

STRAIN-CRYSTALLIZATION OF GUAYULE AND HEVEA RUBBERS

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ABSTRACT

A comparison was made of the room temperature strain-crystallization of naturally-occurring *cis*-1,4-polyisoprenes having varying non-rubber content. A variety of measurements were employed to assess crystallization, including stress relaxation, optical birefringence, and the infrared absorption spectrum. All methods yielded the same result: The strain required to induce crystallization is less for polyisoprenes having larger concentrations of impurities. The ability to crystallize at lower orientation presumably underlies the superior failure properties of guayule rubber and the poorer grades of natural rubber (NR) in comparison to deproteinized NR.

INTRODUCTION

Natural rubber's unusual propensity for strain-induced crystallization¹⁻⁴ was recognized almost two hundred years ago,⁵ and has been the subject of scientific inquiry ever since (for a recent review, see reference 6). A prerequisite for high levels of strain-crystallizability is steric purity of the polyisoprene backbone, which accounts for the better performance of natural in comparison to synthetic polyisoprene.^{7,8} The non-rubber components, especially the denatured proteins and other hydrocarbon-insoluble contaminants, exert an influence on the crystallization behavior, primarily affecting the rate of crystallization. For example, it has been shown that acetone extraction⁹ and deproteinization of natural rubber (DPNR)¹⁰ both reduce the isotropic crystallization rate, presumably by reducing nucleation sites. However, the degree of crystallinity attained in the absence of orientation is governed by the backbone microstructure, specifically the length of *cis*-1,4 sequences, not by the non-rubber constituents.¹¹

Most comparisons of synthetic and natural rubber, as well as studies of the effect of nucleating agents, have focussed on isotropic ("cold") crystallization. At room temperature (RT), this unoriented crystallization continues for decades ($\approx 10^9$ s).¹² Its practical importance is primarily in limiting the use of NR at low temperatures. The failure properties of polyisoprene rubber are governed by strain-induced crystallization. Crystallization of NR under strain transpires through row nucleation of lamellae, whose growth proceeds perpendicular to the strain direction.^{13,14} The latter, secondary crystallization, can be quite slow,¹⁵ and its rate is unaffected by strain.¹³ However, the row nucleation rate is greatly enhanced by orientation, effecting rapid initial crystallization.¹⁶⁻¹⁹ The time for strain-induced crystallization of NR is less than 60 ms at RT,¹⁵ which makes it difficult to compare strain-induced crystallization rates among different compounds. However, the process is expected to be sufficiently fast for any practical application.

Since the presence of impurities primarily affects crystal nucleation rather than growth,^{9,20} the degree of crystallinity and its dependence on strain (see, for example, reference 21) is of less interest in accounting for the failure properties of natural rubber. However, the minimum strain

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required for crystallization determines the stress concentration necessary to induce crystallization in the vicinity of a crack, as well as its spatial extent. Thus, this minimum strain can be expected to play a governing role in NR's failure properties.

The focus in this paper is on the strain at which orientational crystallization commences in various naturally-occurring *cis*-1,4-polyisoprenes. Our purpose is to shed light on the recent finding²² that less pure rubbers have better failure properties than cleaner or deproteinized NR, notwithstanding the smaller intrinsic flaw size of the latter.

EXPERIMENTAL

The *cis*-1,4-polyisoprenes (Table I) are identical to those used in the earlier study,²² consisting of a high purity NR (SMR-L), a lower purity grade NR (SMR-10), a deproteinized natural rubber (DPNR-S from the H. A. Astlett Co.), and an ASTM 2227 "grade 5" guayule rubber (GR) from S. F. Thames of the University of Southern Mississippi. The only compounding of the rubbers was the addition, using a two-roll mill, of an antioxidant and dicumyl peroxide. The quantity of the latter was adjusted to give the same equilibrium modulus (= 1.1 MPa at 30% elongation) for all four compounds. The rubbers were cured at 160 °C for 60 minutes in a compression mold. Thin films were cast from cyclohexane solutions containing the peroxide and antioxidant. After overnight drying, the deposited film was preheated in a pressurized mold at 80 °C for 1.5 hours, then cured at 160 °C for 1 hour. The modulus of these films was determined to be equivalent to that of the thicker, compression molded samples.

All properties were measured at room temperature. Stress-strain data (ASTM D4482 specimens) was obtained using an Instron 4206, with strains determined with a non-contacting optical extensometer. The mechanical hysteresis was calculated from the area under extension-retraction curves, obtained at a cross-head speed of 5 mm/min. Stress relaxation experiments also employed the Instron, since our interest was limited to the long time behavior.

Infrared spectroscopy was carried out on cast films, typically 30 μm in thickness. Specimens were maintained in a strained condition for 24 hours (*in vacuo* to minimize ozone degradation) before measurement, with the elongation determined from fiducial marks. Unpolarized Fourier transform infrared (FTIR) spectra were obtained using a single beam Nicolet Magna FTIR Spectrometer-750 at 1 cm^{-1} resolution. Each spectrum was averaged over 200 scans.

Birefringence measurements were also made on cast films (*ca.* 100 μm thick). These were deformed 15 minutes prior to the measurement. It was determined that within the accuracy of the measurements, this period of time gave results sufficiently close to mechanical equilibrium. The films were kept under vacuum at all times, in order to maintain optical clarity. The stress corresponding to each strain was independently measured. The birefringence (Δn) was determined

TABLE I
cis-1,4-POLYISOPRENES

| | SMR-10 | GR | SMR-L | DPNR |
|--------------------------------|--------|--------|--------|-------|
| solubles (%) | 2-3 | — | 2-3 | 2-3 |
| insolubles (%) | 3-4 | 3-4 | 3-4 | < 1 |
| dirt (%) | < 0.10 | < 0.05 | < 0.03 | 0.003 |
| ash (%) | < 0.75 | < 0.60 | < 0.50 | 0.09 |
| nitrogen (%) | < 0.60 | < 0.60 | < 0.60 | 0.08 |
| dicumyl peroxide (phr) | 2.5 | 2.9 | 2.5 | 2.8 |
| antioxidant ^a (phr) | 1 | 1 | 1 | 1 |
| modulus ^b (MPa) | 1.08 | 1.13 | 1.05 | 1.10 |
| C^c (GPa^{-1}) | 2.08 | 1.94 | 1.95 | 1.79 |

^a polymerized 2,2,4-trimethyl-1,2-dihydroquinoline

^b ratio of stress to strain at 30% extension

^c Equation (3)

from the rotation (θ) of an analyzer polarizing filter using²³⁻²⁵

$$\Delta n = \frac{\theta}{\pi} \times \frac{\lambda}{l} \quad (1)$$

where λ (= 632.8 nm) is the wavelength of the HeNe laser radiation and l is the film thickness.

RESULTS

The earlier study²² determined that these four rubbers attain equal degrees of isotropic crystallization. Their failure properties, including tensile strength, tear strength, cut growth resistance, and fatigue life, fell in the order²²

$$\text{GR} > \text{SMR-10} > \text{SMR-L} > \text{DPNR.}$$

This performance is inversely correlated with the size of the intrinsic flaw deduced from the same failure properties.²² Notwithstanding this anomaly, the issue to be addressed is the extent to which the above relative failure performance reflects differences in the rubbers' strain-induced crystallization behavior.

A variety of techniques have been developed to study strain-crystallization. Probably the most often employed is x-ray diffraction.^{21,26-30} Usually the maximum intensity of the crystalline peak is taken as a measure of the crystallinity, although this "crystallinity index" is proportional to the degree of crystallinity only if the peak breadth is constant. In fact, the latter is influenced by the size, perfection, and orientation of the crystallites.

The density change accompanying crystallization provides a means to measure its progress dilatometrically.^{7,9,20,31} A correspondence has been demonstrated between results obtained on stretched NR by x-ray diffraction and by dilatometry.³² Thermal analysis, a facile technique for isotropic crystallization studies, is less useful for oriented samples; nevertheless, a few differential thermal analysis (DTA) studies of strain-induced crystallization in rubber have been reported.^{33,34} Nuclear magnetic resonance (NMR) has been applied to the study of NR cold crystallization³⁵; however, in the presence of orientation a simple demarcation into "mobile" amorphous fractions and "immobile" crystalline domains is not possible.^{36,37}

Chain segments become elastically inactive when crystallized, which means that stress decay can be a useful probe of strain-crystallization.³⁸⁻⁴⁰ A correlation between crystallinities deduced from stress relaxation and measured dilatometrically has been demonstrated.² A comparison has also been reported of the results on NR obtained from stress relaxation measurements with those from x-ray diffraction experiments.⁴¹

In this study three techniques were employed to assess strain-crystallization: the mechanical response, the infrared absorption spectra, and the optical birefringence.

STRESS RELAXATION AND HYSTERESIS

In Figure 1 are shown representative extension-retraction curves for the SMR-10. Below *ca.* 250% strain, the resilience is quite high, as expected for unfilled compounds deformed at slow rates (about 10^{-3} s^{-1} herein). At moderate strains, mechanical hysteresis is observed, which increases to very high values (>40% in GR) at the highest strains. This hysteresis is due to crystallization.^{42,43} From measurements on the four rubbers in the manner shown for SMR-10, we obtain the results in Figure 2. The suggestion from these results is that in terms of the strain required to induce crystallization, the strain-crystallizability of the rubbers follows the order

$$\text{GR} > \text{SMR-10} > \text{SMR-L} > \text{DPNR.}$$

The energy dissipation observed in a tensile retraction experiment can also be probed using transient stress-relaxation measurements. Figure 3 illustrates stress relaxation data for the SMR-10 at various strains. Two aspects of a stress relaxation measurement reflect crystallization, the time for the stress to decay and the value of the stress associated with mechanical equilibrium. Note that at the highest strains in Figure 3, substantial stress decay continues after the initial hour of relaxation.

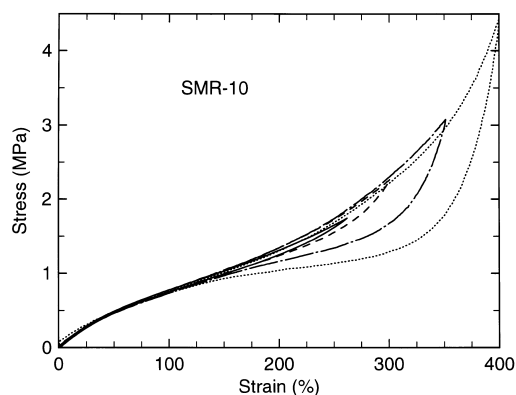


FIG. 1.—Extension of the SMR-10 to various strains, followed immediately by retraction. Each curve represents a new test specimen. The increasing magnitude of the hysteresis loop reflects the development of strain-induced crystallinity.

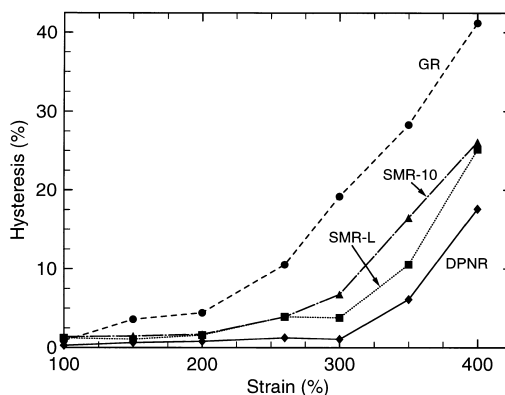


FIG. 2.—The mechanical energy dissipated relative to the total input strain energy for the four elastomers stretched to various extent. Strain crystallization at *ca.* 250% or higher results in more marked hysteresis.

In Figure 4 we plot the stress at mechanical equilibrium for the four rubbers as a function of strain. The data overlap at low strains (by design of the compounds, see Table I), while diverging at higher strains. The rank ordering of the higher strain moduli is

$$GR > SMR-10, SMR-L > DPNR.$$

Although this equilibrium stress *per se* is related to the degree of crystallinity, interpretation is difficult. Crystalline chain segments are elastically inactive, but the presence of inextensible crystallites stiffens the rubber,^{38,44} resulting in an upturn in a stress-strain curve at high extension.⁴⁵⁻⁴⁷

A better reflection of the strain-crystallization process is the time scale of the stress decay.^{2,41} While purely viscoelastic relaxation takes place at all strains, the additional decay arising from

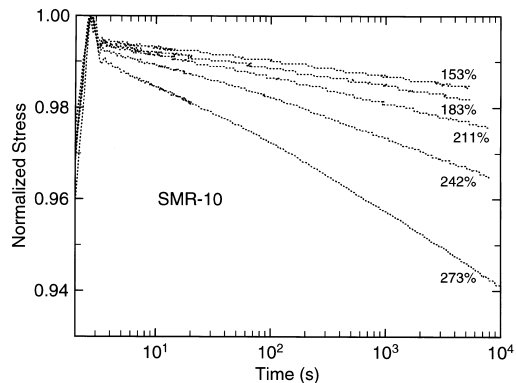


FIG. 3.—Stress measured for the SMR-10 after imposition of tensile strains of the indicated magnitude (normalized by the peak stress for clarity). The initial over-shoot is an artefact of the Instron cross-head motion. While approaching a plateau value at lower strains, the stress continues substantial decay at higher strain. This is a consequence of strain-induced crystallization.

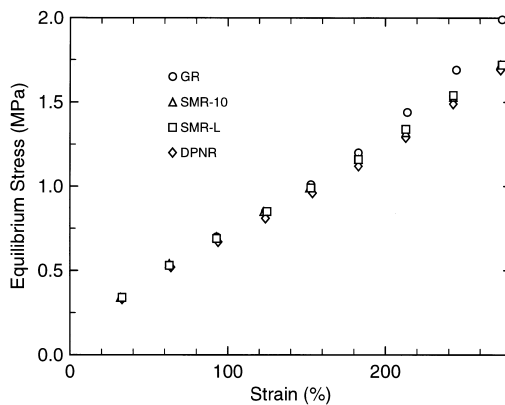


FIG. 4.—The stress measured at mechanical equilibrium for the four rubbers. At low strains the moduli are equal, by design.

the elastic inactivity of crystalline stems causes an increase in the relaxation time. This can be seen in the stress relaxation data for SMR-10 in Figure 3. In Figure 5 we plot the relaxation time (defined as the period required for stress relaxation to be >99% complete) as a function of extension for the four rubbers. From these results we conclude that their susceptibility for strain-crystallization rank as

$$\text{GR} > \text{SMR-10} > \text{SMR-L} > \text{DPNR},$$

in agreement with inferences from the hysteresis data.

INFRARED SPECTROSCOPY

Infrared measurements were carried out for each rubber over a range of strains, with a representative spectrum of unstretched SMR-10 shown in Figure 6. The arrow indicates the position of the backbone C-H out-of-plane mode. Upon crystallization this peak shifts upfield about 10 wavenumbers.⁴⁸ Thus, in semi-crystalline *cis*-1,4-polyisoprene, two peaks are observed, each specific for the amorphous or crystalline phase.

We can fit the spectrum in this region, using a Lorentzian function to describe the absorbance A of each curve^{23,49}

$$A(\omega) \propto \frac{\Delta}{\Delta^2 + (\omega - \omega_{\text{max}})^2} \quad (2)$$

where ω is frequency, and Δ and ω_{max} are respectively the half-width and central frequency of the peak. In Figure 7 this fitting is illustrated for partially crystallized SMR-10. There are also two neighboring resonances of weak intensity; these showed no systematic change with crystallization. While the intensity of the main two peaks was directly dependent on degree of crystallinity, both the frequency and breadth were essentially independent of strain, $\omega = 835.5\text{cm}^{-1}$ and $\Delta = 18.5\text{cm}^{-1}$ for the amorphous peak, and $\omega = 844.6\text{cm}^{-1}$ and $\Delta = 4.5\text{cm}^{-1}$ for the crystalline resonance.

The relative integral intensity of the crystalline band yields a measure of the degree of crystallinity. The results obtained in this manner for the four polyisoprenes at various strains are displayed in Figure 8. With respect to the strain at which significant crystallinity becomes apparent, the strain-crystallizability of the rubbers are in the order

$$\text{GR} > \text{SMR-10} > \text{SMR-L} > \text{DPNR}.$$

These results are consistent with conclusions drawn from the hysteresis and the stress relaxation experiments.

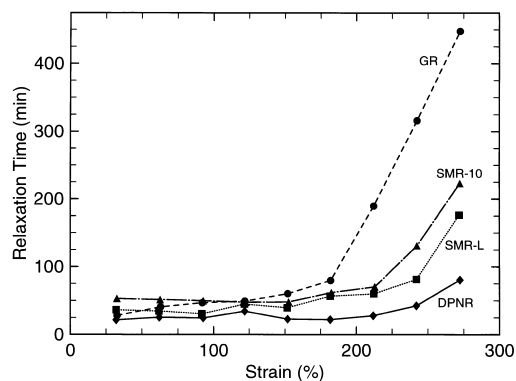


FIG. 5.—The time over which stress decay was observed for the four rubbers. Initially viscoelasticity governs the relaxation time; at higher strains crystallization commences.

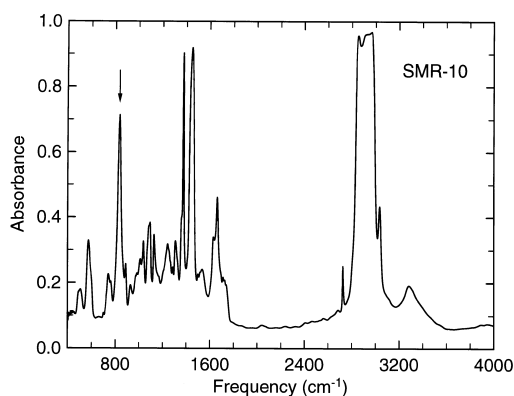


FIG. 6.—The infrared spectrum of unstretched SMR-10; the arrow denotes the crystallization-sensitive peak (backbone C-H out-of-plane bending) used in the analysis.

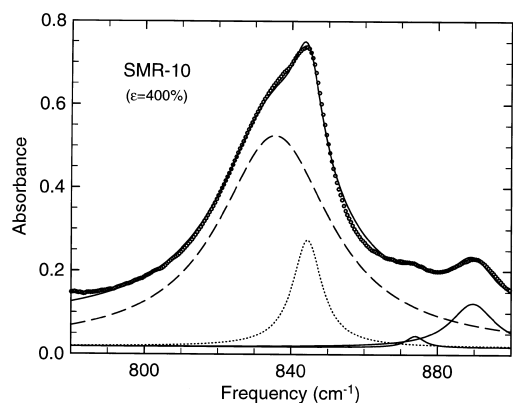


FIG. 7.—The infrared spectrum of SMR-10 stretched to 400% strain. The experimental data (o o o) is well-described by the sum (solid line) of the best-fits of Equation (2) to the amorphous and crystalline resonances (dashed and dotted lines respectively). Only the peak intensities were dependent on the degree of crystallinity. There are two minor peaks toward higher frequency, which were unaffected by crystallization.

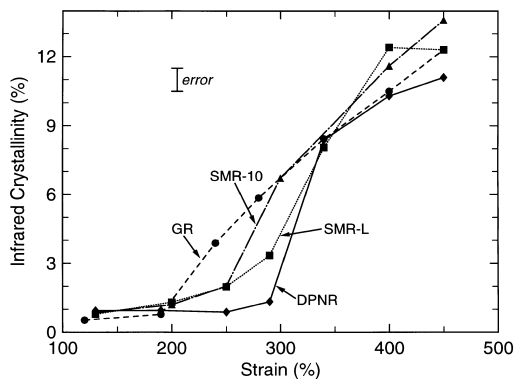


FIG. 8.—The degree of crystallinity determined from infrared spectroscopy for the four elastomers, stretched to various extent.

BIREFRINGENCE

The application of stress to rubber induces optical anisotropy, which can be described by the stress-optical law.^{23,25,50} For uniaxial deformation this has the simple form

$$\Delta n = C \times \sigma \tag{3}$$

where σ is the true stress and C the stress optical coefficient. Although Equation (3) is often regarded as generally valid for amorphous polymers,⁵⁰ exceptions to this law are known.^{28,51,52}

The birefringence was measured for the four rubbers over a range of tensile strains (Figure 9). At low strains, proportionality between Δn and the uniaxial true stress is observed, yielding

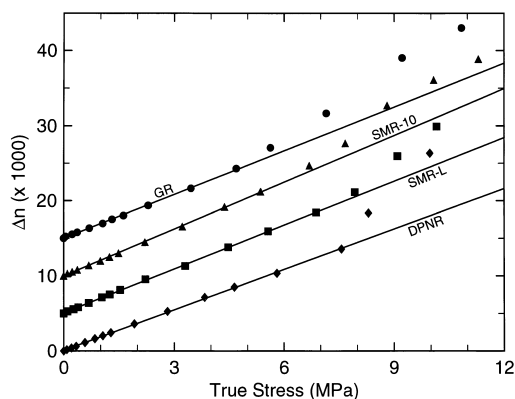


FIG. 9.—The birefringence measured for the four elastomers over a range of strains (the data has been shifted vertically for clarity). The solid lines, whose slopes correspond to the stress optical coefficient, are linear fits to the low strain data. Strain-induced crystallization gives rise to the deviations from linearity at higher stresses.

the values for the stress optical coefficient listed in Table I. There are some small differences in C for the four polyisoprenes. The value for DPNR, $C = 1.79 \text{ GPa}^{-1}$, is somewhat lower than the value of 2.0 GPa^{-1} determined previously for the same material.²⁷ At least a portion of this difference can be ascribed to differences in crosslinking; C has a weak inverse dependence on crosslink density.⁵³ The stress-optical coefficients determined for SMR-L and SMR-10 fall within the range of literature values for natural rubber.^{54,55} On the other hand, C for GR is about 18% smaller than was previously reported for an uncrosslinked guayule rubber.⁵⁶ Since guayule is not a commercial product, different samples are unlikely to be identical.

At higher stresses, the birefringence deviates from the stress-optical law due to crystallization.⁵⁵ The total birefringence is given by^{57,58}

$$\Delta n = \phi_c f_c \Delta_c + (1 - \phi_c) C \sigma + \Delta n_{\text{form}} \quad (4)$$

in which ϕ_c is the degree of crystallinity, f_c the Hermans orientation function for the crystalline domains, and Δ_c their intrinsic birefringence. The form birefringence, Δn_{form} , represents contributions to the birefringence from the interface between the crystalline and amorphous phases.

Equation (4) assumes the stress on the amorphous material equals the total stress, which is only true for low levels of crystallinity.⁵⁹ When $\phi_c \approx 0$, the form birefringence is negligible, and the degree of crystallinity is simply related to the measured birefringence⁶⁰

$$\phi_c = \frac{\Delta n - C \sigma}{f_c \Delta_c} \quad (5)$$

It is usually assumed, but not always correct,⁶¹ that strain-induced crystallization yields nearly perfectly oriented crystallites ($f_c = 1$). Since for natural rubber at room temperature, high orientation is necessary to induce crystallization (strains $> 200\%$), the assumption that $f_c = 1$ is acceptable.

We can use Equation (5) to calculate the minimum crystallinity observable *via* optical birefringence. To do this requires a value for the intrinsic birefringence of the crystals. Literature values for *cis*-1,4,-polyisoprene, which can be calculated from bond polarizabilities, span the range $0.13 \leq \Delta_c \leq 0.28$ ^{55,62}. From the data for SMR-10 in Figure 9, we note that at a true stress equal to 6.7 MPa, $\Delta n = 0.1468$. This corresponds to the first datum deviating from the stress optical law. Using the C in Table I, from Equation (5) we then calculate that $0.6\% > \phi_c > 0.3\%$ (corresponding to the range of literature values for Δ_c). Thus, optical birefringence can detect the onset of strain crystallization at levels lower than most experimental methods. This is verified herein. For example, while the data in Figures 2, 5, and 8 suggest GR strain-crystallization requires strains $\geq 200\%$, crystallization is first evident in Figure 9 at a strain of 125%.

As seen in Figure 9, the rubbers exhibit deviation from the stress optical law at different stresses, implying their relative strain-crystallizability is

$$\text{GR} > \text{SMR-10} > \text{SMR-I, DPNR.}$$

Once again, it is found that crystallinity is induced by orientation most readily in the guayule rubber, with DPNR representing the opposite extreme.

SUMMARY

A variety of experimental techniques were used to determine the onset of strain-crystallization in naturally-occurring *cis*-1,4-polyisoprenes. Although differing somewhat in details, all methods yielded the same result: guayule crystallizes at lower strains than natural rubber, and deproteinized natural rubber requires the highest strains for crystallization to be induced. Their propensity for strain-crystallization thus correlates with the relative failure properties of these rubbers.²²

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