Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

PRESSURE DIFFERENTIAL SCANNING CALORIMETRY*

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(Received February 26th, 1970)

ABSTRACT

A system is described for obtaining differential scanning calorimetry (DSC) data under reduced (to 10 microns) or elevated (to 1000 psi) pressure. Applications illustrating vapor–liquid equilibrium, competitive reactions, relative oxidative stability and pressure induced reactions are discussed.

INTRODUCTION

Differential Scanning Calorimetry (DSC) is a technique which has gained remarkable popularity in the last five years as one of the more valuable thermal analytical methods. DSC can be generically defined as a differential thermal analytical method in which the ordinate value at any given temperature (or time) is directly proportional to the differential heat flow between a sample and reference material and in which the integrated area under the measured curve is directly proportional to the total differential caloric input. The term "Scanning" implies that usually the temperature of both sample and reference is varied during the run at some known function of time (usually linear). Because of its quantitative nature and the increased need for numerical values in thermal analytical measurements, DSC has to a large part replaced conventional DTA techniques. A second factor, that of ease in sampling handling, further increased the utilization of DSC, even in those areas where quantitative data were not necessary. This came about because, by design, in DSC, the differential thermal sensors must be located external to the sample container in order to obtain quantitative results. This resulted in a simple sample container, unencumbered by the need of a temperature sensor in direct contact with the sample, which greatly facilitated sample preparation.

Commercially available DSC units offer a great deal of flexibility in varying the temperature, heating rate, atmosphere composition and thermal history imparted to a sample in order to obtain a complete thermal-energy profile under varying experimental conditions. Their pressure and vacuum capabilities, however, have been limited to working at pressures close to ambient and at reduced pressures down to approximately 1 torr.

The only way of achieving higher than ambient pressures was to encapsulate

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*Presented at the Symposium on Recent Advances in Thermal Analysis, American Chemical Society Meeting, Houston, Texas, U. S. A., February 23–27, 1970.

the sample of interest in a hermetically sealed container and to allow the pressure to build up as the temperature was increased. This method had the severe limitation that pressure was uncontrolled and depended solely upon the vapor pressure of the sample at any given temperature.

Since the ability to vary pressure, as well as temperature, has far-reaching application in elucidating thermal behavior of materials, it was the purpose of the work described in this paper to design, evaluate and apply a Differential Scanning Calorimeter module capable of operation to elevated and reduced pressure limits far in excess of anything presently available.

DESCRIPTION

The resulting unit consists of what is, in effect, a regular Du Pont DSC Cell[1], enclosed in a specially designed pressure housing, complete with all necessary valving and plumbing. This unit is shown in Fig. 1.

Fig. 1. Pressure DSC Cell.

Both the top and cylinder are removable by simply unscrewing the three bolts with the fingers. Normally only the top is removed for loading and unloading samples. No tools are utilized in assembly or disassembly to completely avoid the possibility of stripped threads, *etc.*, which would compromise the structural integrity of the enclosure. Any resistance encountered in loosening the bolts is an automatic indication of residual pressure and an instant danger warning signal. "O"-ring seals set in grooves in the top and bottom portions of the enclosure seat against the side wall of the cylinder and increase their contact as either pressure or vacuum is applied. All fittings are of high-pressure type and a special hermetically sealed glass-to-metal feed-through is used to provide electrical connections.

The assembly is designed to operate at a maximum working pressure of 1000 psig and to attain a vacuum of under 10 microns with a good pumping system attached. A large safety factor is designed in to prevent any possible failures. The cell, valving and connections are diagrammed in Fig. 2.

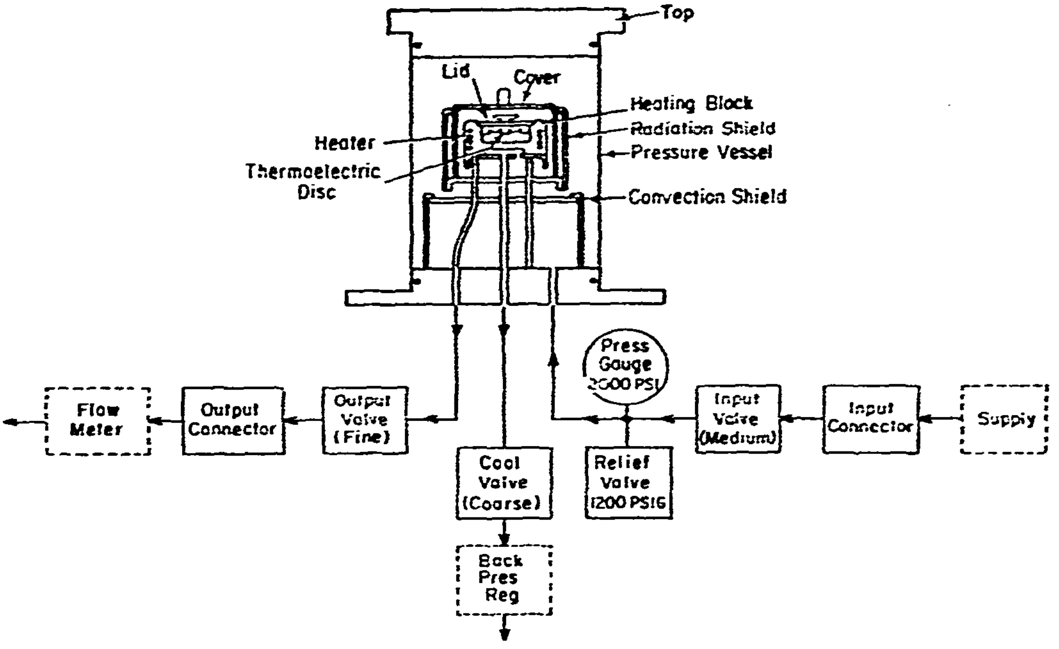

Fig. 2. Block diagram–Pressure DSC Cell.

The supply gas (connected to a tank regulator set at 1000 psi or under) enters the cell through the input connector and is controlled by the input control valve. This valve is a medium-thread (7 turn) high-pressure needle valve and is mainly used to regulate the rate at which the cell is pressurized. The incoming gas enters the cell directly through a hole in the baseplate, and floods the entire internal volume of the enclosure. A spring-loaded safety valve is in the supply line between the valve and baseplate and is set to open at 1200 psi. In addition, a pressure gauge with a maximum range of 2000 psi is also connected at this point.

Gas exiting the cell during purging enters the sample chamber through a hole in the silver lid, passes over the sample, through an orifice in the side wall of the sample chamber and down through a tube connected to the baseplate. This exhaust gas is controlled by the output control valve, which is a fine-thread (14 turn) high-pressure needle valve, and passes out of the cell via the output connector. Control of gas flow rate during purging is accomplished by use of this output valve. A flowmeter may be connected to a line from the output connector. Extreme care must be exercised that conditions never exist in which the flowmeter could become pressurized, or explosion may result. A pressure-flow rate correction must be made to convert readings made on the flowmeter, which vents to ambient, to velocities flowing over the sample at elevated pressure.

A third valve, labelled "cool control valve", is connected internally in the cell to a point under the heating block outside of the sample chamber. This is a coarse-thread (3 turn) stop valve which is used to rapidly release pressure from the cell after a run is completed. Since it has the largest orifice, it is the point at which a vacuum system is normally connected to the unit. The term "cool" derives from the fact that, when not being used otherwise, this valve may be connected to a source of compressed air to allow cooling of the heater for rapid turn-around. This procedure is carried out with the top of the pressure housing removed.

Under normal operating conditions the cell is first purged by opening the output and cool control valves and allowing gas to flow for several minutes into the cell through the input valve. The output and cool valves are then closed and the cell brought up to operating pressure. If complete exclusion of air is desired, a procedure of alternate evacuation and filling with the gas of interest may be employed.

The input valve is normally closed after filling. This produces what is, in effect, constant volume conditions. During a run, as the temperature rises, the internal pressure will increase. This is usually negligible since a relatively small volume within and adjacent to the heating block actually achieves the temperature of the experiment. If true constant-pressure conditions are required, an auxiliary regulator may be connected to the system (shown connected to the cool control valve in Fig. 2) which would release all pressure above the value set on the regulator.

PERFORMANCE

At ambient pressure, performance of the Pressure DSC is identical to that of a regular Du Pont DSC Cell. At elevated pressures, there is some change in the value of the calibration coefficient used in the calculation of energies from that found at ambient pressure. This variance is less than 10% over the entire pressure and temperature range (−190 to 650°C), and is probably due to the increased density of the gas causing a change in the thermal resistance path to the sample. For maximum calorimetric accuracy it is advisable to calibrate the cell (using metal samples) in the pressure range of interest.

Baseline performance under pressure is extremely good, even at maximum sensitivity. A typical baseline, run on two empty aluminum cups at maximum sensitivity, is shown in Fig. 3.

When running under vacuum below 1 torr there is some loss of sensitivity and resolution due to the increase in thermal resistance between the constantan thermoelectric disc and the sample pan. At temperatures under 200°C, sensitivity and resolution equivalent to that found at higher pressures can be obtained by applying a thin layer of thermally conductive grease (similar to that used to heat sink transistors) between the disc and the pan.

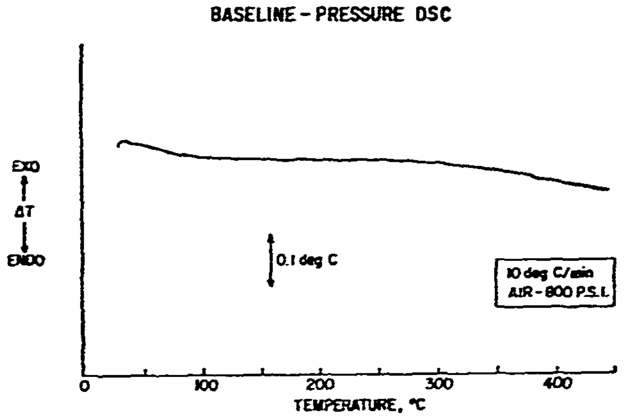

Fig. 3

APPLICATIONS

The ability to vary pressure of inert or reactive gas in the DSC technique opens up a large avenue of possible applications heretofore not feasible. Several studies carried out in our laboratory are discussed here.

Probably the first affect which comes to mind, when one considers varying pressure, is the ability to shift the boiling points of liquids. Such an illustration is shown in Fig. 4. The upper curve shows the normal melting (122 °C) and boiling (251 °C) points of benzoic acid. The lower curve, run at 200 psig in nitrogen, shows the unshifted melting point and the elevated boiling point of 378 °C at this pressure. In order to avoid sublimation and evaporation, and to insure equilibrium conditions, the above samples were run in a small hermetically sealed aluminum sample pan which had a small (~0.002 in) hole punched in the top to equalize pressure.

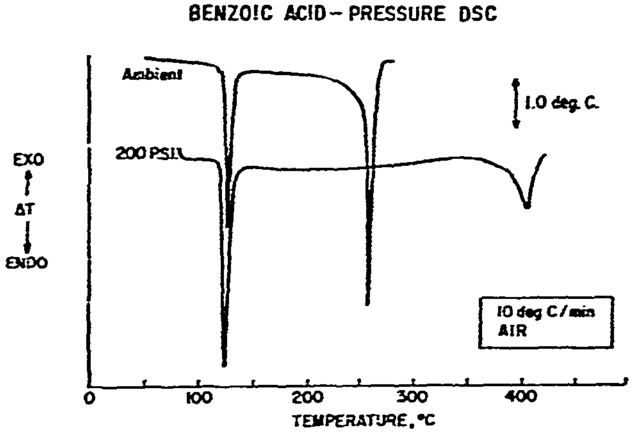

Fig. 4

The relationship between temperature and equilibrium vapor pressure illustrated above is, of course, given by the familiar Clapeyron–Clausius equation:

$$[\ln p = \frac{\Delta H_v}{RT} + C]$$

It was decided to test the linear relationship between ln p and $1/T$ using the Pressure DSC Cell. Since extensive pressure–temperature information is readily available on water[2] (*i. e.* steam tables), the water–steam system was used. The pin-hole, hermetic-cup arrangement described above was employed. A comparison of pressure, observed temperature and the steam table value is given in Table 1, for values of p from ambient to 1000 psi. The same data are plotted in Fig. 5. Agreement with the steam-table data is excellent and the remarkable straight line slope of the log p *vs.* $1/T$ plot yields a value of 529 cal/g for the latent heat of vaporization of water which compares favorably with the accepted value of 539 cal/g.

TABLE 1

BOILING POINT OF WATER AS A FUNCTION OF PRESSURE -PRESSURE DSC CELL

P (GAUGE) (P.S.I.)	P (ABSOLUTE) (P.S.I.)	T (OBSERVED) (°C)	T (STEAM TABLES) (°C)
0	14.7	100	100
50	65	147	148
100	115	177	170
200	215	193	198
400	415	232	231
600	615	252	254
800	815	272	271
1000	1015	289	286

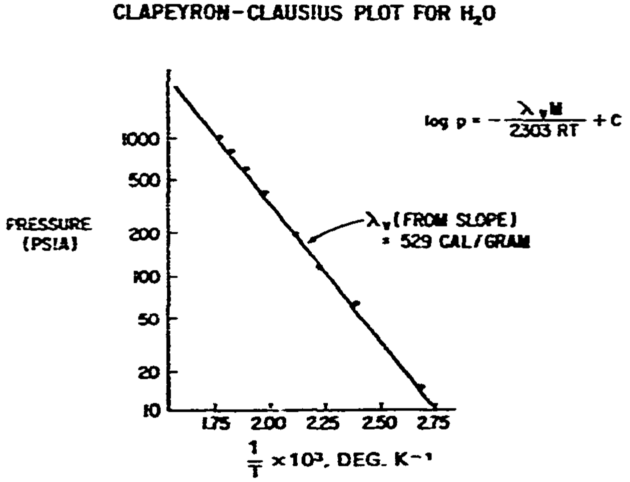
CLAPEYRON-CLAUSIUS PLOT FOR H_2O

Fig. 5

The ability to shift pressure-sensitive transitions can be used to great advantage in the case where two thermally dependent reactions are competitive at approximately the same temperature. If one is pressure-sensitive and the other is not, or if there is a difference in degree of sensitivity, the reactions may be resolved from each other by modifying the pressure. Such a condition is shown in Fig. 6. The upper curve is a DSC scan at ambient pressure in N_2 of a phenolic resin. The exothermic cure reaction and the endothermic vaporization of water in the system are competitive in the 100–200 °C range. The net energy change detected by DSC does not yield significant information. By raising the pressure to 800 psig, the water vaporization is shifted out of the phenolic-cure region and a two-stage curing exotherm is observed.

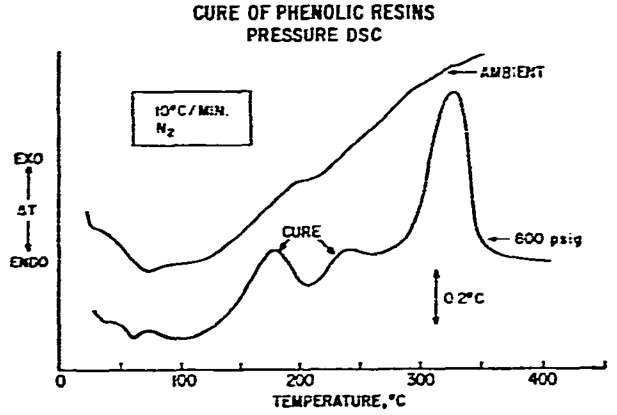

Fig. 6

Another case of competitive reactions is shown in Figs. 7–10, for a sample of orange oil, an essential oil. In running DSC at ambient pressure in air, it was observed that sometimes the reaction seemed endothermic, other times exothermic and, at times, both. Fig. 7 illustrates four repetitive scans on identical samples. The same sample run at ambient pressure in nitrogen always gave an endotherm at 182 °C (see Fig. 8). It was felt that the 182 °C transition in N_2 was the normal boiling point of

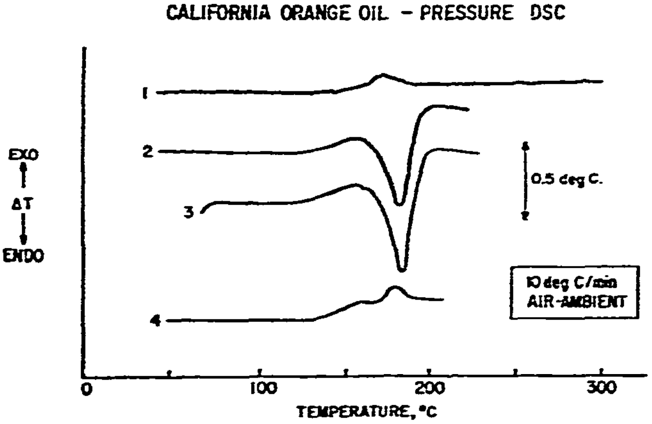

Fig. 7

the oil, and that this transition, which appears in two of the four scans in Fig. 7, was competitive with an exothermic oxidation reaction at the same temperature. Increasing the pressure in nitrogen to 50 psig simply shifted the transition up to 249 °C, indicating the behavior of a regular liquid–vapor equilibrium. This is shown in Fig. 9. Increasing the pressure in air, however, to 35 psig (Fig. 10) produced a large exotherm, starting at 125 °C, which supported the theory that a competitive oxidation reaction existed. Fig. 10 also shows a small endotherm at 260 °C which can be attributed to boiling at the increased pressure.

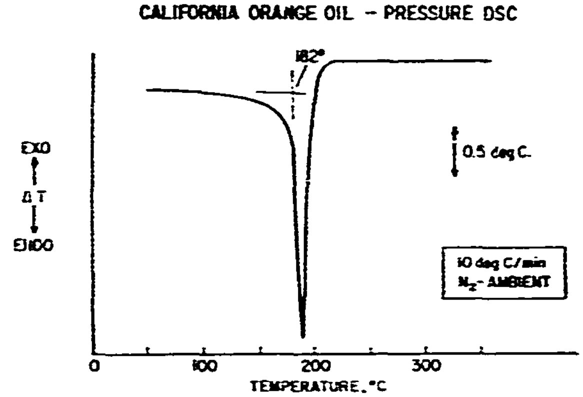

Fig. 8

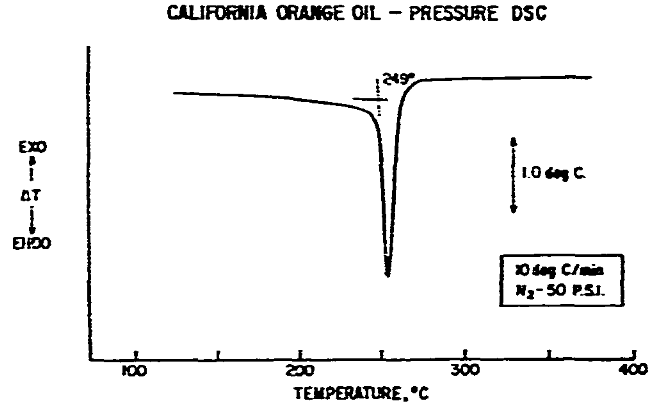

Fig. 9

The use of increased oxygen or air pressure to indicate relative oxidative stabilities of comparable compounds is demonstrated in Figs. 11–13. These scans were run on three competitive automotive hydraulic brake fluids. Fig. 11 indicates no significant differences between ambient and elevated pressure on one of these materials when run in nitrogen. The same was true of the other two samples. Some differences can be noticed in the scans of the three brands when run in air at ambient pressure (Fig. 12), but these differences are not significant enough to discriminate between the samples. By raising the pressure in air to 600 psig (Fig. 13), all three materials were shown to exhibit an exothermic oxidation, the onset temperature of which allowed us to rank the materials in order of oxidative stability, brand *Z* being the most stable.

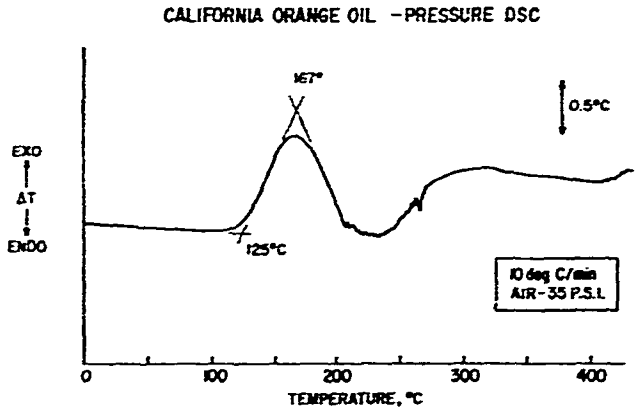

Fig. 10

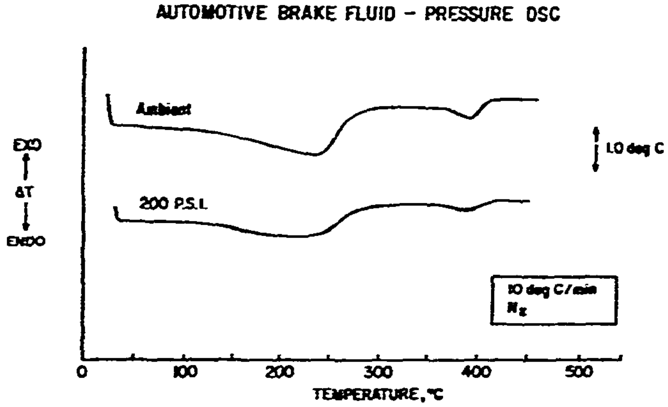

Fig. 11

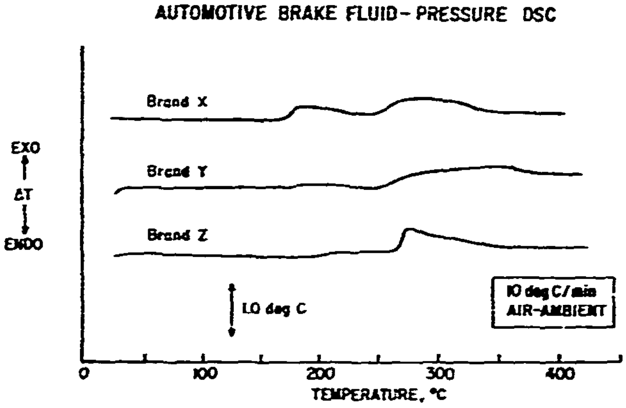

Fig. 12

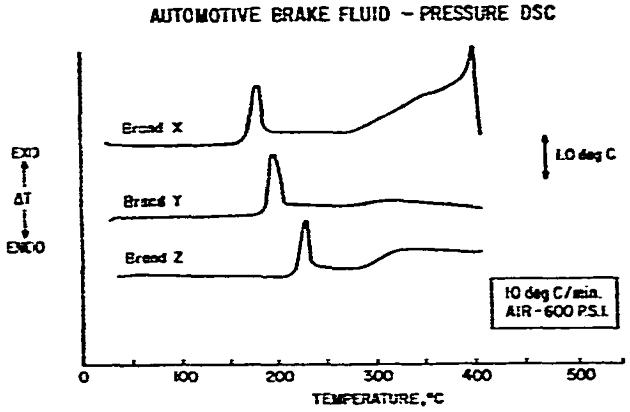

Fig. 13

A similar oxidative reaction occurring at higher oxygen partial pressures is illustrated in Fig. 14. This shows a scan in nitrogen and three scans in air, at successively higher pressures, of an automotive motor oil. The appearance of an oxidative

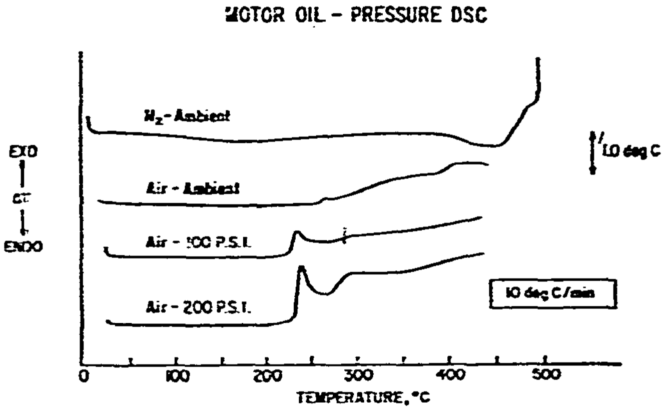

Fig. 14

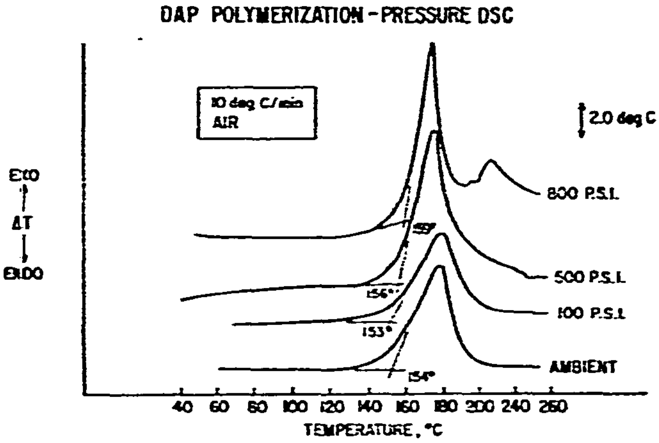

Fig. 15

exotherm at approximately 230°C, which grows in magnitude with pressure, is evident. It is interesting to note that a value of 232.2°C is given as the flash point of motor lubricating oil in the literature[3].

The final application study discussed here involves the use of pressure to produce additional reactions or alternate reaction paths, which do not appear to occur at lower pressures. Such an example is given in Fig. 15. This set of scans shows the effect carrying out the polymerization of diallylphthalate (DAP) during a DSC scan at several pressures. Significantly, as the pressure is raised above several hundred psi, the major exothermic peak tends to sharpen up and move upward in temperature. At higher pressures, first a shoulder can be noticed on the upper temperature side of the major peak (500 psig) and at still higher pressure (800 psig) several new higher-temperature peaks appear. These would indicate pressure induced secondary reactions either concurrent with or following the initial reaction, as the temperature is raised.

CONCLUSION

The above are only a few of the many possible areas in which pressure DSC can be put to use. It is our hope that we have generated enough interest that others will attempt to put this new ability to change an old variable into practice.

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3 Ref. 2, p. 42.