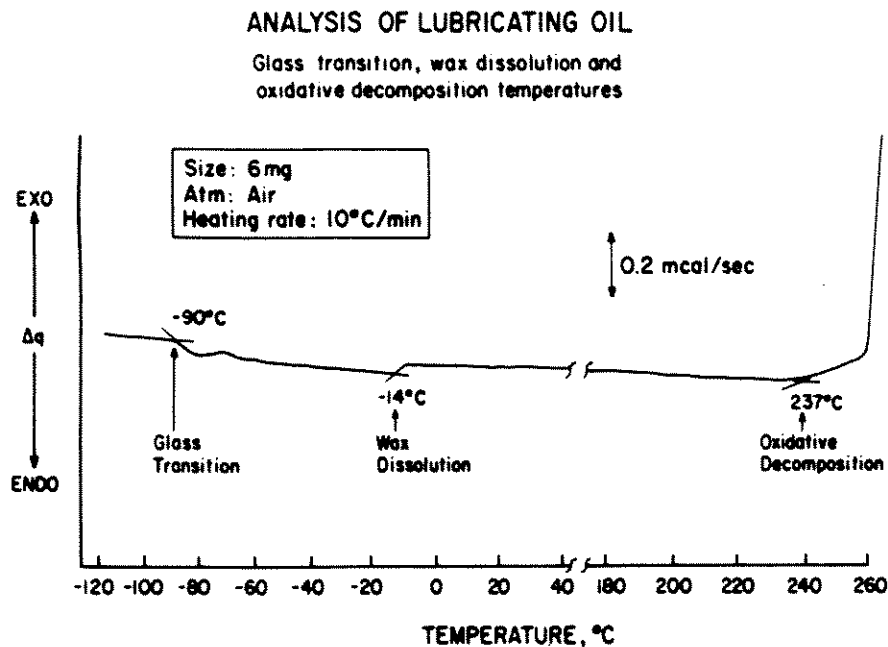


Figure 9

LUBE OIL WAX CONTENT CRYSTALLIZATION and MELT

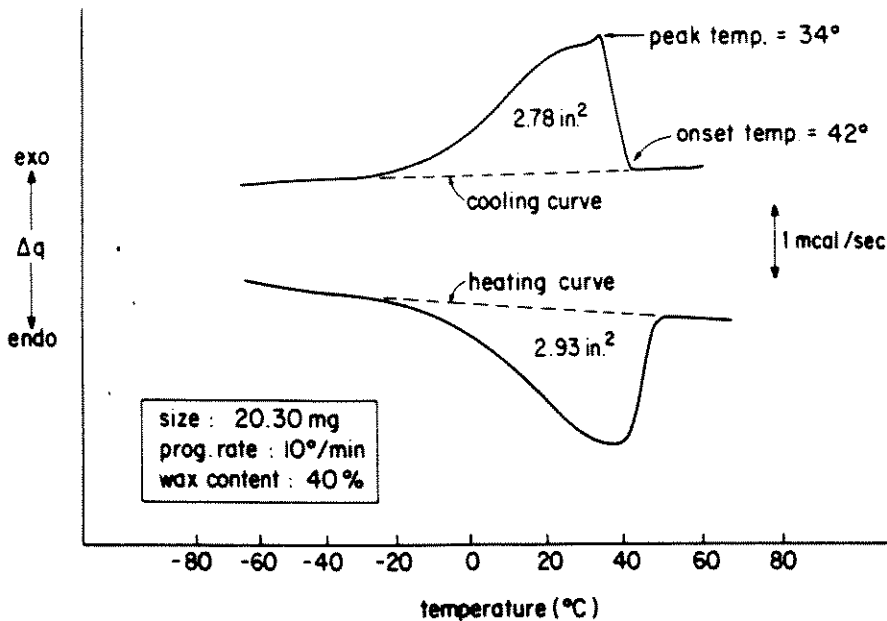


Figure 4

A correlation between wax content as prepared and determined by DSC is shown in Figure 5. A straight line correlation passing through zero is obtained. Giavarini and co-workers have similarly demonstrated a linear relationship between this heat of crystallization and wax content, as determined by the ASTM method (D-721).

In addition, the melting and crystallization ranges of

the wax content can be measured from the same scan much more accurately than by conventional ASTM methods (D-938, D-127, and D-87)³.

Probably the most widely used thermal analytical technique applied to lubricants is that of oxidative stability. The useful lifetime of a lubricant is related to its oxidation to nonlubricating products. In order to improve a lubricant's longevity, antioxidants are added. In order to keep the costs of products down, only enough antioxidant is added to retard oxidation. A measurement of a particular oil's oxidative stability is important, then, both to quality control and cost reduction.

Oxidative stability is quickly and easily determined by using pressure DSC. An unweighed sample is placed in a pressure DSC cell and the cell pressurized to 500 psig with oxygen. The sample is isothermally stepped to 167 deg and simultaneously a time based scan is started. The elapsed time to the extrapolated onset of exothermic oxidation, as shown in Figure 6, is a measure of oxidative stability. Of course, the same type of experiment can be carried out at atmospheric oxygen pressure at a considerable sacrifice of analysis time.

Some lubricants do not show a well marked oxidation exotherm from which an extrapolated onset can be obtained. Some workers have successfully used the first noticeable deviation from baseline as a measure of oxidative stability of such samples.

Figure 7 illustrates the results of a number of tests obtained for grease samples containing various levels of an antioxidant. From tests such as these, an optimum level of antioxidant can be determined. Extrapolated onset and first deviation from baseline, as demonstrated

WAX CONTENT OF LUBRICANT

Calibration Curve

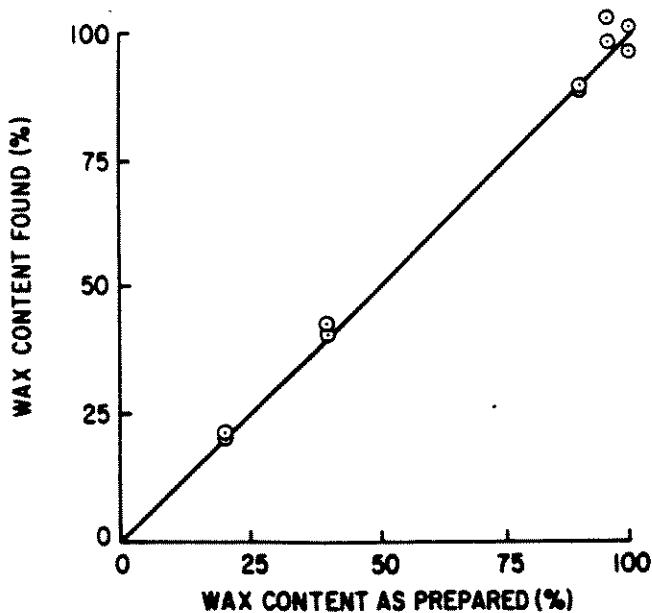
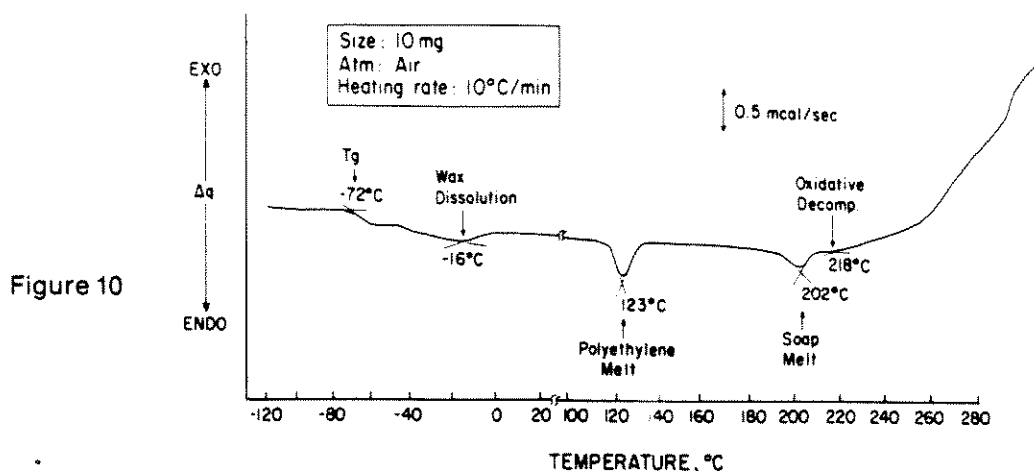


Figure 5

ANALYSIS OF GREASES

Quality Parameters



the polyethylene melt and the lithium stearate (soap) melt. For greases, the soap melt defines the high useful temperature limit and the glass transition defines the low useful temperature limit. In addition, the percent composition of the polyethylene and soap can be determined from the area under their respective melt peaks.

Thus, from this one DSC scan, six different quality control parameters can be determined: 1) lower useful temperature, 2) upper useful temperature, 3) wax content, 4) polyethylene content, 5) soap content, and 6) oxidative stability.

Summary

Thermal analysis techniques, particularly DSC and pressure DSC, have demonstrated their usefulness to the lubricant chemist. A wide variety of physical parameters, of interest to both quality control and research, can be quickly and easily determined. Among such parameters are: glass transition, specific heat, wax dissolution temperature, wax crystallization onset temperature, wax

crystallization peak temperature, wax melting range, heat of wax crystallization, heat of polyethylene melt, heat of soap melt, oxidation onset temperature, and oxidation onset time.

These parameters are related directly to important lubricant quality indicators: lower use temperature limit, upper use temperature limit, wax content, polyethylene content, soap content, viscosity cloud point, pour point, oxidative stability, and boiling point range.

References

1. Levy, P. F., *Amer. Lab.*, 46 (January 1970)
2. Noel, F., *Thermochim. Acta.*, 4, 377 (1972)
3. Giavarini, C., and Pochetti, F., *J. Therm. Anal.*, 5, 83 (1973)
4. Blaine, R. L., *Amer. Lab.*, 18 (January 1974)
5. Razo, M. L., and Asomosa, P. M., *Revista del Instituto Mexicano del Petroleo*, 6, 34 (1974)
6. Noel, F., *J. Inst. Petrol.*, 57, 354 (1971)
7. Giavarini, C., Pochetti, F., and Savu, C., *Riv. Combust.*, 23, 496 (1969)
8. Stearns, R. S., Duling, I. N., and Johnson, R. H., *Ind. Eng. Chem., Prod. Dev.*, 5, 306 (1966)
9. Wendlandt, W. W., *Thermal Methods of Analysis*. John Wiley, 1974, 505 pages

About the Author



R. L. BLAINE

obtained his BS degree from the University of Washington in 1965 and his PhD degree in analytical chemistry from Oregon State University in 1969 majoring in scientific instrumentation. He is presently an applications chemist in Du Pont Instrument's thermal analysis laboratory and is the author of a number of papers on the application of thermal analytical techniques to the electronic packaging, lubricants, fossil fuels and consumer protection industries. His present interests are in the areas of polymer physical properties testing and in the use of computers to enhance thermal analytical techniques.