

# Stress Evolution Analysis in Postforming Cooling

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## Synopsis

An interaction between heat transfer, shrinkage, and stress relaxation during postforming cooling of thermoplastic materials was studied. In order to arrive at a treatable mathematical formulation, while retaining the basic physical effects, the one-dimensional case was analyzed with the relaxation spectrum approximated by a single relaxation time depending on temperature. An effective relaxation parameter  $\beta$  controlling the postforming behavior was identified. Its dependence upon the relaxation time, rate of heat transfer, and a temperature interval was established. An analytical approximation for a maximal tensile stress was developed. This result enables an understanding of the interaction between cooling conditions and material behavior.

## INTRODUCTION

The postforming behavior is recognized as an important element of the polymer processing. Cooling of melt-spun fibers was analyzed by Bell and Edie<sup>1</sup> applying the finite-element Galerkin method. The method allowed the handling of the temperature-dependent physical and mechanical properties important for the pertinent temperature range. The analysis underlines the importance of the ambient temperature on the development of the internal stresses.

Build-up of stresses during cooling of the injection-molded specimens was studied by Titomanlio et al.<sup>2</sup> Their article suggests a model connecting the pressure history during the cooling with the stress distribution in the specimen.

Hornberger and Derries<sup>3</sup> and Siegmann et al.<sup>4</sup> studied the effect of fabricating conditions on development of the thermal stresses, and their influence on a performance of polymeric materials.

An excellent overview of the thermoforming process by Throne<sup>5</sup> provides detailed information regarding its applications, including cooling analysis.

This work originated from the numerical analysis<sup>6</sup> of the cracking of a specific thermoformed part while cooling on the mold. The plane strain model of complex geometry was developed. The coupled problem of transient heat transfer and thermal shrinkage was modeled. The development of the cracking was predicted in a portion of the part where developing tensile stresses acceded the critical stress value of the material at the processing temperature. Conclusions of the study underline the sensitivity of the cracking to competing mechanisms of stress build-up and relaxation.

The sensitivity of the phenomenon to minute changes in material composition led to our concentration on the material mechanisms involved in the process of postforming cooling. The study of the problem progressed through

a quantitative characterization of basic material mechanisms, an identification of governing parameters and, finally, a numerical simulation of the postforming cooling for a specific part. This article will concentrate on identification of basic material parameters.

### FORMULATION OF THE PROBLEM

The postforming cooling process involves complex thermal and kinematical boundary conditions. A formed part is attached on one side to the mold and has its other surface free and exposed to the ambient air.

The cooling of the part will be sensitive to the contact between the surface of the mold and plastic.<sup>5</sup> The heat transfer to the mold depends on its material properties, its thermal inertia and cooling. Since, at this interface, conduction is the main heat-transfer mechanism, the imperfections in the contact might lead to the activation of the radiation and convection as secondary mechanisms. The heat transfer to the outside air is done mostly through convection, and as such is a much slower process than the conduction to a metal mold, though this may change if the mold is made from a nonmetallic material such as epoxy/fiberglass.

Relative motion between mold surface and plastic surface can take place due to differences in a thermal expansion during cooling. As a first approximation, we will ignore this motion. However, motion of the surface exposed to the air is unrestricted.

In addition to the nonsymmetric heat-transfer and kinematic boundary conditions leading to nonuniform strain during cooling, the specific geometry of a thermoformed part can lead to a stress concentration in certain areas.

The coupling between the heat transfer and stress evolution, requires a simultaneous solution of the coupled equations:

#### Heat transfer:

$$\partial(\rho C_p T)/\partial t = \nabla(k(T)\nabla T),$$

where  $\rho$  is the density,  $C_p$  is the heat capacity,  $k$  is the thermal conductivity,  $T$  is the temperature,  $\nabla$  is the linear differential operator, and  $t$  is the time.

#### Stress evolution:

$$\nabla\sigma^T - \alpha E(T)/(1 - 2\nu)\nabla T(\mathbf{x}, t) + \nabla \int_0^t \mathbf{I}(\sigma) d\tau/\lambda_r(T) = 0 \quad (1)$$

describes stress build-up due to the shrinkage created by the cooling, and the relaxation controlled by the temperature-sensitive relaxation time  $\lambda_r$  and the appropriate component of the stress invariant  $\mathbf{I}(\sigma)$ ;  $\sigma^T$  is the transposed stress tensor,  $\alpha$  is the coefficient of thermal expansion,  $E$  is the elastic modulus, and  $\nu$  is the Poisson ratio.

Equation (1) is based upon a very simple approximation for the isothermal stress relaxation:

$$d\sigma/dt = -\mathbf{I}(\sigma)/\lambda_r(T),$$

where the relaxation time  $\lambda_r(T)$  is treated as an effective relaxation time at the temperature  $T$ .

The heat transfer boundary conditions:

$$\mathbf{n}\nabla(kT) = h_\gamma(T_\gamma - T),$$

with  $\gamma = 1, 2$  for the two surfaces,  $\mathbf{n}$  denoting the normal vector at the appropriate interface, and  $T_1$  and  $T_2$  standing for the ambient air temperature and, possibly transient, temperature of the mold at the interface with the formed part. To account for time variation of  $T_2(t)$ , it is necessary to solve simultaneously the heat transfer problem in the mold. The discussion of the associated effects on the postforming cooling can be found elsewhere.<sup>5</sup>

The appropriate initial and boundary conditions should be applied:

The heat transfer initial conditions:

$$T = T_o(\mathbf{x}),$$

where temperature distribution  $T_o(\mathbf{x})$  is determined by the preheating of the formed part,

Traction boundary condition at the free surface is given by:

$$\mathbf{T} = \mathbf{n}\sigma = 0,$$

and a "no slip" condition at the mold surface is assumed.

### ANALYSIS OF ONE-DIMENSIONAL MODEL

To arrive at a treatable mathematical formulation, the one-dimensional case was analyzed. The model can be visualized as a narrow strip of material, with the initial temperature  $T_o$ , held in adiabatic mechanical grips with one long side open and exposed to the outside environment with a constant temperature  $T_1$ .

Assuming the stress invariant  $I(\sigma) \equiv \sigma$ , the material model for the isothermal stress relaxation is approximated as

$$d\sigma/dt = -\sigma/\lambda_r,$$

and the stress Eq. (1) takes the form

$$\sigma = E\alpha(T_o - T) - \int_o^t \sigma/\lambda_r d\tau.$$

Changing the integration variable from  $\tau$  (time) to  $\theta$  (temperature):

$$\sigma = E\alpha(T_o - T) + \int_T^{T_o} \sigma/\lambda_r d\theta/\theta', \quad (2)$$

where  $\theta'$  is the time derivative of the temperature  $\theta$  (i.e., the cooling rate).

Also during the postforming, cooling temperature is initially higher than the glass transition temperature  $T_g$ ,  $T_o$  was selected as a temperature 10–15°C below  $T_g$ , where the value of the elastic modulus  $E$  reaches a plateau after the rapid build-up in the vicinity of the glass transition temperature. Figure 1

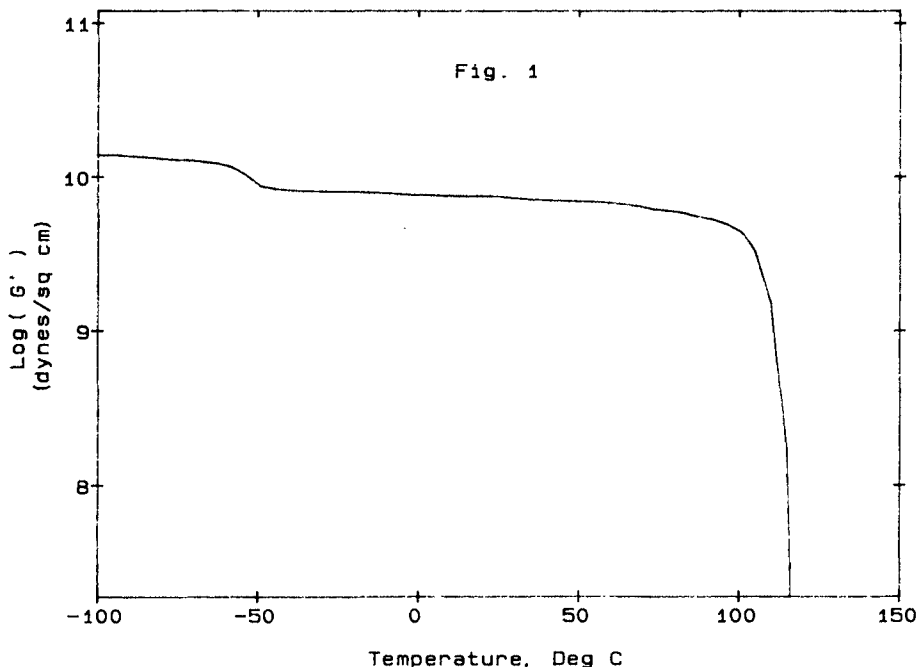


Fig. 1. Change of the elastic modulus  $G'$  with the temperature  $T$  for a rubber-modified styrene acrylonitrile polymer.

illustrates the notion, allowing us to neglect contributions to the thermal stress  $\sigma(T)$  for temperatures above  $T_g$ .

The solution of the integral Eq. (2) is presented as

$$\sigma(T) = E\alpha\phi(T) \int_T^{T_0} \{d\xi/\phi(\xi)\}, \quad \text{where } \phi(\xi) = \exp\left[-\int_\xi^{T_0} d\theta/(\theta'\lambda_r)\right].$$

For the one-dimensional case, the heat-transfer problem formulated at the center of the strip; far away from the narrow insulated sides, renders an exact solution,<sup>7</sup> which can be presented as an infinite series

$$A_n X_n \exp(-\kappa \xi_n^2 t), \quad (3)$$

where  $X_n = \cos(\xi_n x) + h/\xi_n \sin(\xi_n x)$  is the function of the coordinate  $x$  measured across the width of the narrow strip;  $\xi_n$ —the  $n$ -th solution of

$$\tan(\xi l) = 2\xi h/(\xi^2 - h^2)$$

where  $l$  being the width,  $\kappa$  standing for the diffusivity, and  $h$  for the film coefficient. The important notion is that all characteristic times

$$(\lambda_t)_n = 1/(\kappa \xi_n^2), \quad n = 1, 2, \dots$$

depend upon the dimension,  $l$ , the material properties,  $\kappa$ , and the intensity of the heat transfer at the outer edge characterized by the coefficient  $h$ .

The solution (3) is applicable for a material with temperature-independent diffusivity  $\kappa$ . The case of  $\kappa(T)$  can be reduced to this condition applying an integral transformation<sup>8</sup> to temperature and diffusivity and introducing a new variable  $\theta$ :

$$\theta = 1/\kappa_o \int_T^{T_o} \kappa(T) dT.$$

Using two first terms of the time series (3), temperature  $T$  can be expressed as

$$T = \{(T_o - T_1)\exp(-t/\lambda_t) + T_1\}. \quad (4)$$

Stress relaxation time  $\lambda_r$  can be approximated as

$$\lambda_r = \lambda_o \exp(y(T_o - T)), \quad (5)$$

where  $\lambda_o$  is the relaxation time at the temperature  $T_o$ . The sensitivity of the stress relaxation to the temperature variation can be seen in Figure 3 where  $\lambda_r(T)$  is plotted for a number of different materials.

Substituting (4) and (5) into the expression for  $\phi(\zeta)$ , we obtain

$$\phi(\zeta) = \exp \left[ -\lambda_t/\lambda_o * \int_{\zeta}^{T_o} \exp(y(\theta + T_o))/(\theta - T_1) d\theta \right] \quad (6)$$

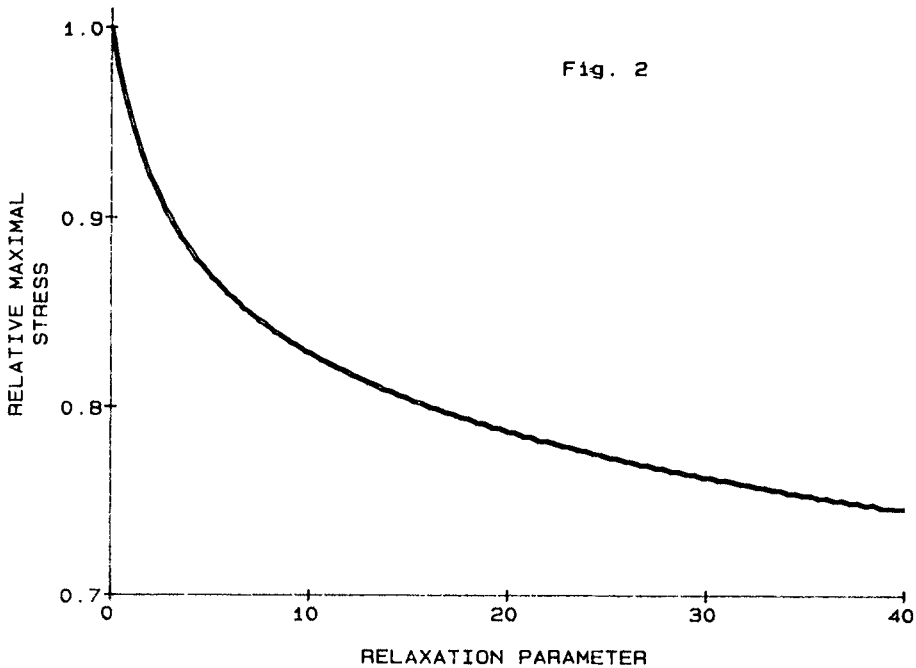


Fig. 2. Dependence of a nondimensional maximal stress on a relaxation parameter.

The singularity of kernel in (6) at  $T = T_1$  implies that

$$\phi(\zeta) = 0 \quad \text{at} \quad \zeta = T_1,$$

that is, that after an infinite time, which it takes according to (4) to reach this temperature, the stress will totally relax. Since no experiments can be conducted on such time scale, this singularity is unattainable and can be omitted. Most of the contribution to the value of the integral comes from the vicinity of  $T_o$ . Thus, the kernel can be approximated as

$$\exp(y(\theta - T_o))/(T_o - T_1).$$

The resulting expression for the stress is

$$\sigma(T) = E\alpha/y \exp[\beta Ex(T)] \int_{Ex(T)}^1 \exp(-\beta x)/x dx, \quad (7)$$

where  $Ex(T) = \exp(y(T - T_o))$ , and

$$\beta = \lambda_i/\lambda_o/[y(T_o - T_1)]$$

is the nondimensional relaxation parameter which depends on the ratio of the heat-transfer time scale and the reference stress relaxation time  $-\lambda_i/\lambda_o$ . The parameter is normalized with respect to the temperature interval multiplied by the temperature sensitivity parameter  $y$  of the stress relaxation time.

Changes of the relaxation parameter  $\beta$ , achieved by a variation of cooling conditions or by changes in a material composition, are very important for the postforming behavior as can be seen in Figure 2 where the maximal values of  $\sigma/[E\alpha(T_o - T_1)]$  are plotted for identical temperature interval ( $T_o$  and  $T_1$ ) and material parameters  $E$  and  $\alpha$ .

The integral in (7) can be presented as a difference of exponential integral functions<sup>9</sup>

$$E_1(\beta Ex(T)) - E_1(\beta)$$

and, since values of  $E_1(x)$  are tabulated, its numerical evaluation is readily available. As an alternative, it can be approximated as

$$\begin{aligned} \int_{Ex(T)}^1 \exp(-\beta x)/x dx &= y(T_o - T) - \beta(1 - \exp[y(T - T_o)]) + \dots \\ &+ (-\beta)^n/n!(1 - \exp[ny(T - T_o)])/n + \dots \quad (8) \end{aligned}$$

Also the infinite series (8), generated through the integration by parts, satisfies the Weierstrass sufficient condition for the uniform convergence of functional series:

$$\begin{aligned} ABS[a_n(T)] &= (\beta)^n/n!(1 - \exp[ny(T - T_o)])/n \\ &\leq (\beta)^n/(n!n) \rightarrow 0 @ n \rightarrow \infty, \end{aligned}$$

where  $ABS[\dots]$  stands for the absolute value of the argument.

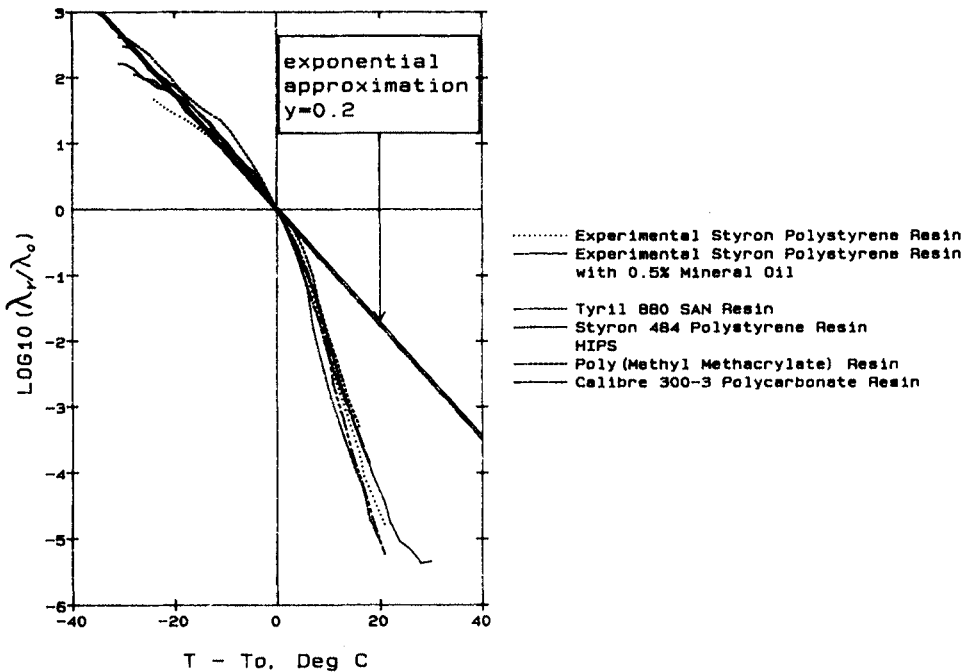


Fig. 3. Family of nondimensional relaxation times presented as a function of a temperature shifted by individual values of  $T_o$ . ("Styron" and "Calibre" are trademarks of the Dow Chemical Co.)

Expression (8) is acceptable only for  $\beta \leq 10$ . For larger values of the relaxation parameter, extremal terms of the series become too large for numerical handling.

### IDENTIFICATION OF CHARACTERISTIC MATERIAL CONSTANTS

In a follow up to the modeling of the cracking problem,<sup>6</sup> a careful analysis of material properties was conducted to identify reasons for the differences in a postforming performance for a number of rubber-modified styrene acrylonitrile polymers. It was found that value of the stress relaxation time  $\lambda_o$  varied by two decades, while the rest of the properties displayed only minor variations.

Since the relaxation parameters  $\lambda_o$  and  $y$  are not readily available below  $T_g$ , and since their interpolation from above the glass transition temperature can be misleading,<sup>5</sup> these values were obtained for different materials.

Fig. 3 shows graphs of the normalized relaxation times,  $\lambda_r(T)/\lambda_o$ , plotted versus  $T - T_o$  for a number of materials. These data were obtained using a Rheometrics 7700 Dynamic Mechanical Spectrometer. Dynamic properties for frequencies between 0.016 and 16 Hz were measured from  $T_o - 30^\circ\text{C}$  to  $T_o + 30^\circ\text{C}$  at  $2^\circ\text{C}$  increments. The ratio  $\lambda_r(T)/\lambda_o$  was obtained from the time-temperature shift factors<sup>10</sup> used to superimpose the data taken at different temperatures. Values of  $\lambda_o$  were measured in a step strain experiment at  $T_o$  on the same instrument.

TABLE I  
 Summary of Stress Relaxation Parameters:  $T_o$ , the shift temperature ( $^{\circ}\text{C}$ ),  $y$ , the temperature sensitivity ( $1/^{\circ}\text{C}$ ), and the relaxation time  $\lambda_o$  (s), at  $T = T_o$ .

Material	$T_o$	$y$	$\lambda_o$
Experimental Styron <sup>a</sup> Polystyrene Resin	95	0.2	50
Experimental Styron <sup>a</sup> Polystyrene Resin + 0.5% mineral oil	95	0.2	30
Tyrl <sup>a</sup> 880, SAN	95	0.2	1000
Styron <sup>a</sup> 484, HIPS	88	0.2	40
Poly(methyl methacrylate)	91	0.2	50
Calibre <sup>a</sup> 300-3 Polycarbonate	141	0.2	200

<sup>a</sup>Trademark of The Dow Chemical Company.

The observed similarity of the shapes for the curves in Figure 3 justifies the selection of material parameters  $T_o$ ,  $y$ , and  $\lambda_o$  for description of the temperature dependent stress relaxation.

Table I presents values of  $T_o$ ,  $y$ , and  $\lambda_o$  for six thermoplastic materials. As it was pointed out by Kubat and Rigdahl,<sup>11</sup> a single relaxation time is not sufficient for a quantitatively accurate description of the relaxation behavior. The present analysis for a one-dimensional case is intended to reveal the interrelation between material and cooling conditions and as such provides a comparative differentiation of the postforming performance of different materials. For this reason, values of  $\lambda_o$  and  $y$  are rounded off to a first digit.

The coefficient of the temperature sensitivity  $y$  is approximately constant, for the tested materials, and equal to  $0.2\ 1/^{\circ}\text{C}$ . The reference temperature  $T_o$  varies between  $88^{\circ}\text{C}$ , for Styron\* 484, HIPS, and  $141^{\circ}\text{C}$ , for Calibre\* 300-3 Polycarbonate. The value of the stress relaxation time  $\lambda_o$  varies over almost two decades, from 30 to 1000 s.

### IMPLICATIONS OF THE ANALYSIS

The obtained expression for the relaxation parameter  $\beta$

$$\beta = \lambda_t / \lambda_o / [y(T_o - T_1)]$$

includes two processing-independent material parameters:  $\lambda_o$ , the stress relaxation time at the reference temperature  $T_o$ , and  $y$ , the temperature sensitivity of the stress relaxation approximated as

$$\lambda(T) = \lambda_o \exp(y(T_o - T));$$

one processing parameter  $T_1$ , the ambient temperature, and the characteristic time of the cooling  $\lambda_t$ , which depends upon the thermal properties of the

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formed material, heat-transfer boundary conditions, and characteristic length of the part (thickness).

The obtained expression for the maximal stress

$$\sigma(T) = E\alpha/\gamma \exp[\beta Ex(T)] \int_{Ex(T)}^1 \exp(-\beta x)/x dx$$

where  $Ex(T) = \exp(\gamma(T - T_o))$ , accounts for the interaction of the competing mechanisms of the thermal stress build-up, due to the cooling, and the stress relaxation. Thus, cooling a specific part over a half of an initial cooling time will drop the stress relaxation parameter to 50%. Knowing the value of  $\beta$  for the initial cooling regime, it is possible to predict the relative change in a maximal stress using the curve in Figure 3.

The development of tensile stresses during postforming cooling can lead to failure of the part. This unacceptable development can be controlled by changes in material composition and the processing conditions.

As it follows from Table I, the examined materials demonstrate almost identical values of the temperature sensitivity  $\gamma$ . On the other hand, the values of  $\lambda_o$  demonstrate two decades of change thus providing a strong impact on the value of the relaxation parameter  $\beta$  and, consequently, on the value of the maximal tensile stress.

The values of the reference temperature  $T_o$  do demonstrate significant changes, especially in view of the fact that values of  $\lambda_o$  are measured at these temperatures.

Since values of  $\lambda_o$  and  $T_o$  are sensitive to additives,<sup>10</sup> as well as to a basic material composition, the reduction in a maximal stress can be readily achieved through the study of the sensitivity of these parameters to viable concentrations of different additives. In a course of such changes, other material properties should be taken into consideration as well.

Since parameter  $\beta$  is proportional to the value of  $\lambda_o$ , an obvious method of the stress reduction comes from a slower cooling. For example, this change can take place when the mold material is changed from aluminum to an epoxy/fiberglass composite. The dependence of the cooling time  $\lambda_t$  on the part thickness points to a sensitivity of the stress build-up to changes in a cross-sectional geometry. Variations of the thermal properties to different additives should be mentioned at last, as an additional element of the stress control.

The main qualitative result presented in this work can be summarized as follows: that postprocessing behavior of thermoplastics does not depend solely on material or processing parameters, but presents an interactive process.

Also the above mathematical treatment was developed for the thermoforming process, its applicability to other forming processes for thermoplastic materials, such as injection molding, compression molding, fiber spinning, is straightforward.

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