

# Differential Scanning Calorimetry (DSC)

## A Beginner's Guide

This booklet provides an introduction to the concepts of Differential Scanning Calorimetry (DSC). It is written for the materials scientist unfamiliar with DSC.



DSC family.

The differential scanning calorimeter (DSC) is a fundamental tool in thermal analysis. It can be used in many industries – from pharmaceuticals to polymers and from nanomaterials to food products. The information these instruments generate is used to understand amorphous and crystalline behavior, polymorph and eutectic transitions, curing and degree of cure, and many other material properties used to design, manufacture and test products. DSCs are manufactured in several variations, but PerkinElmer is the only company to make both single and double-furnace styles. We've manufactured thermal analysis instrumentation since 1960, and no one understands the applications of DSC like we do. In the following pages, we answer common questions about what a DSC is, how the instruments work, and what they tell you.

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## 20 Common Questions about DSC

### **Q** What is DSC?

**A** Differential Scanning Calorimetry, or DSC, is a thermal analysis technique that looks at how a material's heat capacity ( $C_p$ ) is changed by temperature. A sample of known mass is heated or cooled and the changes in its heat capacity are tracked as changes in the heat flow. This allows the detection of transitions like melts, glass transitions, phase changes, and curing. Because of this flexibility, DSC is used in many industries including pharmaceuticals, polymers, food, paper, printing, manufacturing, agriculture, semiconductors, and electronics as most materials exhibit some sort of transitions.

The biggest advantage of DSC is the ease and speed with which it can be used to see transitions in materials. If you work with polymeric materials of any type, the glass transition is important to understanding your material. In liquid crystals, metals, pharmaceuticals, and pure organics, you can see phase changes or polymorphs and study the degree of purity in materials. If you are processing or distilling materials, knowledge of a material's heat capacity and enthalpy changes can be used to estimate how efficiently your process is operating. For these reasons, DSC is the most common thermal analysis technique and is found in many analytical, process control, quality assurance and R&D laboratories.

### **Q** What is the difference between a heat flow and a heat flux DSC?

**A** The term differential scanning calorimetry refers to both the technique of measuring calorimetric data while scanning as well as a specific instrument design. The technique can be carried out with other types of instruments. Historically, temperature transitions in materials were first seriously studied for the ceramic industry in the 1800s by differential thermal analysis (DTA). This early work was done by placing a thermometer into a material and heating it in an oven, similarly to the way a meat thermometer is used. There were some serious problems with this as placement of the thermometer was often not reproducible. This was solved by Boersma's development of the fixed thermocouple differential thermal analyzer. Analyzers of this design are still common today and called Boersma DTAs.

In the 1960s, Mike O'Neill of PerkinElmer developed the first double-furnace, or power controlled DSC in order to measure heat flow, the movement of heat in and out of a sample, directly. This instrument uses a feedback loop to maintain the sample at a set temperature while measuring the power needed to do this against a reference furnace. This allows for very precise control of temperature, very accurate enthalpy and heat capacity measurements, and true isothermal performance. Because of its direct measurement of heat flow, it is often called heat flow DSC.



Figure 1. Double-furnace design allows the direct measurement of heat flow.

A Boersma DTA can also be used to calculate heat flow with the right calibrations and is also used for the technique of DSC. However, they do this by measuring temperature differences and changes between a sample and a reference, or the heat flux. These instruments are sometimes called heat flux DSCs. Like all DTA designs, the Boersma really measures the temperature difference ( $\Delta T$ ) and calculates heat flow from calibration data. Because of their single furnace design, heat flux DSCs are less sensitive to small transitions, heat and cool at slower rates than heat flow DSC, and give less accurate values for Cp and enthalpy.

**Q How does the difference affect me?**

**A** For the vast majority of simple applications, the data from both types of instruments are comparable and both instruments can give good data. However, both designs have strengths and weaknesses, and if you are doing more than just looking at simple glass transitions and melts, you may need one or the other. Some of the differences are given in Table 1.

<b>Table 1. Heat Flow Versus Heat Flux DSC.</b>		
	<b>Heat Flow</b>	<b>Heat Flux</b>
Fast Heating (250 °C/min plus)	Yes	No
Modulated Techniques	Yes	Yes
Accuracy of Cp Values	High	Moderate
Delta H Accuracy	High	Moderate
Ease of cleaning	Very	Moderate
OIT Testing	Moderate	Easy
Isotherm Performance	Excellent	Affected by sample

## Q Why do curves point in different directions?

A As shown in Figure 2, this is a convention based on how the instruments work. In a heat flow DSC, the endothermic peaks – those events which require energy point up – because the instrument must supply more power to the sample to keep the sample and reference furnaces at the same temperature. In a heat flux DSC, these same events cause the sample to absorb heat and be cooler than the furnace, so they point down. The reverse logic applies to exothermic events where energy is released. The International Conference on Thermal Analysis and Calorimetry (ICTAC) set the convention that curves should follow this pattern many years ago. Most modern software systems let you flip the curves as you like.

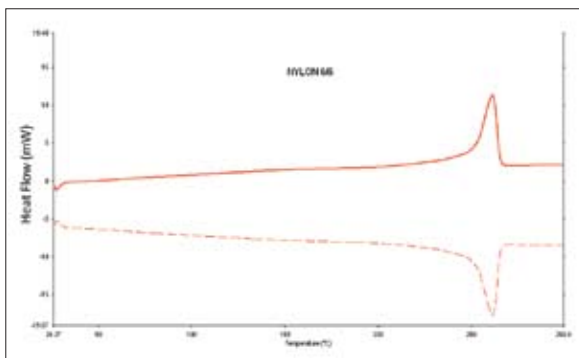


Figure 2. Comparison of curves for a nylon from a double furnace DSC (solid line) and from a single furnace heat flux DSC (Boersma DTA). Endotherms point in opposite directions as explained in the text.

## Q What is heat capacity?

A Heat capacity ( $C_p$ ) is the amount of energy a unit of matter can hold. Think of a can of green pea soup: it's a gelatinous mass at room temperature but as it heats up in a saucepan it becomes more and more fluid. Its heat capacity also increases and the fluid soup at 100 °C can hold more energy than the solid at room temperature. All materials show this increase in heat capacity with temperature. It is reported as either J/g, J/mol, or as calories/g in the older literature.

As heat capacity increases with temperature, the run of a real sample should show a slight upward slope toward higher temperature as well as a step change in the baseline across the melt as the heat capacity of a molten material is higher than that of a solid. Lack of these features suggests some form of data manipulation. Of course, a strong enough peak will dwarf these features.

Heat capacity may seem academic, but it turns out to have lots of practical implications and engineers often need it. For example, when running an extruder for polymeric or food products, knowing the heat capacity of the material can help you figure out how efficient your process is and whether you are using too much energy. You can use it to calculate the energy needed to run a distillation or recycle column or to estimate how much energy is needed to keep something at a certain temperature.

The standard is water with a heat capacity of 1 J/M, which means it takes 1 joule of energy to heat 1 cc of water one degree. Practically, people use sapphire as a standard as it is a stable solid, so it doesn't change much, doesn't get contaminated, and can be made very pure. This allows you to measure heat capacity and obtain very accurate numbers.

### **Q** Why is measuring the glass transition important?

**A** The glass transition ( $T_g$ ) has been called the "melting of amorphous material" and as unscientific as that is, it isn't that bad a description. Amorphous material like glass has no organization in the solid state – it is random. This gives it the transparency that glass has among other properties. As you warm it up, its heat capacity increases and at some point you have enough energy in the material that it can be mobile. This requires a fair amount of energy compared to the baseline increase, although much less than the melting point does. This energy normally appears as a step change in the instrument baseline – pointing up in heat flow instruments and down in heat flux.

In non-crystalline and semi-crystalline polymer of any type – synthetic high polymers like polypropylene and polystyrene, natural polymers like rubber, or biological polymers like proteins – the glass transition is the best indicator of material properties. As the glass transition changes due to either different degrees of polymerization or modification by additives, the physical properties of the material change. The relationship of  $T_g$  to degree of polymerization shown in Figure 3 changes with these alterations.

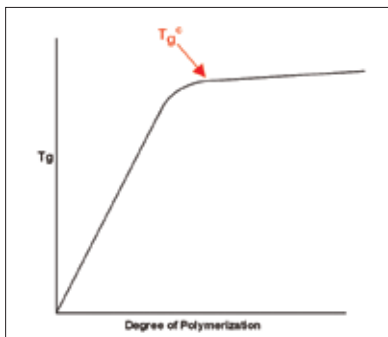


Figure 3. The relationship of  $T_g$  with degree of polymerization showing the  $T_g$  critical where the material develops polymeric properties.

Similarly, material properties also change dramatically above the  $T_g$ . For example, materials lose their stiffness and flow as is the case in molten glass, and their permeability to gasses increases dramatically leading to increased spoilage in food products. Lyophilized materials can collapse and their storage life is shortened as excipient-drug reactions can increase.

## Q Why should I measure melting by DSC?

A As most people know, melting is often measured using a simple melting point apparatus adequately. However, the number is often imprecise and difficult to reproduce. Using a DSC for this task gives you the melting temperature from a calibrated and highly precise system and also gains you considerably more information about the sample. When you measure the melting point ( $T_m$ ) in a DSC, you get not only the onset of melting, the  $T_m$ , but also the peak temperature which corresponds to complete melting in organics and the energy that the melting transition needs in order to occur. This is the enthalpy of the transitions and it is associated with the crystallinity of materials. (Figure 4). ICTAC standards say you should take the onset of the melt peak as the melting point for metals, organics, and similar materials, but the peak value should be used for polymers.

In addition, you can use the enthalpy of melting to estimate both purity and degree of crystallinity for materials. In the case of pharmaceuticals and organics, you can estimate purity of materials with much more accuracy by using the leading edge method. This method is based on the melting point depression caused by impurities and, if you know the molecular weight of your material, it may be possible to use this approach instead of other methods like liquid chromatography.

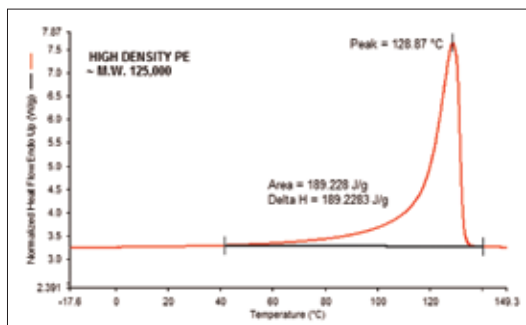


Figure 4. The melting of polyethylene is shown with the melting temperature calculated at the peak, as is standard for polymers. The area and enthalpy of melting are also reported.

## Q What else can I learn from DSC data?

A DSC can detect any change that alters the heat flow in and out of a sample. This includes more than just glass transitions and melting. You can see solid state transitions like eutectic points, melting and conversions of different crystalline phases like polymorphic forms, dissolution and precipitation from solutions, crystallization and re-crystallizations, curing exotherms, degradation, loss of solvents, and chemical reactions.

Table 2 shows the type of transitions detected by DSC sorted by industry and use in that industry.

<b>Table 2. Industry Transitions.</b>		
<b>Industry</b>	<b>Transitions</b>	<b>Purpose</b>
Pharmaceuticals	Tg	Collapse or storage temperature, amorphous content
	Cp	Processing conditions
	Tm	Polymorphic forms, purity, QC
Polymers	Tg	Indicator of material properties, QC, effect of additives
	Tm	Polymer processing, heat history
	Exotherm	Reactions rate, curing of materials, residual cure
	Cp	Energy needed to process
	Tc	Recrystallization times, kinetics
Food	Tg	Storage temperature, properties
	Tm	Processing temperature

### **Q How do I obtain good data?**

**A** Initially, obtaining good data means understanding what good data is. The quality of the data you get is to some degree subjective. A company measuring the Tg of polymers being used for injection molding of toys will have different requirements than someone concerned with the collapse temperature of a lyophilized cake. Good data requires at a minimum a valid calibration with suitable standards, a smooth baseline, and reasonable separation of the sample peak from any noise in the baseline. It should be both repeatable and reproducible.

By calibration, it means the instrument has to be set up against known standards and checked so it gives reasonable values. How tight the value repeat is depends on a decision based on needs of the industry – one company may need a half a degree while another may tolerate a degree in variation of temperature. Similarly, how good a baseline you need is driven by the requirements of your business. The baseline should be smooth – no bumps or spikes, flat – a flat line although in a real sample some slope upward with higher temperature is expected as the heat capacity increases, and repeatable – not changing from run to run.

Assuming you know the calibration is valid and the baseline is acceptable, the transitions should be clearly visible without excessive manipulations. If the peak requires multiple smoothing, is difficult to detect from baseline noise, or is exceptionally distorted, another technique may be indicated.



## **Q** How can I improve my data?

**A** There are several ways to improve a weak signal if everything else is working well. You can most easily increase sample size by running a larger sample, you can run the same sample faster, or you can use one of more advanced techniques, which will be discussed later (Page 13 – Modulated Techniques or Fast Scanning Techniques.) You should remember that if you increase sample size, scanning rate or both, you need to watch for loss of resolution in your data caused by uneven heating of the sample. A large sample should ideally be run at a slower rate and a sample run at faster rates should be smaller. Both of these help because the heat flow is a function of sample mass and scanning rate.

In some cases, a more specialized pan may be the answer. Specialized sample pans exist for many purposes. Samples containing solvents can be run in sealed pans. Samples that evolve gases, such as those containing explosives, may be run in vented pans. Films can be placed in pans that keep them flat. A different material sample pan may be needed to reduce interactions with the sample or to allow a higher temperature to be used. If you look in thermal analysis supply catalogs, you will see a wide variety of pans for all sorts of specialized conditions.



*Figure 5. DSC 8500 with 96-position autosampler.*

## **Q Why doesn't my data agree with other thermal techniques?**

**A** One common question is why DSC data does not always agree with other methods of analysis. This is most commonly raised with the difference in values for the glass transition for DSC and the mechanical methods of Thermomechanical Analysis (TMA) and Dynamic Mechanical Analysis (DMA). There are several reasons for this, but the most important one involves the nature of the glass transition. The glass transition is really a range of behavior where scientists have agreed to accept a single temperature as the indicator per certain standards. Different industries have used different points from the same data set that can vary as much as 15 °C. DSC, TMA, and DMA measure different processes and therefore, the numbers vary. You can see as much as a 25 °C difference in data from a DSC to DMA data reported as peak of tan delta.



Figure 6. DSC 6000 with 45-position autosampler.

## **Q What is the difference between controlled and ballistic cooling?**

**A** Cooling is often an under appreciated property of both DSC and material science in general. How a material is cooled from its melt defines its heat history and the heat history can make a great deal of difference in a material's properties. The classical example is poly-ethylene terephthalate (PET), which becomes nearly all amorphous when cooled rapidly from the melt, but is mostly crystalline when cooled slowly. Since the heat history is so important in how a material behaves, the standard operating procedure in plastics is to run a heat-cool-heat cycle. The first heat shows the material as received, the cooling step – if done with controlled cooling – imposes a standard heat history on the material, and the second heat allows you to compare materials directly to each other.

Controlled cooling is important as you want the cooling rate to be as controlled as was the heating rate to get reproducible data. In controlled cooling, a specific temperature change per minute is specified as a rate somewhere between 0.1 to 500 °C/min, and should be maintained throughout the experiment. This is in contrast to ballistic cooling, where the sample is cooled as fast as possible, by either cutting all power to the DSC furnace or by removing the sample and dropping it into LN<sub>2</sub>. Very high rates of controlled cooling are desirable as some processes have rates of 800 °C /min and high rates allow you to model them.

Controlled cooling allows the greatest degree of separation between overlapping peaks and is more sensitive than melting. Controlled cooling also allows you to do isothermal re-crystallizations studies to see how a material behaves when a process applies large temperature drops on a material. With the isothermal kinetic packages, you can then predict behavior at rates that have not actually been measured.

**Q Why should I care about isothermal performance?**

**A** Isothermal performance means the ability of the DSC to hold a temperature precise with no drift. This is best accomplished in a power controlled DSC as it is designed to control temperature. Many processes in real life are actually done isothermally: baking a cake, curing an aircraft wing, molding plastic parts, etc. Often the material is inserted into a set temperature region at a very different temperature; the cake goes from room temperature to 150 °C or the plastic goes from the molten state in the extruder to room temperature as a blown film. This means that the DSC must not only be able to hold an isothermal temperature precisely, but it must be able to heat and cool to that temperature rapidly with no under or overshoot. This is another area where a power controlled DSC has an advantage due to its design.

**Q How do I study oxidative stability?**

**A** Oxidative Stability or the Oxidative Induction Time (OIT) test is often studied in both DSC and TGA. This is normally done by heating a material to a set temperature under an inert gas and switching to air or oxygen once it has equilibrated. The time needed for the material to begin to burn is then recorded. Normally in a power compensated DSC, a flow-thru cover is used to remove the smoke from the DSC as quickly as possible. (It can also be used to remove reactive gases generated by the sample.) Often it is best to run these tests in a TGA as this experiment is very dirty and these instruments are designed to accommodate such samples.

**Q When do I need to use HP-DSC?**

**A** High Pressure (HP) DSC is used for several reasons: first, an oxidative stability test may take too long at atmospheric pressures to be convenient. An example of that would be looking at an antioxidant package in motor oil. Secondly, some reactions form water or methanol as a byproduct, leading to foaming in the sample. Higher pressure suppresses this. Thirdly, some reaction kinetics are affected by pressure and running the reaction under controlled pressure is needed to study this. Finally, transitions like the T<sub>g</sub> and boiling point are responsive to pressure and running DSC under pressure allows you to study that. For boiling points, pressure DSC allows you to calculate the vapor pressure of the sample.

**Q When should I consider using UV-DSC?**

**A** UV-DSC or Photo-DSC is a DSC that has been adapted to allow the sample to be exposed to UV light during the run. This can be done with several types of light sources, like mercury vapor lamps or LEDs, over a range of frequencies and intensities. UV-DSC allows the study of UV initiated curing systems in the DSC, like those used for dental resins, orthopedic bone cements, hydrogels, paints or coatings, and adhesives. It complements the technique of UV-DMA, which allows you to gain mechanical information on these systems. UV-DSC allows you to study the efficiency of curing and to develop kinetic models for curing systems.

UV-DSC is also used to study the decomposition of materials under UV radiation. This can be for understanding the effects on the storage of pharmaceuticals, on antioxidant packages in polymers and rubbers, on food properties, or on dyes in sunlight. It is possible to use kinetics to model the degradation by UV light. Because of the high intensities of UV available, accelerated testing is possible.



*Figure 7. DSC 6000 with UV-photocalorimeter accessory.*

**Q How are kinetic studies done with a DSC?**

**A** Kinetic studies on the DSC can be done using scanning methods, where the sample is either heated through a temperature ramp, or isothermally, where the sample is held at a set temperature. In the latter case, the ramp rate to that temperature should be as fast as possible to minimize the effect of the ramp. Data from these methods can be exported to Excel® or another program for analysis or run through several commercially available programs. The advantage of using DSC for kinetic studies is it tends to be faster and more straightforward than other methods.

## **Q What is Modulated Temperature DSC?**

**A** Modulated Temperature DSC (MT-DSC) is the general term for DSC techniques where a non-linear heating or cooling rate is applied to the sample to separate the kinetic from the thermodynamic data. In StepScan™ DSC, this is done by applying a series of heating (or cooling) micro-steps followed by an isothermal hold. This allows you to separate the data into an Equilibrium Cp curve that shows the thermodynamic response of the sample and an isokinetics baseline that shows the kinetic response. Unlike some other techniques, these are calculated independently. This technique removes kinetic noises from transitions, like enthalpic overshoot or the curing exotherm, from an overlapping Tg.

## **Q What is Fast Scan DSC or HyperDSC®?**

**A** Fast Scan DSC is the generic term for DSC techniques that apply very high heating rates to a sample to increase the sensitivity of a DSC or to trap kinetic behavior. Fast scan heating rates range from 100-300 °C/min., where HyperDSC heating rates range from 300-750 °C/min. Heating at high rates was originally developed in power controlled DSC thanks to the small furnace mass and the best results are still obtained in these instruments. When heating rates of 100-750 °C/min are applied, the response of the DSC to weak transitions is enhanced and it is possible to see very low levels of amorphous materials in pharmaceuticals, measure small amounts of natural products, freeze the curing of thermosetting compounds, and inhibit the cool crystallization of polymers as well as the thermal degradation of organic materials.

## **Q What hyphenated techniques work with DSC?**

**A** DSC is not normally hyphenated as frequently as is TGA but hyphenation has been used. DSC-IR has been used to look at the evolved solvents from pharmaceuticals while DSC-MS has been used to look at the composition of meteorites and lunar rocks. DSC has also been coupled to FT-IR microscopy to look at changes in a sample during a DSC run.

Probably the most promising hyphenated technique is DSC-Raman, where a sample is irradiated by a Raman laser as the sample is run in DSC profile. Because of the nature of the Raman spectrometer, it is ideally suited for this as it does not require any processing of reflectance spectra nor the use of a special transmission path cell.

DSC-Raman shows great potential for the study of polymorphic materials, polymeric re-crystallization, chain movements at the glass transition, and for hydrogen bonding polymers.

# Glossary

## Annealing

is the slow controlled cooling of a material from its melt temperature to room temperature. This employs controlled cooling rates below 5 °C/minute. This is used to further study the effects of structural ordering within the material.

## Crystallization Temperature

is an exothermic event where a liquid changes to a solid. This is depicted as a peak. The extrapolated onset and peak temperature characterize this event.

## DMA – Dynamic Mechanical Analysis

measurement of stiffness and modulus using forced oscillations as a function of time, temperature, stress, strain, or frequency.

## DSC

is an analytical technique that measures the heat flow rate to or from a sample specimen as it is subjected to a controlled temperature program in a controlled atmosphere.

## DTA – Differential Thermal Analysis

a simpler form of DSC often called heat flux or single furnace DSC.

## Endothermic Event

is a thermal event of a material where energy is absorbed by the material, i.e. melting.

## Exothermic Event

is a thermal event of a material where energy is expelled by the material, i.e. crystallization.

## Fast Scanning DSC

is a DSC technique that employs controlled heating rates above 100 °C/minute. It is used to observe subtle thermal events.

## Glass Transition (T<sub>g</sub>)

is an endothermic event, a change in heat capacity that is depicted by a shift in the baseline. It is considered the softening point of the material or the melting of the amorphous regions of a semi-crystalline material.

## Heat

is a form of energy. Heat is not temperature.

## Heat Capacity (C<sub>p</sub>)

is the amount of heat required to raise a unit mass of a material one degree in temperature.  $C_p = Q/m\Delta T$ , where:  $C_p$  = specific heat,  $Q$  = heat added,  $m$  = mass of material,  $\Delta T$  = change in temperature.

## Heat History

is the last thermal excursion the material has experienced. In polymers, heat history is erasable by heating the material slightly above the melt temperature and then quenching or annealing a material to below its glass transition temperature.

## Heat of Fusion (hf)

is the amount of heat per unit mass needed to change a substance from a solid to a liquid at its melting point.  $hf = Q/M$ , where: hf = heat of fusion, Q = heat added, m = mass of material.

## Isothermal

holding at a certain temperature and observing material changes in respect to time. An application of an isothermal experiment is the examining the curing time of an epoxy.

## Isothermal Kinetics

kinetics calculated using isothermal temperatures instead of ramping rates.

## Joule

is the amount of heat required to raise one gram of H<sub>2</sub>O by 1 °C.

## Melting Point (Tm)

the temperature at which a materials melts. It is measured as the peak temperature of an endothermic event. For metals and pure organics, it is not the peak temperature, but the extrapolated onset temperature (To) of the endothermic event.

## Morphology

refers to the crystalline properties and non-crystalline (amorphous) properties of materials.

## Quench Cooling

is a DSC technique that employs rapid cooling rates above 100 °C/minute. This is used to further study the effects of rapid crystallization of a material.

## Scanning

heating or cooling at a controlled rate.

## Specific Heat

see heat capacity. For engineering purposes, specific heat and heat capacity can be assumed to be equal.

## Start-up Transient

is the initial change in the baseline at the very beginning of a scanning run before the instrument is in complete scanning rate control.

## Temperature

is the degree of heat measured on a definite scale.

### **TGA – Thermogravimetric Analysis**

tracking the change in the mass of a sample as a function of time and/or temperature.

### **TMA – Thermal Mechanical Analysis**

measurement of changes in sample size or volume as a function of temperature.

### **Watt**

is the power expended when one joule of work is done in one second of time.

## **Additional References**

ASTM® E 2161-08 Standard Terminology Relating to Performance Validation in Thermal Analysis.

ASTM® E 473-08 Standard Terminology Relating to Thermal Analysis and Rheology.

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