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The Use of Differential Scanning Calorimetry in the Identification of Synthetic Fibers

Thermal methods of analysis have attained a position of prominence recently, particularly in applications to fibers, plastics, and other synthetic polymeric materials [1]. This is principally due to the development of several instruments designed to analyze submilligram specimens which yield satisfactory quantitative and qualitative data [1]. Among the instruments commercially available is the Perkin-Elmer differential scanning calorimeter (DSC). We have successfully used the DSC to identify most synthetic fibers in significant amounts in case materials submitted for analysis.

The merits of this technique, compared with pyrolysis, gas liquid chromatography, and infrared spectroscopy, were simplicity of operation and suitability to the analysis of fiber blends and mixtures. In most instances the method was nondestructive in terms of additional instrumental analysis. Resin coatings or dyestuffs, unlike the situation occasionally encountered with solubility or microscopic methods, introduced no interfering effects.

Differential scanning calorimetry provides a measurement of the rate, magnitude, and temperature at which chemical or physical changes occur in a substance or system during heating or cooling. The DSC differs from classical thermal analytical instruments in that it measures the difference in electrical power required to maintain the specimen pan and empty reference pan at a linearly increasing (or decreasing) temperature. This differential power input, recorded as a function of temperature, is directly proportional to the energy involved in the thermal transitions.

Experimental

In the characterization of semicrystalline polymeric fibers measurements were made of the following quantities: melting temperature, heat of fusion, temperature of reaction, and heat of reaction. The melting point has been defined as the peak of the fusion endotherm, that is, the temperature at which the absorption of heat proceeds at its maximum rate (T_m). The integral of the fusion curve obtained by direct measurement with a planimeter represents the total energy absorbed by the specimen during the transition (ΔH). When expressed in calories per gram the area represents an approximation of the heat of fusion (H_f).

Operating Parameters

Range: 2 mcal/s per full scale deflection

Scan rate: 20 deg C/min

Chart speed: 4 in./min

Nitrogen flow rate: 20 ml/min

Specimen size: 0.3 to 3.0 mg

Calibration checked daily using tin and lead standards

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Procedure

After being weighed on a microbalance, each specimen was encapsulated and heated at a rate of 20 deg C/min from 50 C to approximately 40 C above the melting point, producing the first fusion endotherm. The specimen was then recrystallized by cooling at 20 deg C/min down to 50 C. The recorder was not activated for this step. After this first thermal history had been imposed on the specimen, another program to approximately 40 C beyond the melting point was applied to yield the second fusion endotherm. A second thermal history quench cooling was imposed by removing the specimen from the heated chamber and allowing it to cool rapidly to room temperature. Finally, the specimen was returned to the cooled specimen holder and programmed again to yield the third fusion endotherm.

In addition to the sample weight before encapsulation, the following information was recorded from the three scans obtained:

- a. The melting point and heat of fusion from the second fusion endotherm or, as in the case of polyamides (see below), from the third fusion endotherm.
- b. The positions and heats of reaction of any other endotherms or exotherms.
- c. A visualization of peak morphology.

Results and Discussion

General Observations

Invariably, the first fusion peaks represented larger ΔH values than subsequent fusion endotherms, presumably due to the high degree of crystallinity imparted by the manufacturers' spinning and drawing processes. The shape of the first peak was not always reproducible for a given fiber. This was thought to be partially caused by the presently uncontrollable geometric configuration of the fiber in the specimen capsule. Once the initial fusion had been made, subsequent fusion endotherms were invariably reproducible in shape and position (± 1 C). Accuracy in the quantitative data was sacrificed to some extent to accommodate the minimal specimen size and to complete the three scans in a reasonable period of time; for example, the H_f estimates were within ± 20 percent of the true values.

Characteristics of Fiber Classes and Variations within Classes

Polyamides—Nylons were readily differentiated from other classes on the basis of the presence and position of characteristic double peaks apparent on the second scan (Fig. 1). White [2] first described the double-peak occurrence in drawn nylon 66 and attributed the lower peak to misorientation of crystallite regions prior to fusion. Gray and Casey [3] interpreted the occurrence of similar peaks as the result of prior annealing of the crystallizing polymer. Their argument was that the assumed linear cooling rate was in fact nonlinear because of the large exothermic heat of crystallization, which caused transient annealing in the slowly cooling polymer. My own observation that the amplitude of the first peak varied inversely with the prior cooling rate supported this explanation.

The four major varieties of nylons were differentiated from one another on the basis of T_m and H_f values as illustrated in Table 1.

Polyesters—Members of the polyester class could be recognized quickly by the presence of a solid phase crystallization exotherm in the 120 to 160 C region following quench cooling (Fig. 2). Of all the fiber-forming polymers presently in commercial use, the polyesters are the best example of ones which do not crystallize rapidly on cooling and can therefore be quenched into an essentially amorphous condition [4,5]. Following the

TABLE 1—Summary of data for endotherm yielding classes.

Class	Generic or Trade Names	Fusion Endotherms			Solid Phase Crystallization Exotherm	Cyclization Cross-Linkage Exotherm				
		Description	T_m , deg C	H_f , cal/g						
Polyamides	Nylon 6 Nylon 66 Nylon 11 Nylon 610	<i>Second Endotherm</i>		<i>Third Endotherm</i>	nil	nil				
		double	217	12						
		double	257	14						
		double	185	10						
		double	218	14						
		(first peak small)								
Polyesters	Regular PET ^a Terylene Dacron Fortrel Enka Polyester Kodel 411 Vycron 5 Vycron 2 PCDT ^b Kodel 211	<i>Second Endotherm</i>		<i>Second Endotherm</i>	140 to 150 140 to 150 140 to 150 140 to 150 140 to 150 140 to 150 150 to 160 120 to 145	nil nil nil nil nil nil nil nil				
		single	249	7.5						
		single	249	7.5						
		single	249	7.5						
		single	249	7.5						
		single	249	7.5						
		single	226	5.0						
		single	280	7.8						
		Triacetates	Arnel and Tricel	first, single			296	4.5	206	nil
				second, single			285	3.0	nil	nil
third, single	278			2.2	239	nil				
Polyolefins	Polyethylene Branched Linear Polypropylene Isotactic Syndiotactic	<i>Second Endotherm</i>								
		single	102	14	nil	nil				
		single	128	35	nil	nil				
		triple	156	15	nil	nil				
		single	156	18	nil	nil				
Polyvinyls	Saran Nitril Vinyon Vinal	<i>Second Endotherm</i>								
		double	162	4.0	nil	nil				
		T_g at 180 C	nil	nil	nil	350				
		nil	nil	nil	nil	irregular at 316				
		T_g at 200 C	nil	nil	nil	nil				

^a Polyethylene terephthalate.^b Polycyclohexylene dimethylene terephthalate.

resumption of heating over a specific temperature range, the random molecular configuration was replaced by highly crystalline arrangements and produced the described exotherm.

The regular, largely homopolymer, polyethylene terephthalates (PET), such as Dacron, Terylene, Fortrel, Kodel 411, and Vycron 5, produced similar patterns, with the described exotherm at 140 to 150 C, the second fusion endotherm at 249 C, and an H_f of 7.5 cal/g. The copolymeric Vycron 2 (PET/isophthalate) differed significantly with a T_m of 226 C and an H_f of 5.0 cal/g. Polycyclohexylene dimethylene terephthalates (PCDT) such as Kodel 211 were readily distinguishable by the second fusion endotherm at 280 C and a slightly higher H_f of 7.8 cal/g (Table 1).

Triacetates—Arnel, Tricel, and other triacetates displayed a solid phase crystallization exotherm on the first and third scans at approximately 205 C and 235 C, respectively

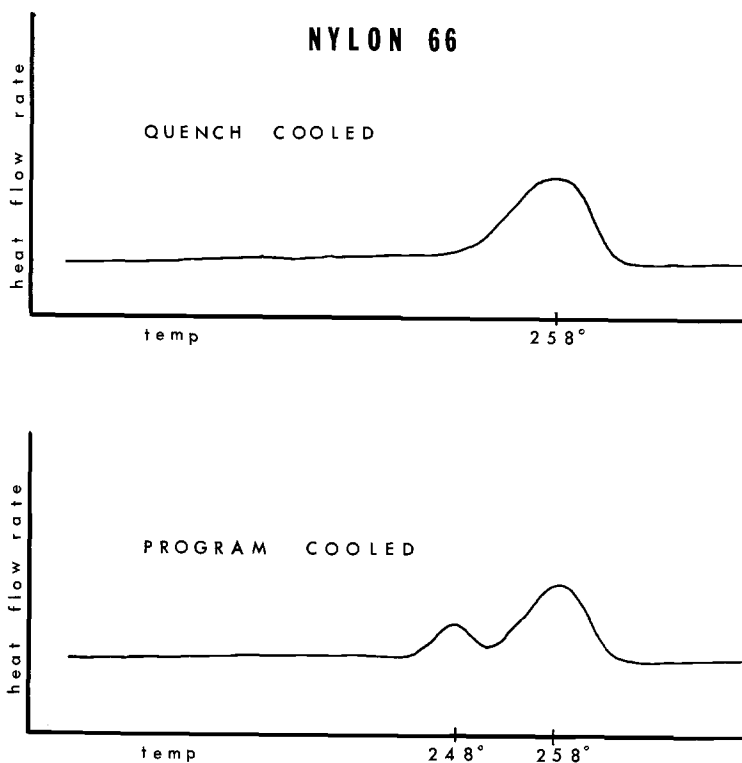


FIG. 1.—DSC thermograms of nylon 66 following quench and program cooling.

(Fig. 3). Whenever the fabric was heat set (annealed) the exotherm was absent or much reduced on the first scan.

The first fusion endotherm occurred in the 295 to 303 C range with an H_f of 4.0 to 5.0 cal/g. As each triacetate specimen was repeatedly melted and recrystallized, the melting point decreased, the temperature of the crystallization exotherm increased, and the H_f values decreased. The successive alterations noted could well be due to specimen loss and impurity buildup as a result of the degradation of acetylcellulose by sulfuric acid released during the saponification of sulfoesters [6]. That appreciable thermal decomposition occurs in triacetates heated beyond 280 C has been shown in thermal gravimetric analysis (TGA) studies [7].

Polyolefins—Branched polyethylene consistently melted at 102 C with an H_f of 14 to 15 cal/g. Linear polyethylene, with its higher degree of crystallinity, repeatedly melted at 128 C with an H_f of 35 cal/g (Fig. 4).

Syndiotactic polypropylene characteristically melted at 156 C with an H_f of 18 cal/g. The one polypropylene known to be isotactic produced three distinct endothermic maxima (140, 148, and 156 C) following programmed cooling. Kamide [8], in his studies of annealed, recrystallized, unoriented, isotactic polypropylene, interpreted the multiple peak phenomenon in terms of partial melting followed by recrystallization resulting in thicker lamellae formation.

Polyvinyls—Sarans displayed a low energy fusion endotherm at 162 C with an H_f of 4.0 cal/g. The second fusion endotherm consisted of two well defined peaks similar to those of

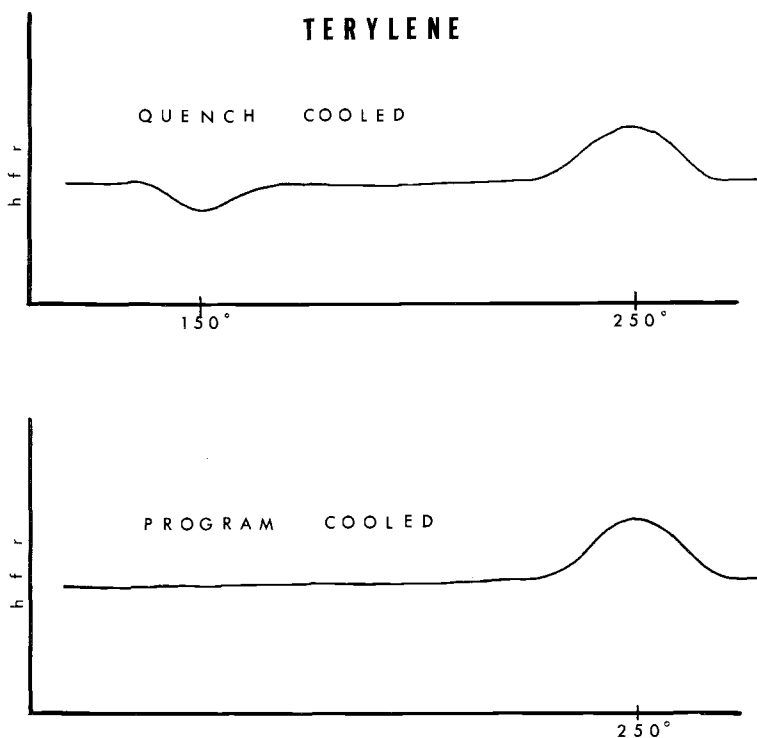


FIG. 2.—DSC thermograms of terylene following quench and program cooling.

the polyamides but at lower temperatures and lower H_f . The nitrils produced an endothermic reaction at 180 C and an exotherm at 350 C. On the first scan the glass transition at 180 C appeared endothermic because of the high degree of order in the glassy state as a result of annealing. The findings were similar to Schwenker's [9] in that the second and third scans lacked the endothermic peak patterns and reverted to the typical glass transition base line shift indicative of an increase in the heat capacity. A pronounced high energy exothermic reaction at 316 C was obtained with the vinyons. The fact that this exotherm was highly irregular in shape prevented any confusion between these and the acrylonitriles. Vinals displayed an endothermic peak at 227 C on the first scan; on subsequent scans this reaction was found to be indicative of a glass transition similar to that found with the nitrils.

Polyacrylonitriles—As expected, the acrylics did not have fusion endotherms but displayed a characteristic irreversible high energy exothermic reaction in the 300 to 330 C range (Fig. 5). Studies have suggested that this thermal degradation involved intermolecular cross-linking and intramolecular cyclization to a conjugated system as well as additional oxidative reactions [10]. The practical significance of the oxidative contribution to the exotherms became apparent when achievement of reproducible peak maxima and heat of reaction data was repeatedly unsuccessful. Nitrogen was used as the purge gas in order to minimize the simultaneous oxidative reactions, but obviously an undetermined and variable amount of air was being encapsulated nonhermetically with the fiber. Consequently, I replaced the nitrogen with air to standardize the oxygen concentration in contact with the fiber specimen. This resulted in an acceptable degree of reproducibility (± 2 C)

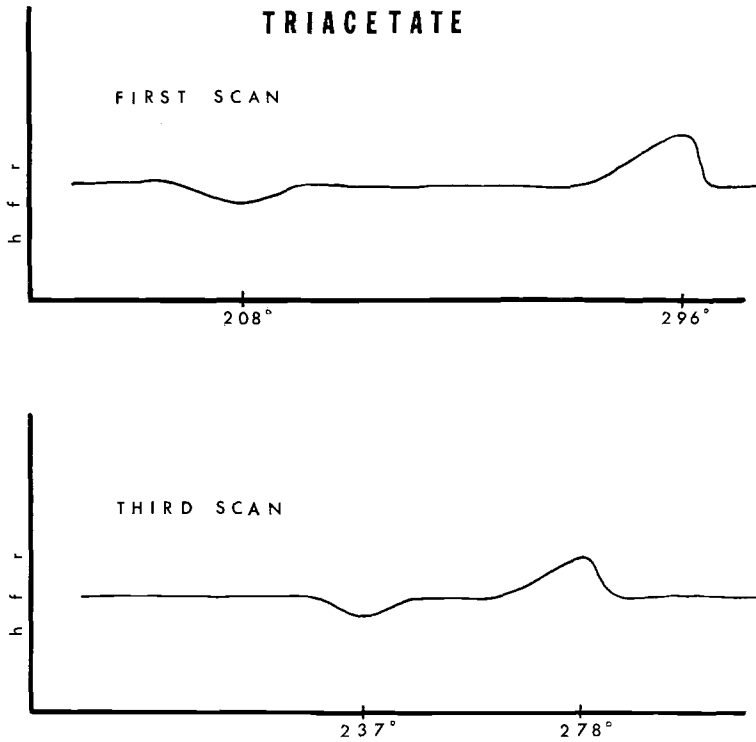


FIG. 3—DSC thermograms of triacetate; first and third scans.

that permitted differentiation of many of the various fibers within the acrylic class on the basis of position of exotherm maxima (Table 2).

TABLE 2—Polyacrylonitriles with air purge (specimen size 0.3 to 0.5 mg).

Trade Name	Cyclization and Cross-Linkage Exotherms, deg C
Orlon 41	325
Orlon 44	300
Orlon 42	337
Orlon 28	336
Orlon 21	336
Orlon 75	335
Zefkrome	323 (narrow exotherm)
Zefran 1200	317 (narrow exotherm)
Zefran 1203	323 (narrow exotherm)
Zefran 1207	320 (narrow exotherm)
Zefran Q1254	331
Creslan 61	329
Creslan 63	326
Creslan 58	336
Creslan BB	333
Creslan 68	313
Acrilan 16	322 (shallow exotherm)
Acrilan 36	336 (shallow exotherm)
Courtelle (type unknown)	300
Dralon (type unknown)	325
Redon (type unknown)	318

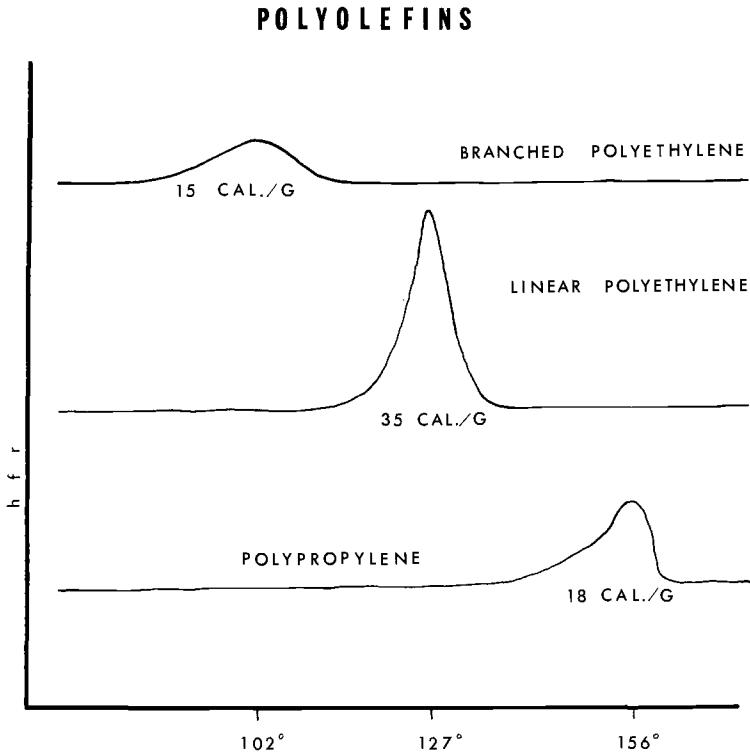


FIG. 4—DSC thermograms of branched and linear polyethylene and syndiotactic polypropylene following program cooling.

Modacrylics—The modacrylics, Verel and Dynel, produced highly characteristic patterns consisting of what appeared to be fusion endotherms at 230 C and 268 C, respectively, immediately followed by high energy degradation exotherms typical of acrylonitrile component polymers or copolymers (Fig. 6).

Fiber Blends and Mixtures

Assessment of the relative proportions of two or more fiber types in a yarn or thread has obvious value in the comparison of textile materials. Manual methods of separation by teasing and weighing have been found to be time consuming, tedious, and often inaccurate. Providing the endotherms or exotherms resulting from one component of a blend were at least 10 C from those of the other components, scanning calorimetry provided a simple, fast, and reasonably accurate method of determining the percentage by weight of each fiber type. Tarim and Cates [11], among others, showed that in most instances the blend thermogram was a simple sum of the thermal spectra of its constituents. The only exception to this rule found in this study was a mixture of poly(vinyl chloride) and nylon, in which the nylon endotherms were suppressed following the initial fusion scan.

Percentages by weight were calculated using the total weight of each specimen, the heats of fusion given in Table 1, and ΔH measurements obtained from each endotherm. Results obtained on fabric and yarn blends of known composition are shown in Table 3. Wool and cotton were inert over the temperature range of interest.

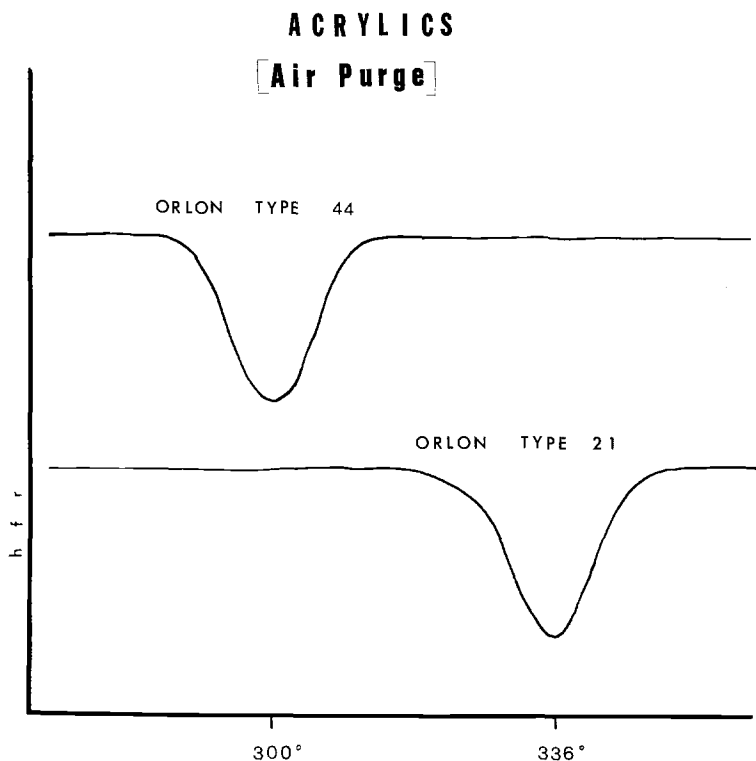


FIG. 5—DSC thermograms of orlon 44 and orlon 21 utilizing air as the purge gas.

TABLE 3—Fiber blends and mixtures.

Specimen	Calculated Percentages, wt %	Manufacturers' Specifications, wt %
Liliana	15% nylon 6 85% acetate	18% nylon 6 82% acetate
Novlan	42% nylon 66 58% wool	43% nylon 66 57% wool
Ponemal	52% vycron 2 48% rayon	50% vycron 50% rayon
Mx-36	56% nylon 66 44% acrylic	50% nylon 50% acrylic
Fabric blend (Koratron treated)	64% regular PET 36% cotton	65% PET 35% cotton

Summary

The use of differential scanning calorimetry (DSC) in the identification of synthetic fibers has been described. Results from each applicable class have been presented with an outline of criteria for differentiation and characterization; in several instances further individualization within a class has shown to be possible. Applications have also been made to the quantitative analysis of fiber blends.

MODACRYLICS

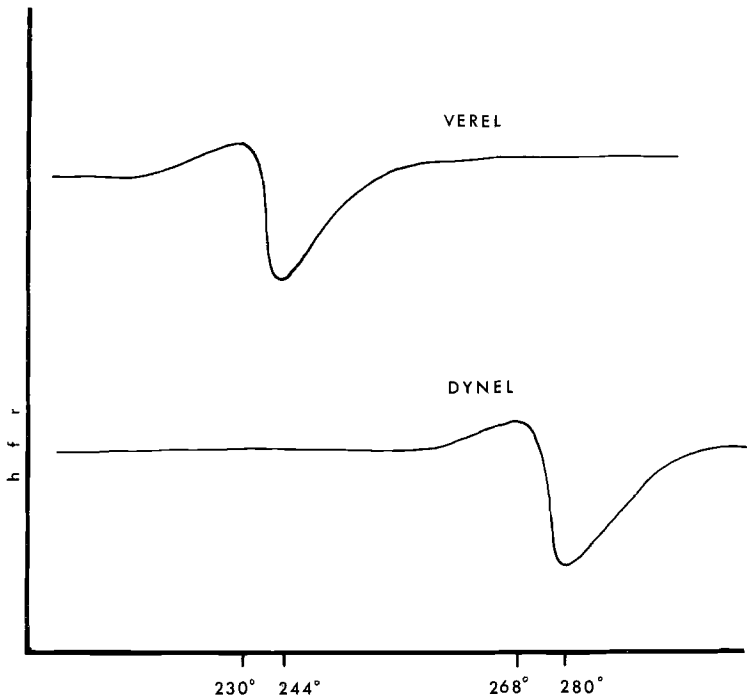


FIG. 6—DSC thermograms of Verel and Dynel.

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