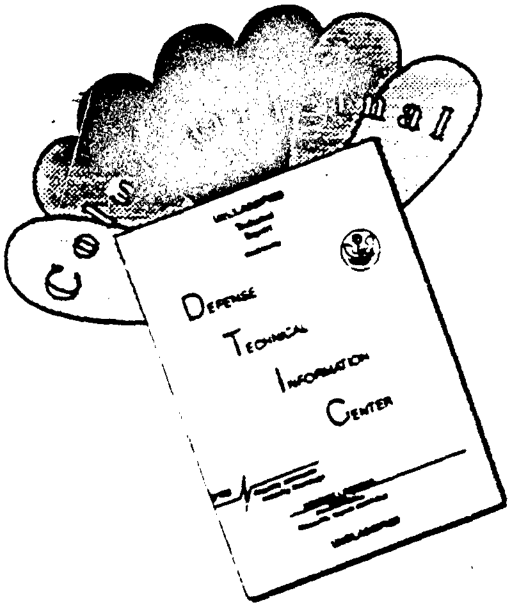
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THERMAL ANALYSIS OF SELECTED COMMERCIAL THERMOPLASTIC RESINS (U)

by

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ABSTRACT

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were used to characterize and identify several commercial thermoplastics used or considered for use in Canadian C4 gas masks. The goal was to build a data base from which unknown thermoplastic samples could be fingerprinted. A secondary goal was to characterize the thermal transitions of the polymers to determine the effect of processing.

Both TGA and DSC demonstrated characteristic thermal transitions of the particular polymer used in the sample. In some cases, the presence and amount of inorganic fillers could be detected, as well as polymer blend composition. The effect of thermal history was also determined for Noryl and Valox resins by heating and then quench cooling the samples. The thermal transitions of the more crystalline Valox were dependent on the thermal history whereas the amorphous Noryl could be repeatedly heated and cooled, maintaining reproducible thermal transitions.

RÉSUMÉ

L'analyse thermogravimétrique (ATG) et le calorimétrie par balayage différentiel (CBD) ont charactérisés et identifiés plusieurs plastiques commerciaux utilisés ou considerés pour utilisation dans le masque C4 canadien. Le but était de construire une banque de données de laquelle l'empreinte digitale d'un thermoplastique inconnu pouvait être prise. Un but secondaire était de charactériser la transition thermique du polymère pour déterminer l'effet du processus de fabrication.

Et l'ATG et la CBD ont démontré les charactéristiques de transition thermale de polymères spécifiques utilisés dans les échantillons. Dans certains cas, la présence et la quantité de matière inorganique ont pu être détectées de même que la composition de mélanges de polymères. L'effet de l'histoire thermique fut aussi déterminé pour le Noryl et le Valox en chauffant et trempant les échantillons. Les transitions thermiques de la résine plus crystalline, le Valox, dépendaient de l'historique thermique tandis que la resine amorphe, le Noryl, a pu être chauffée et refroidie en maintenant des transitions thermiques reproduisibles.

EXECUTIVE SUMMARY

Commercial thermoplastics used in C4 mask components are generally poorly characterized by suppliers. The thermal behaviour of these plastics determines their processing conditions, stability and degradative behaviour, but there is little information available on particular brands. Often, the polymers can be identified and fingerprinted by their thermal transitions. To this end, a variety of commercial thermoplastics used or considered for use in mask components were characterized by differential scanning calorimetry and thermogravimetric analysis. The goal of this work was to build a database to be used in the identification of unknown thermoplastic samples, and to characterize thermal transitions for the purpose of processability. It was determined that the commercial thermoplastics could be easily identified by these techniques.

TABLE OF CONTENTS

PAGE

1.0 INTRODUCTION

A number of different rubbers and plastics are used in gas masks. In particular, the Canadian C4 mask has several thermoplastics including polyester elastomers and polyphenylene oxides modified with high-impact polystyrene. Several other thermoplastics consisting of polyamides and acetal resins were considered, but are not currently being utilized in masks. In addition, a number of elastomers are used, including bromobutyl, silicone and natural rubbers. Each of these has different material and chemical-resistant properties, all of which need to be thoroughly tested prior to use in the mask.

Thermal analysis is a series of techniques that yield qualitative and quantitative information on the thermal properties of the polymer. Two of these techniques, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measure the thermal transitions of the polymer such as the glass transition temperature, Tg, where the polymer changes from a hard, glassy state to a soft, rubbery state, the melting temperature, Tm, and finally the decomposition temperature Td. The temperatures of these transitions are usually indicative of the particular polymer used in the sample. Samples with more than one polymeric component will either exhibit transitions of each component part, or exhibit intermediate transitions. Thus, DSC and TGA are valuable tools in fingerprinting and identifying unknown polymer samples and determining blend compositions.

Differential scanning calorimetry monitors the endothermic or exothermic changes of a polymer sample as the temperature is raised. The heat flowing in or out of the polymer sample is measured in reference to a standard. Thermal transitions are recorded as either a peak or simply a baseline adjustment in the thermogram. The glass transition is usually seen as a slight endothermic shift in the baseline at a particular temperature, melting appears as an endothermic peak, and decomposition appears as a very large peak, either endothermic or exothermic. If the polymer is highly crystalline, exothermic crystallization peaks may be seen. These transitions may be dependent on the polymer's thermal history, so DSC has limited application in identifying particular polymers. However, it is very useful for determining thermal history and kinetics of thermal transitions.

Similarly, TGA heats the polymer sample, but the weight loss is monitored instead of heat flow. TGA is useful in determining decomposition temperatures and mechanisms of thermal decomposition. This technique is most useful for identifying and quantifying component parts of a mixture, since different polymers and/or fillers may have different decomposition temperatures.

However, even though DSC and TGA are very commonly used in polymer science, no identification database yet exists. We report the TGA and DSC data for several commercial thermoplastics, especially those used or considered for use in C4 gas mask components. The ultimate goal is to develop a database for these plastics that may identify and characterize not only plastic and rubber components of Canadian-made equipment but also those from foreign equipment.

2.0 EXPERIMENTAL

Table I lists the commercial thermoplastics used in this study. Each of these was available in either pellet or plaque form.

A Dupont 910 Differential Scanning Calorimeter and a 951 Thermogravimetric Analyzer were utilized for the thermal analysis, with associated Dupont software and hardware. The TGA experiments were performed in a nitrogen atmosphere. The evolved gases were not analyzed. Several heating rates were used in TGA and the temperature of each transition was extrapolated back to zero heating rate. The DSC experiments were all performed at 5°C/min.

3.0 RESULTS AND DISCUSSION

3.1 THERMOGRAVIMETRIC ANALYSIS

A typical TGA plot of Zytel-101L is shown in Figure 1. This sample begins to decompose at approximately 380°C, with rapid weight loss occurring at 400 to 500°C. The derivative curve shows a single peak at 463.5°C, with a total weight loss of 99.6%. This data suggests that Zytel-101L either has a single, homogeneous polymer or copolymer, or that the components of the blend decompose at the same temperature. There are no substantial quantities of inorganic additives (e.g. carbon black or glass fibres) in the plastic since there is nearly 100% weight loss. The presence of these additives would appear as a residue, resulting in a weight loss of significantly less than 100% (e.g. 60 to 80%).

TGA data for each sample is listed in Table II. The average standard error for each reported decomposition temperature, Td, is approximately 2%. All Td's in Table II are reported at the extrapolated heating rate of 0°C/min.

Several important trends are observed in the data. First, the thermoplastics can be identified by their decomposition temperatures. For example, the polyamides (Rilsan and Zytel) usually decompose between 435 and 456°C, except for the nylon copolymer Zytel 330 NC-10. These can be easily differentiated from, for example, the polyester Valox compounds, which have decomposition temperatures at 390 to 395°C. Second, thermoplastics with significant amounts of inorganic additives can be easily distinguished from those with no additives.

TABLE I

Commercial Thermoplastics Studied

Name	Manufacturer	Polymer Type
Zytel 101L	Dupont	polyamide (66 nylon)
Zytel 330 NC-10	Dupont	polyamide (nylon copolymer)
Zytel 70G 33 HS1-L	Dupont	polyamide (glass-reinforced 66 nylon)
Zytel ST-801	Dupont	polyamide (toughened nylon)
Zytel ST-8018	Dupont	polyamide (glass-reinforced toughened nylon)
Zytel 72G 33 L	Dupont	polyamide (glass-reinforced 66 nylon)
Hytrel 4056	Dupont	polyester elastomer
Delrin 500 DE 8020	Dupont	acetal resin (polyoxymethylene)
Delrin II-500	Dupont	acetal resin copolymer
Noryl N300	GE	polyphenylene oxide modified with polystyrene
Noryl SE1	GE	polyphenylene oxide modified with polystyrene
Noryl SE1-GFN2-701	GE	glass-reinforced, modified polyphenylene oxide
Noryl SPN410-701	GE	modified polyphenylene oxide
Valox 420-SE0-7001	GE	glass-reinforced polyester
Valox 310-SE0-3262	GE	polyester
Valox DR48-7001	GE	glass-reinforced polyester
Celcon	Hoechst Celanese	acetal resin copolymer
Rilsan BMN P40	Atochem	polyamide (nylon 11)

TABLE II

Thermogravimetric Analysis Data for Commercial Thermoplastics Data Extrapolated to 0°C/min

Name	Decomposition Temperature °C	% Weight Loss
Zytel 101L	447.8	93.5
Zytel 330 NC-10	135.7 468.1	2.6 91.6
Zytel 70G 33 HS1-L	440.9	62.0
Zytel ST-801	435.6	93.0
Zytel ST-8018	435.9	78.1
Zytel 72G 33 L	456.2	62.5
Hytrel 4056	404.9 653.5	94.4 3.2
Delrin 500 DE 8020	332.0	99.8
Delrin II-500	356.1	98.1
Noryl N300	370.2 452.7	6.4 58.7
Noryl SE1	449.9	75.6
Noryl SE1-GFN2-701	446.7	56.8
Noryl SPN410-701	446.7	83.3
Valox 420-SE0-7001	393.2	58.1
Valox 310-SE0-3262	390.5	74.0
Valox DR48-7001	395.8 488.8	64.4 4.2
Celcon	334.7	98.9
Rilsan BMN P40	250.0 430.6	9.0 83.7

For example, the glass-reinforced Zytel 70G 33H-SiL shows a total weight loss of only 62.0%, whereas the non-reinforced Zytel 101L has well over 90% decomposition. Finally, the presence of small amounts of polymeric or other organic additives can be detected. In some samples, very small peaks with less than 7% weight loss are observed; however, it is difficult to identify these peaks based on TGA data alone.

The disadvantage of this technique is that it has limited usefulness. The decomposition temperature range is broad (50 to 100°C) and the decomposition temperature can be calculated and reported a number of different ways. In this report, we list the inflection midpoint (i.e., the derivative maximum) of the temperature, but the onset point, the half-height midpoint, the half-width midpoint or the half extrapolated tangential midpoint could have been reported, each with a different value. Furthermore, these numbers seem only accurate to within 10 to 20°C, making exact identifications difficult.

3.2 DIFFERENTIAL SCANNING CALORIMETRY

Table III lists the DSC data obtained for the thermoplastic samples. Like TGA, the samples can be grouped by type of polymer and identified. Often, the glass transition temperature (Tg) was either difficult to see (as expected for highly crystalline polymers) or else below ambient temperatures. However, the melting temperatures agree reasonably well with those published in the literature (1), and the decomposition peaks are in the same area as those measured by TGA. The heat of melting is simply the integration of the melting peak, and trends also appear in these values.

DSC is somewhat more useful than TGA in determining the nature and kinetics of thermal transitions of the polymer. It is especially good for determining the nature of transitions in the operating temperature range of the gas mask and whether these transitions will affect the performance of the components. In this study, while no measurements were made below 20°C, the thermoplastics all appeared to be stable from 20 to 50°C.

The effectiveness of DSC in fingerprinting samples is demonstrated in Figure 2. Two similar acetal resin copolymers made by Dupont and Hoechst Celanese are compared and significant differences are observed in Tm and Td. These differences are likely due to slightly different additives or copolymer compositions. Nevertheless, the heat of melting values (244.4 and 258.6 J/g) are comparable, which indicates the base copolymers are at least similar in structure. Thus, it is possible to identify these two resins by their DSC behaviour.

Thermal transitions are very dependent on factors such as quantity and type of additives, heating rate, and especially the thermal history of the sample. The rate of heating and cooling of the polymer, as well as the annealing conditions will impart a thermal history and subsequently may affect glass transition, crystallization and even melting temperatures. Thus, the DSC plot may look completely different for the same thermoplastic before and after processing. Unfortunately, this will certainly limit the

TABLE III

Differential Scanning Calorimetry Data for Thermoplastic Samples

Name	Tg °C	Tm °C	Heat of Melting (J/g)	Td °C
Zytel 101L	-	261.9	114.4	428.2
Zytel 330 NC-10	76.29	149.5	18.8	458.6
Zytel 70G 33 HS1-L	-	260.7	78.8	416.1
Zytel ST-801	-	261.7	86.4	423.0
Zytel ST-8018	-	261.0	77.9	419.4
Zytel 72G 33 L	-	236.2	69.1	421.1
Hytrel 4056	-	147.8	29.2	388.7
Delrin 500 DE 8020	-	175.2	269	358.7
Delrin II-500	-	176.3	251.4	356.6
Noryl N300	172.9	362.8	128.6	423.5
Noryl SE1	137.3	-	-	429-447
Noryl SE1-GFN2-701	130.0	409.4	112.5	446.5
Noryl SPN410-701	-	-	-	415.6
Valox 420-SE0-7001	-	221.8	48.0	373.3
Valox 310-SE0-3262	-	221.6	42.7	374.3
Valox DR48-7001	-	221.9	44.5	382.8
Celcon	-	162.8	229.6	350.2
Rilsan BMN P40	-	181.8	81.8	417.5

ability of the DSC to fingerprint a compound, but may provide valuable information on the degree of crystallization and the morphology of the thermoplastic.

The effect of thermal history on Noryl and Valox resins was studied by first heating each sample at its Tm for 10 minutes, then quench cooling the sample in liquid nitrogen, allowing the sample to reach ambient temperature and finally running a DSC scan. This scan was compared to a scan of the unaltered sample and the effect of thermal history was determined by comparing the melting and glass transition temperatures.

The results for the Noryl sample are shown in Figures 3 and 4. This thermoplastic does not have clear DSC features, but the apparent melting point and the glass transition temperature are essentially identical for both samples. This indicates that the sample is highly amorphous since the thermal history has little effect. Thus, Noryl samples can be easily and reproducibly identified through this method.

In contrast, the thermal history has an effect on the Valox polymers. The results shown in Figures 5 and 6 demonstrate differences in Tm between the quenched sample and the control sample. In effect, the melting peak has been resolved into two peaks. This is probably due to different crystalline formations in the quenched sample, which result in two apparent melting peaks. However, these closely-spaced melting peaks are in the same vicinity as the single melting peak of the control sample and thus the thermal history imparted by this experiment has a minor effect.

4.0 CONCLUSIONS

A small thermal analysis database consisting of DSC and TGA data has been established for thermoplastics which are used or considered for use in gas mask components. The thermal transitions were characterized, the effect of thermal history was examined, and the polymers were identified by these techniques. However, precise identification is not always possible since there are limitations in the precision of thermal analysis.

Two of the more important thermoplastics used in mask components, Noryl and Valox resins, were extensively studied by DSC. A simple test of thermal history showed no effect on Noryl and a minor effect on Valox. Noryl was determined to be mostly amorphous, while the behaviour of Valox suggested the formation of crystalline domains.

5.0 RECOMMENDATIONS

1. A more extensive and useful database should be established which contains data on all polymeric materials used in individual Chemical Warfare protective equipment.

2. DSC data should be obtained on all thermoplastic materials used as components before and after processing to determine the effect (if any) of thermal history on the properties of the material.

3. To increase the effectiveness of TGA as a fingerprinting tool, a mass selective detector should be utilized with the TGA to identify evolved gases from the thermal decomposition of the polymer sample.

6.0 REFERENCES

1. "Thermal Characterization of Polymeric Materials", Edith A. Turi, ed., Academic Press, Inc., Orlando, Florida, 1981.

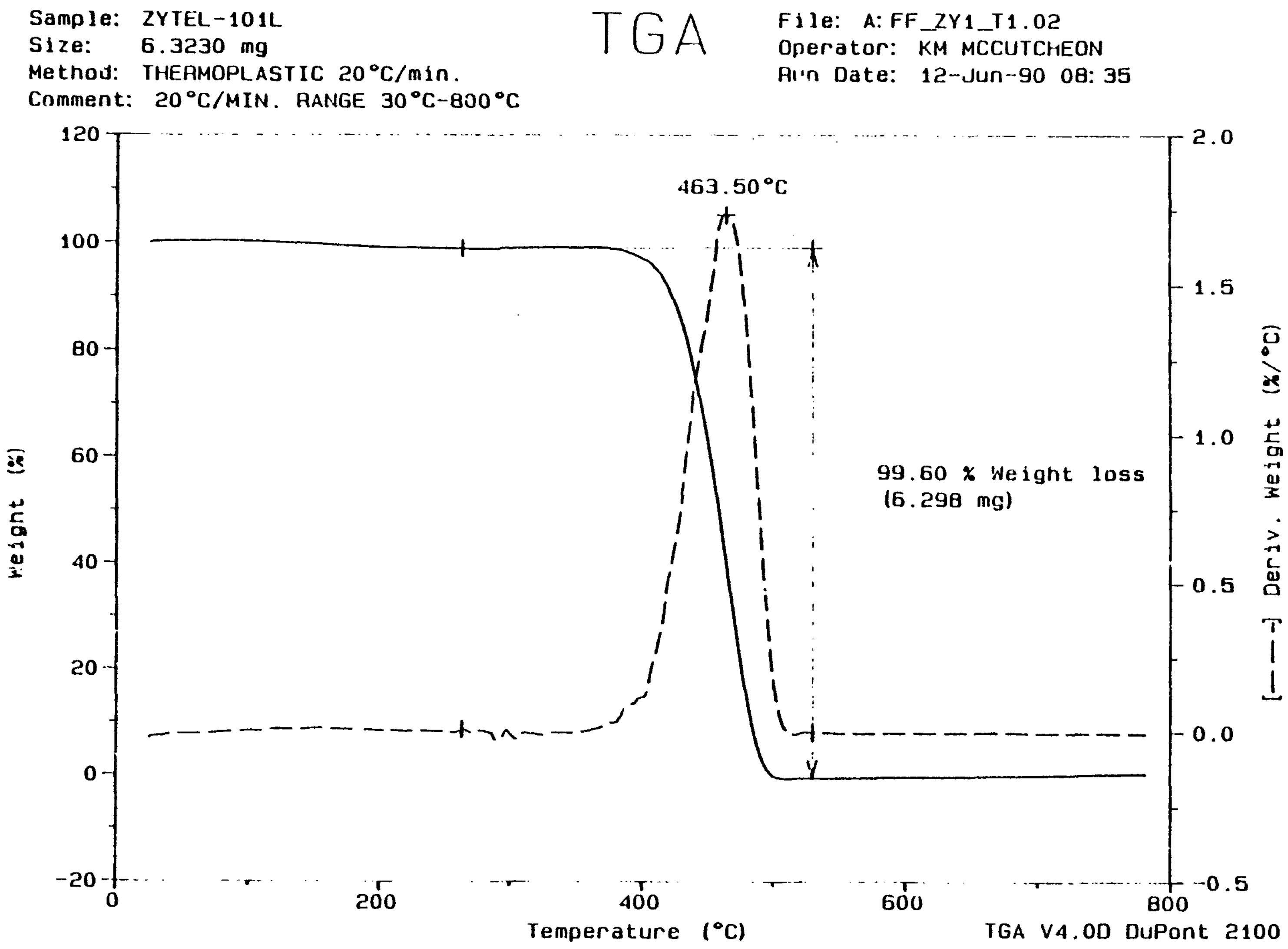

Figure 1: TGA of Zytel-101L.

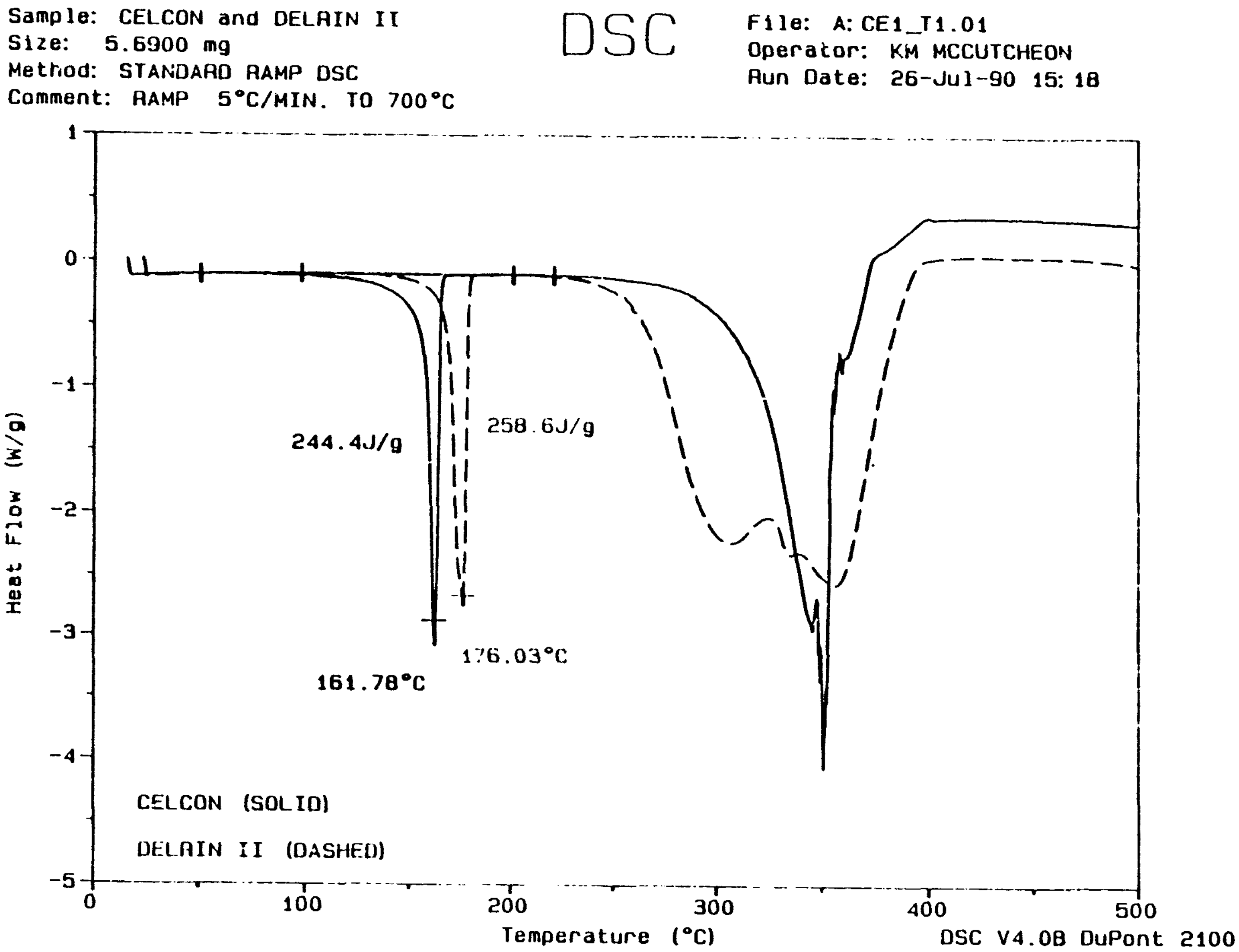

Figure 2: DSC curves of two acetal resin copolymers: Celcon and Delrin II.

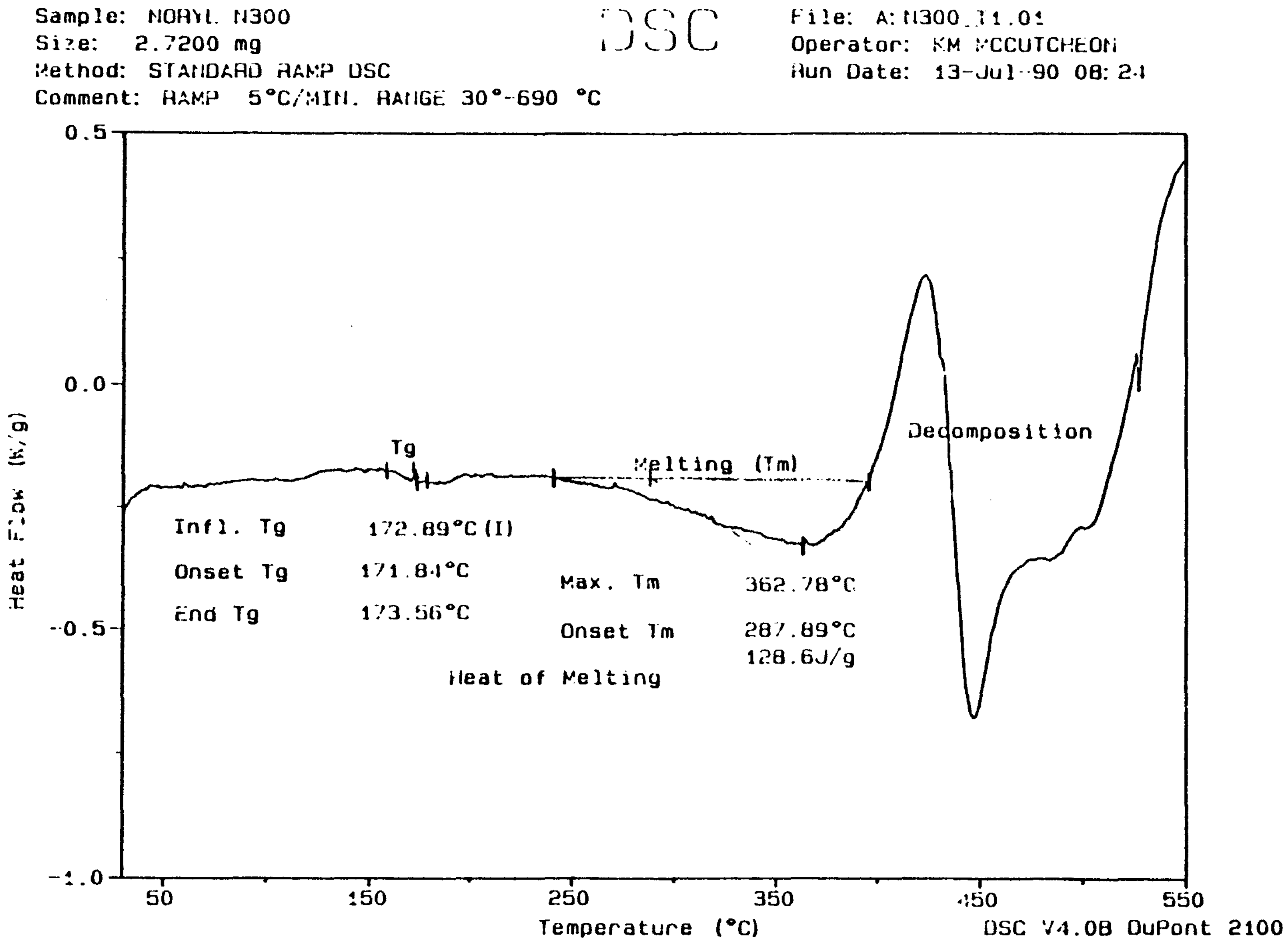

Figure 3: DSC of Noryl N300.

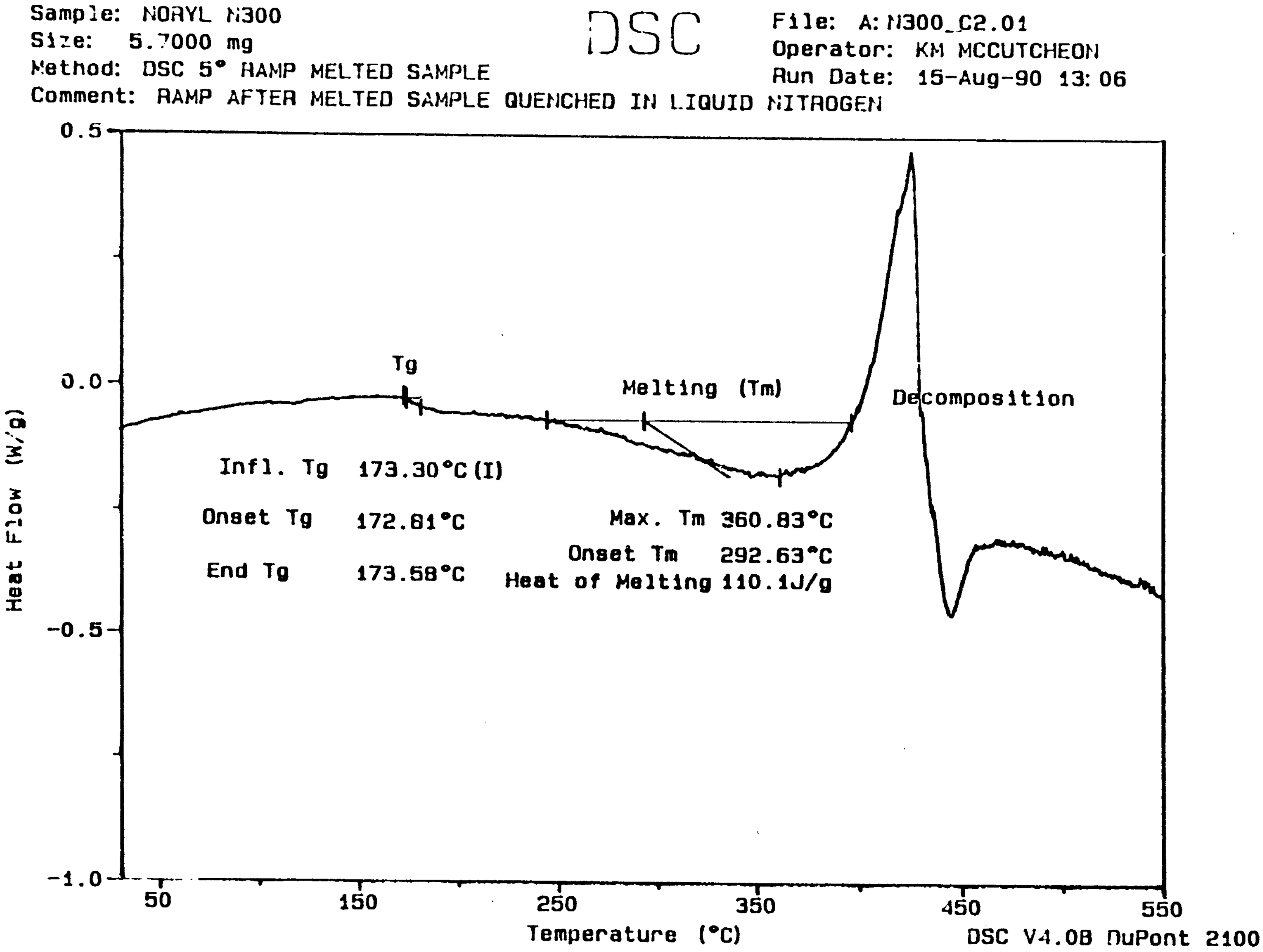

Figure 4: DSC of Noryl N300, after the melted sample quenched in liquid N_2.

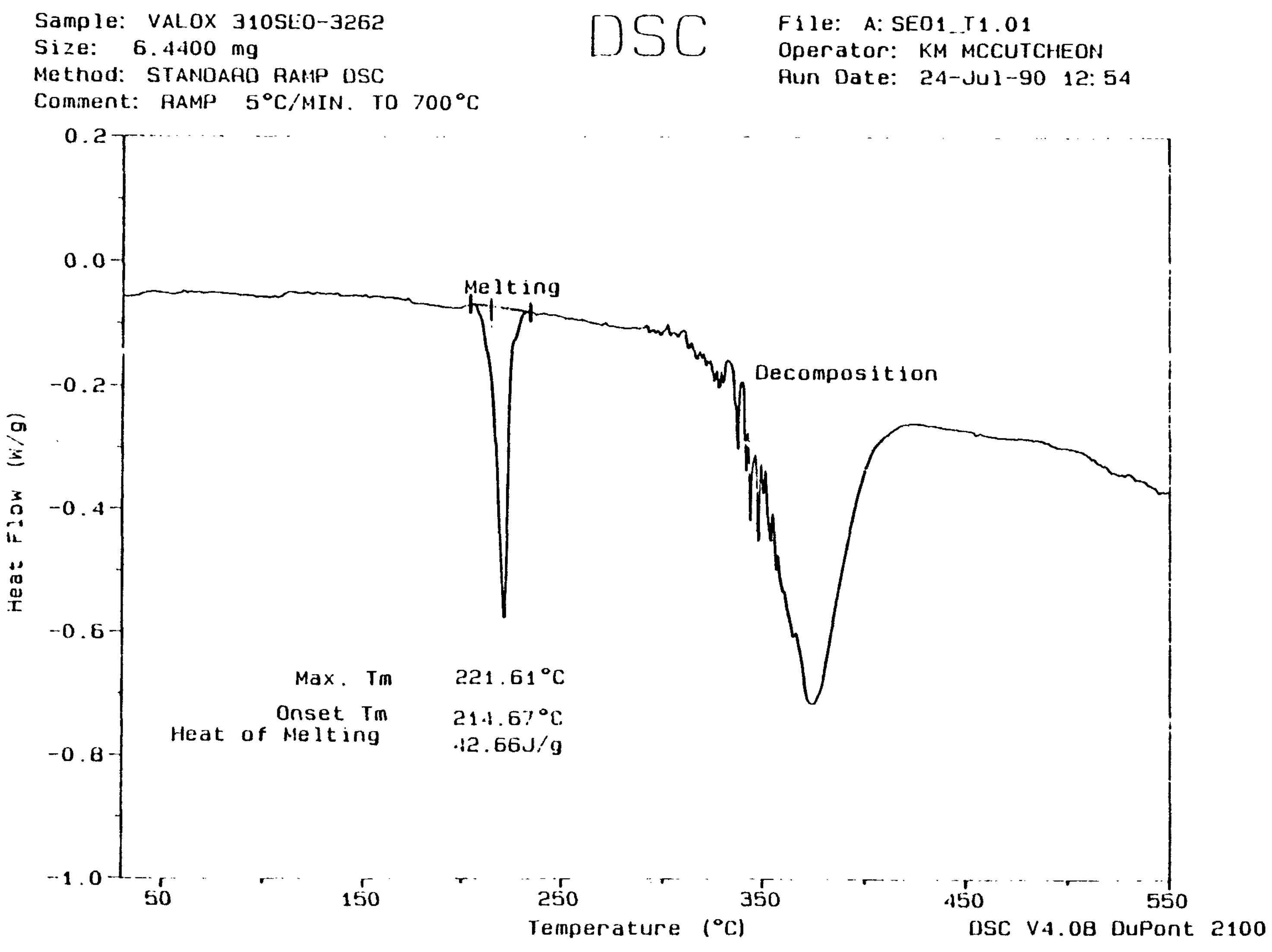

Figure 5: DSC of Valox 310SEO-3262.

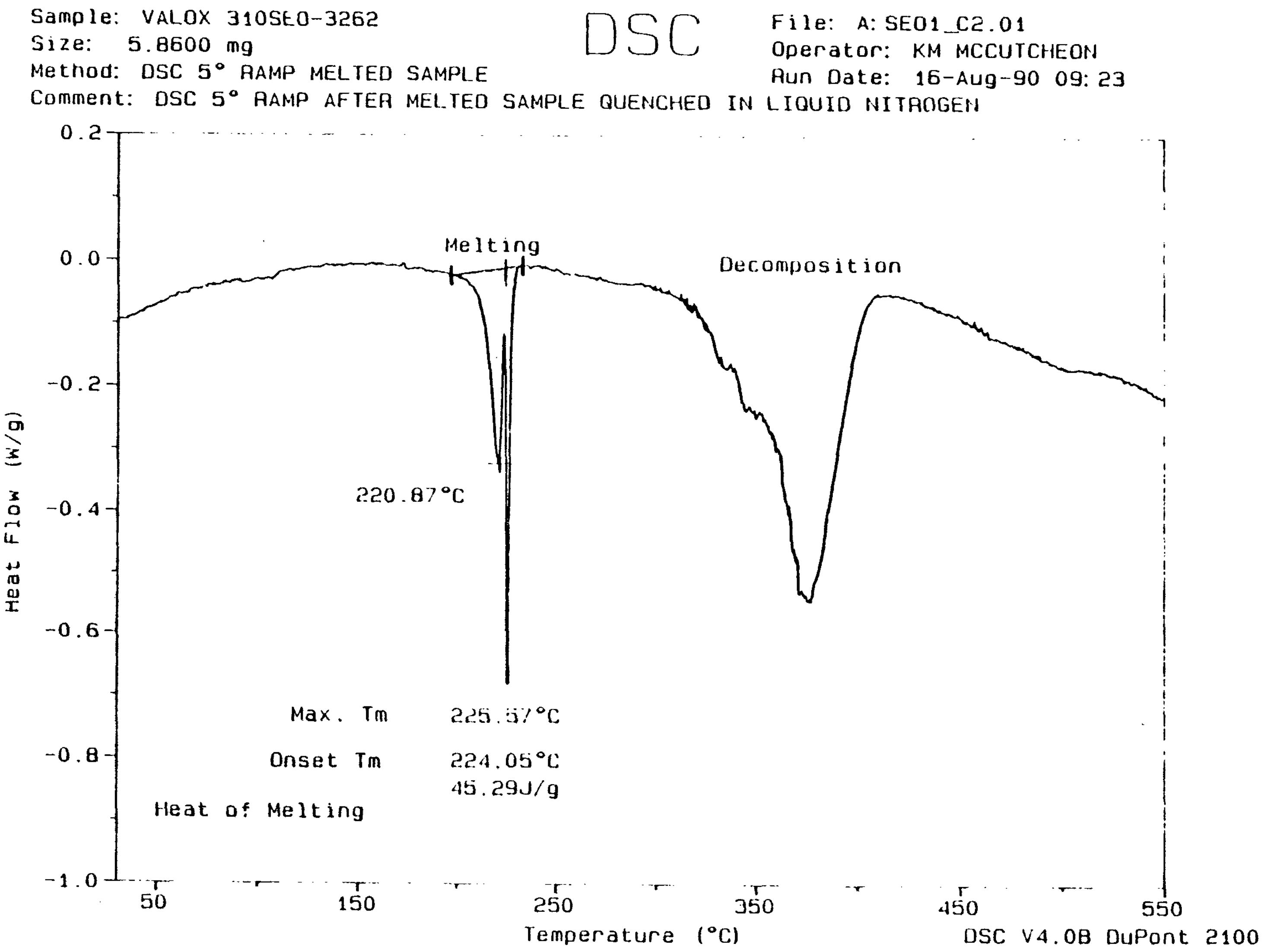

Figure 6: DSC of Valex 310SEO-3262, after the melted sample quenched in liquid N_2.

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