Laser media based on coloured polyurethane

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Abstract. The advantages of a polyurethane matrix over other polymers, which are widely used as active media for dye lasers, are analysed. This matrix exhibits the photostability, service life, radiation resistance, conversion efficiency, and homogeneity of the dye distribution that surpass these properties for active media based on polyurethane acrylate, which has close physical and operation properties. These advantages result not only from the milder polymerisation conditions but also from a lower probability of the formation of ion pairs and dye aggregates. A substantial suppression of these processes in polyurethane is explained by its greater polarity and solvation ability compared to polyurethane acrylate.

Polymer laser media (PLMs) doped with organic dyes have a number of operation advantages compared to liquid media [1, 2]. However, to realise these advantages, the photophysical and photochemical properties of dyes should not degrade at least in passing from a solution to a polymer. This concerns first of all the spectral and lasing properties, photostability, and the service life of PLMs. Polymethyl methacrylate (PMMA) and its modifications [3 – 6], polyuretaneacrylate (PUA) [2, 7], and various epoxides are most widely used as polymers for dye-doped active media.

The PMMA and PUA matrices are hardened by the method of radical polymerisation. Free radicals that are present in the system induce side radical reactions involving dye molecules, which results in the destruction of the latter. Epoxy polymers are hardened in the reaction of polycondensation. However, hardeners used in these reactions possess either base or acid properties, which is unacceptable for organic compounds of many classes, because these properties cause irreversible chemical decomposition of organic molecules.

The authors of paper [10] proposed to use cross-linked polyurethane (PU) as a polymer matrix for passive laser switches (PLSs) based on dyes. Polyurethane is hardened, as epoxy polymers, upon polycondensation. However, in the first case, this reaction proceeds under mild conditions

– at room temperature and in a neutral medium – so that dyes of any classes can be added to polyurethane during its polymerisation without being decomposed (even partially).

The aim of this paper is to study the possibility of using PU as a matrix for PLMs doped with organic dyes. We examined the basic operation parameters of PLMs fabricated from PU and PUA matrices, which have similar physical properties. We found that PU is transparent within a broad spectral range from 0.32 to 2.20 μm, which virtually covers the entire spectral region where dyes are used. The short-wavelength edge of the absorption spectrum shown in Fig. 1 indicates that PU matrices can be used in PLMs pumped by standard coherent sources such as a 337-nm nitrogen laser and longer-wavelength lasers. On the other hand, PUA cannot be used in PLMs pumped in the near UV region because of its strong absorption in this region. By varying the ratio of the initial components in the PU matrix, we can fabricate a highly elastic composition with the refractive index that can be changed from 1.48 to 1.52. The levelling of the refractive indices of the polymer and an optical substrate (glass, quartz) allows us to minimise the passive loss by fabricating PLM in the form of a triplex.
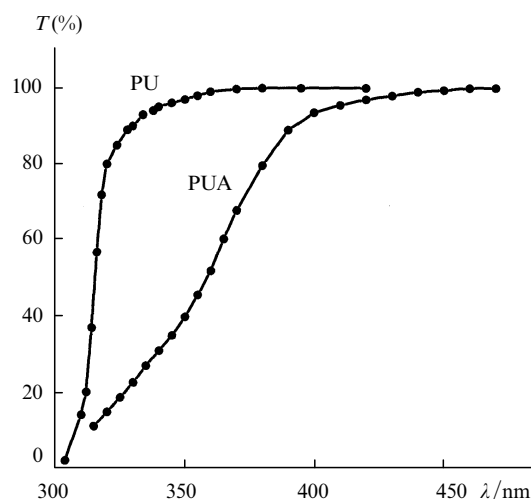
Figure 1. The short-wavelength edge of the transmission spectrum of PU and PUA matrices of thickness 1 mm.

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The radiation resistance of the PU matrix was measured at the second-harmonic wavelength of 532 nm of a single-mode Nd:YAG laser operating in a single-pulse regime. The single-pulse damage threshold E_d was 15 J cm^{-2} for a

pulse duration of 15 ns and the diameter of the irradiated area of 200 μm, which exceeds by a factor of 1.5 the threshold for PUA [2] measured under the same conditions.

Note that polymer matrices of active media experience stronger radiation and thermal loads than PLSs upon the interaction with the pump and lasing radiation. This is explained by the fact that the dye concentration used in active media is at least an order of magnitude higher than in passive media, which substantially increases the probability of their aggregation. The aggregation of dyes results in the degradation of the photostability, service life, and luminescent properties of coloured media [11]. As the dye concentration increases, the probability of formation of ion pairs also increases. In particular, the contact pairs are formed [12] in which electron phototransfer from an anion to a cation can occur [13], resulting in the formation of active neutral radicals.

PLMs require significantly higher power densities for their pumping than the power densities used for the PLS bleaching. This is explained by the fact that to obtain the efficient lasing, it is necessary to produce the level population inversion as great as possible, whereas to perform Q-switching, it is only necessary to obtain equal populations of the ground and excited levels. In addition, the energy load in PLMs is also higher than in PLSs because the radiation is absorbed at two wavelengths (pump and lasing). It is known that the radiation resistance of polymer matrices decreases with decreasing the pump wavelength [14]. The PU-based PLS fabricated by us were tested in solid-state lasers at wavelengths 694 [15], 1060, 1079 [10, 16], and 1320–1350 nm [17, 18], i.e., at substantially longer wavelengths than the wavelength $\lambda = 532$ nm used here.

Most laser polymer materials have intense absorption bands in the region of two-photon transitions for pump frequencies often used in experiments. For example, the energy of the electronic transition in a polymer with the 266-nm absorption band is equal to the absorbed energy of two 532-nm pump photons. Therefore, the degradation of PLMs upon high-power pump can be also caused by two-photon absorption.

The purposeful studies [1, 3, 4] of the mechanism of laser damage of polymer matrices showed that it is necessary to use elastic materials, which exhibit substantial elastic deformations in a broad temperature range. Thus, the introduction of low- and high-molecular additions into PMMA made it possible to obtain the high radiation resistance that satisfied the operation parameters [3, 4].

PLMs based on cross-linked PUA [2, 7, 19, 20] and especially PU studied here have highly elastic properties in a broad temperature range. Such laser elements can operate upon high-power pulsed pump without the addition of plasticisers to the polymer.

Both types of the active media, which differ by polymer matrices, were fabricated in the form of a triplex – a polymer layer contained between two substrates. The PUA elements were fabricated by the method described in papers [2, 7, 19]. The method of fabrication of PU elements is described in our papers [10, 17, 21]. We have chosen for our experiments three organic dyes from three classes of lasing dyes: rhodamine 6G (R6G) (xanthene dye), astraphloxine (HIC) (polymethine dye), and pyrromethine 597 (PM597) (pyrromethine dye).

The main operation parameters of PLMs are the operating resource N, the lasing efficiency η, and photostability. To study the photostability, we fabricated triplexes with silica substrates. The thickness of PU and PUA films doped with dyes in photostability experiments was 300 μm. The optical density D at the maximum of the main transition was about unity. Samples were irradiated by a xenon lamp, which has the continuous emission spectrum in the UV and visible regions. The radiation power density on a sample was 50 mW cm^{-2}. The dependence of the optical density of polymer samples on the incident radiation dose E was measured at the maximum of the absorption band of the dye with a Shimadzu UV-3100 spectrophotometer. Fig. 2 shows the dependences of photodissociation of dyes in polymer matrices on the irradiation energy. One can see that the photostability of dyes substantially increases in passing from PUA to PU.
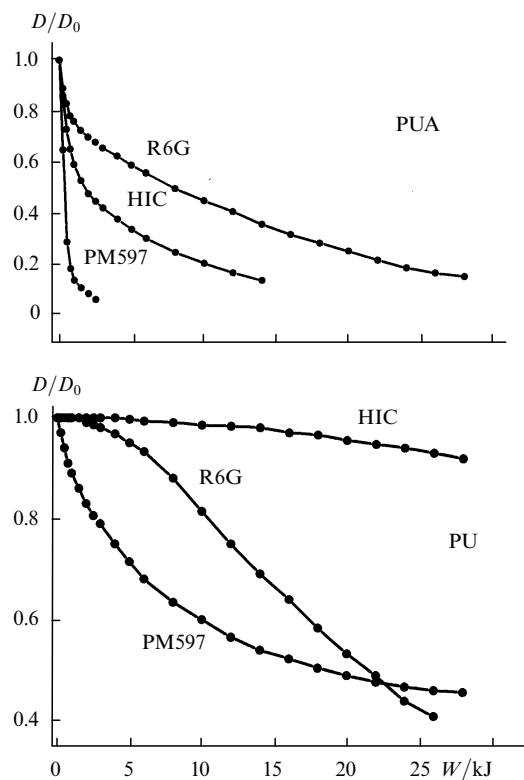
Figure 2. Dependences of the normalised optical density D/D_0 of polymer elements on the irradiation energy W for dyes R6G, HIC , PM597 in PUA and PU.

The PM 597 dye with the skeleton molecular structure proved to be unexpectedly most unstable in both polymers, whereas the HIC dye with an open polymethine chain, which is highly sensitive to photochemical reactions, was most photostable. The PM597 dye exhibited rather strong absorption in the region between 320 and 420 nm, whereas absorption of HIC in this region was very weak (Fig. 3).

Thus, we can conclude that the photochemical dissociation of the PM597 dye exposed to the UV irradiation is mainly determined by electronic transitions to higher electronic states. This circumstance should be taken into account in the synthesis of photostable dyes. The high excited electronic states of dyes can undergo nonradiative deactivation due to vibrational relaxation and internal conversion via high vibrational states of polymers with the formation of free radicals of macromolecules. Because the absorption
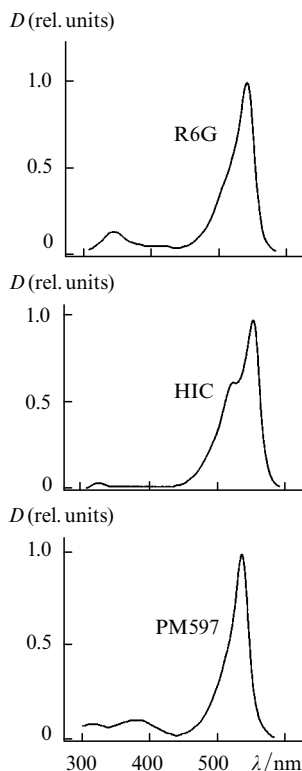
Figure 3. Absorption spectra of R6G, HIC, and PM597 in PU.

bands of dyes in the UV region are overlapped with the absorption band of PUA stronger than with that of PU (Figs 1 and 3), the probability of formation of free radicals in PUA should be higher, which is confirmed by photodissociation curves in Fig. 2.

To study the operating resource of PLMs and the conversion efficiency of the dye laser, we fabricated samples in the form of a triplex. The thickness of a coloured polymer layer placed between glass substrates was 2 mm. The optical density at the pump wavelength was $D(\lambda_p) = 5$. Lasing of PLMs was obtained in a dispersionless cavity of length 16 cm, which consisted of dielectric mirrors with reflectivities $R_1 = 99\%$ and $R_2 = 30\%$. The quasi-longitudinal pumping was used. The angle between the pump and dye laser beams was 15°. Laser elements were place near an output mirror at the Brewster angle to the laser beam. The dye was pumped by the 532-nm second harmonic of a Nd^{3+}:YAG laser operating in the multimode regime. The pump pulse energy and duration were 35 mJ and 18 ns, respectively. The pump beam was focused to a spot of diameter 1.75 mm by a lens with a focal distance of ~ 1 m. This provided the radiation power density on a polymer sample equal to 1.45 J cm^{-2}. The average pump power density was 4.35 W cm^{-2} at a pulse repetition rate of 3 Hz.

The PLM resource is known [5] to depend on the energy density and the average pump energy. To test the operation of our laser elements upon high-power pump and to obtain information on their resource, we specially applied such strict conditions. We used in our experiments thin coloured polymer layers placed between glasses.

In thick polymer layers, for example, in PMMA samples, the resource parameters substantially improve [22]. This is explained first of all by the reduction of side concentration defects and weaker heating of the polymer layer. As the dye concentration decreases, the polymer layer thickness

increases, resulting in the retention of the optimal optical density. The operating volume increases with increasing layer thickness. Therefore, the heat capacity and heat conduction of the working volume also increase. This prevents the overheating of this volume. Thus, the thickness of the PMMA layer in paper [22] was 20 – 30 mm. The high radiation resistance of both PU and PUA allowed us to perform high-power pumping of thin layers of these polymers at the same point, without scanning a pump beam over their area.

The resource dependences of the radiation conversion efficiency η on the number of pump pulses N are presented in Fig. 4. The conversion efficiency is defined as the ratio of the output energy of the dye laser to pump energy. A decrease in η for all the samples with increasing N was caused by the dye bleaching, the polymer matrix being undamaged. For the dyes studied, the operating resource in the PU matrix was greater than in the PUA matrix.
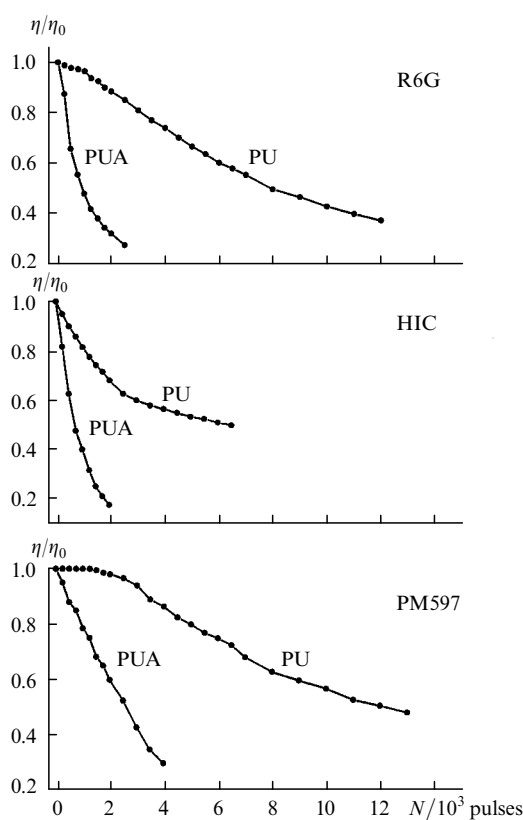

Figure 4. Normalised resource dependences of the lasing efficiency for R6G, HIC, and PM597 in PUA and PU.

The initial conversion efficiency η_0 in PU elements was higher than for PUA elements. The values of η_0 for three dyes in these polymer matrices are presented in Table 1. The dye destruction that we observed during fabrication of PUA elements [7] was later confirmed in [23], where PMMA elements were fabricated using the radical reaction of hardening with the help of benzoyl peroxide. The products of the dye destruction absorb in the lasing region.

To detect the absorption related to the dye destruction products, we examined the long-wavelength parts of the absorption spectra of PUA oligomer compositions before their hardening (left curves in Fig. 5) and after hardening (right curves in Fig. 5). We found the bathochromic shift of the
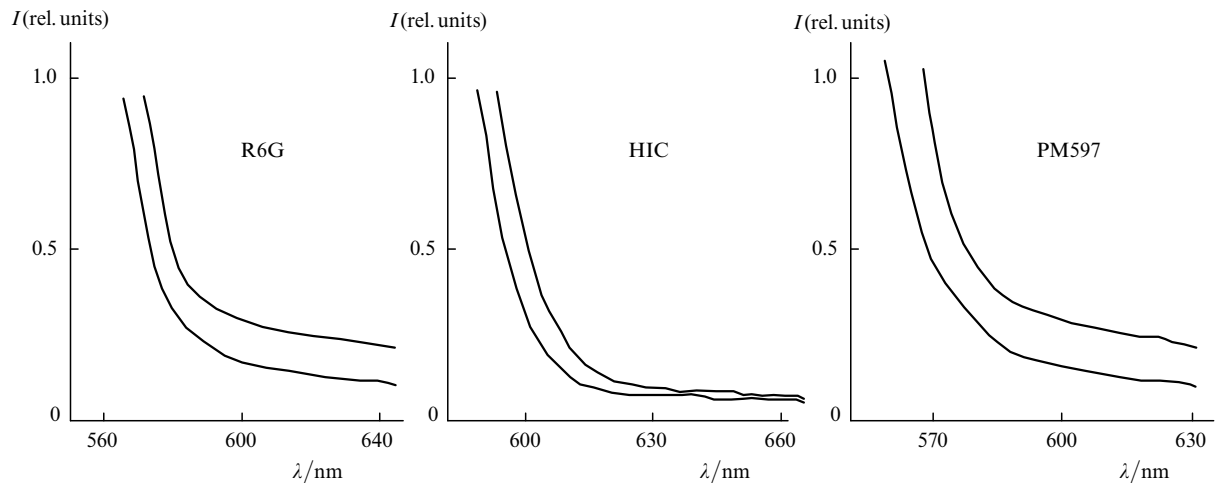
Figure 5. Long-wavelength parts of the absorption spectrum of dyes R6G, HIC, and PM597 in oligomere composites of PLMs based on PUA before (left curves) and after (right curevs) hardening.

absorption band and the additional absorption in the lasing region, which is caused by the dye decomposition products and affects the conversion efficiency η. We do not present here similar spectra for PU before and after the polymer hardening, because no variations in these spectra were observed after hardening.

The greater initial conversion efficiency η_0 in PU compared to PUA can be explained by the absence of the dye decomposition in the PU matrix during its fabrication. The HIC dye in the PUA matrix undergoes only weak destruction, which is accompanied by a weak absorption in the lasing region (see Fig. 5). This explains a small difference in η_0 for HIC in PU and PUA matrices (see Table 1).

Table 1. Basic operation parameters of PLMs.

PLM type	η_0 (%)	$N_{1/2}$	$E_{1/2}/kJ\ cm^{-2}$
R6G in PUA	29	900	8.0
R6G in PU	34	8000	23.0
HIC in PUA	30	700	2.0
HIC in PU	32	6500	160.0
PM597 in PUA	58	2200	0.3
PM597 in PU	75	12200	18.5

N o t e : $N_{1/2}$ – is the number of pulses at which η_0 decreases by half; $E_{1/2}$ is the radiation dose at which D decreases by half.

An important parameter of PLMs used for producing narrow-line lasing is the optical homogeneity of the medium, both with respect to the refractive index and the dye concentration [24]. Because during fabrication of the PUA-based PLMs by the method of photohardening, dyes are decomposed, we studied the distribution of the dye over the element thickness.

For this purpose, the oligomer composition was placed in layers between thin (0.6 mm) quartz substrates during the PLM fabrication. The thickness of an individual polymer layer was 200 μm. Thus, the PLM represented a polyplex consisting of 10 polymer layers and 11 substrates. The hardening was performed by irradiating the PLM with a LUF-4 lamp from the side of the first substrate, the irradiation time being equal to that used for the fabrication of PLMs with a single

polymer layer of thickness 2 mm. After polymerisation, the sample was divided into 10 individual polymer layers, and we measured the optical density D of each layer at the pump wavelength $\lambda_p = 532$ nm.

Fig. 6 shows the histograms of the optical density distribution in layers before and after hardening of the PM597 dye in PUA. Because the dye concentration is linearly related to the optical density, the distribution of the dye concentration in the sample with a monolayer thickness of 2 mm is similar, i.e., it is quite nonuniform. Therefore, the distribution of the dye in PLMs fabricated by the method of radical photopolymerisation is nonuniform due to the dye photodecomposition. The analysis of histograms showed that the initial amount of the R6G, HIC, and PM597 dyes in PUA decreased during radical photohardening due to their decomposition by 13 %, 6 %, and 19 %, respectively.

We found that HIC in PUA has a lower photostability than R6G (Fig. 2). In addition, the time required for the
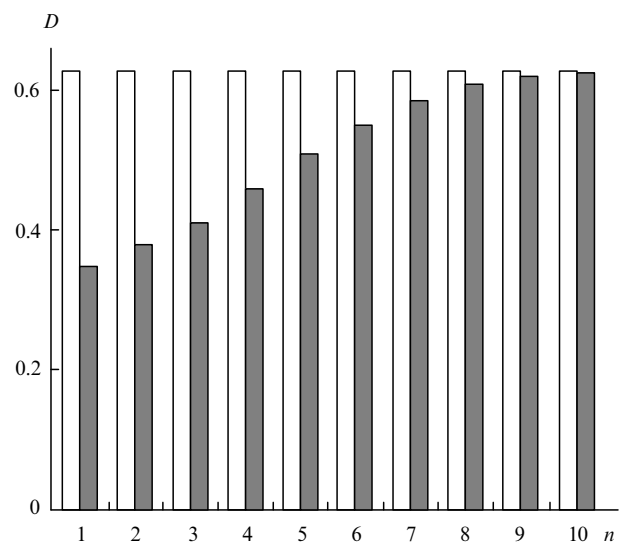
Figure 6. Distribution of the optical density of the PM597 dye in layers before (light columns) and after (hatched columns) hardening. The PLM was irradiated from the side of the first layer. Vertical bars indicate the layer boundaries; n is the layer number.

hardening of the oligomer composition with this dye is shorter by a factor of six (due to the absence of absorption of the dye in the region from 320 to 420 nm) than that for the R6G dye. This explains only a weak decomposition of HIC in PUA during the PLM fabrication and a small difference between the initial conversion efficiencies of these matrices. No destruction of the dye molecules occurs during fabrication of PU matrices, which indicated that the dye molecules are uniformly distributed in the polymer matrix.

Therefore, we can conclude that the photostability, the operating resource, the conversion efficiency, and the uniformity of the dye concentration distribution over the thickness of the PUA matrix are smaller than for the PU matrix. This is caused by a substantially greater decomposition of dyes in the former case. On the one hand, this occurs due to a partial decomposition of dyes in PUA already during polymerisation owing to the radical reaction, which favours the further activation of radical reactions upon the interaction of PLMs with light.

On the other hand, the advantage of PU is not only in the method of its polymerisation but also in its high polarity [12]. Because the permittivity of PU is higher than that of PUA, epoxides, and PMMA [12], the salt-like dyes are dissociated in PU in a greater degree than in the above-mentioned polymers. The separation of counter ions in PU is also facilitated by the presence of many highly nucleophilic functional groups in its chains.

These groups subject dye cations to the nucleophilic solvation, by producing a solvation shell around them [12]. As a result, the probability of formation of contact ion pairs in PU is much lower than in PUA, epoxides, and PMMA, and, hence, the probability of the electron phototransfer and of the association of contact ion pairs due to the electrostatic attraction of their opposite charges in PU is minimal, in contrast to the above-mentioned polymers [12].

Indeed, the replacement of the chloride anion in HIC by tetrafluoroborate, which is more nucleophilic and has a greater electron affinity, virtually does not affect the spectral, lasing, and resource parameters of dyes in PU, whereas in PUA, the absorption band slightly broadens and exhibits a hypsochromic shift, and the dye photostability increases. The dependence of these characteristics on the counter ion type indicates [12] to the formation of contact ion pairs in PUA (in contrast to PU).

Note that the PM597 dye, which is most unstable among the dyes studied, has the greatest operating resource (Fig. 4 and Table 1). This fact is another confirmation of the involvement of highly-lying excited estates of the PM597 dye in processes of its photochemical decomposition. The matter is that the resource parameters were studied upon excitation only into the main absorption band, whereas the photostability was examined upon excitation both into the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ absorption bands.

The intraion PM597 dye represents a chemically bonded contact ion pair, which cannot dissociate at any polarity of a polymer. However, the charges in this pair are well separated. In addition, because of a substantial electronegativity of fluorine atoms, the negative charge is localised at the borofluoride bridge, so that the intermolecular phototransfer of an electron from boron to nitrogen in PM597 is hindered in a greater degree than in chemically uncoupled contact pairs of cationic dyes HIC and R6G, where counter ions can either approach or move away from each other depending on the polarity and solvation ability of the medium.

As a result, the PM597 dye has a greater operating resource in PU and PUA than HIC and R6G. As in salt-like cationic dyes, the electrostatic attraction between the opposite charges of the intraion PM597 dye can favour the formation of aggregates. For the reasons considered above, these processes in PU are much less probable than in PUA. This circumstance in a combination with mild polymerisation provides the better resource characteristics of PM597, HIC, and R6G in PU.

Therefore, PU is a promising material both for PLSs and PLMs based on organic dyes. Unlike other polymers, doping of PU with dyes of any classes is not accompanied by their decomposition. According to criteria formulated for coloured polymer laser media in review [11], PLMs based on PU have a great potential for improvement of photochemical, resource, and lasing parameters by optimising coloured matrices.

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