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Influence of spoliation in poly(2-hydroxy ethyl methacrylate) soft contact lens on its free volume and optical transparency

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Abstract The calcification in poly(2-hydroxy ethyl methacrylate) contact lens was investigated using positron annihilation spectroscopy (PLS). The two poly(2-hydroxy ethyl methacrylate) (PHEMA) lenses of different companies were calcified employing a simple mechanism of calcification in abiotic aqueous solutions. The calcium deposit was analyzed using energy dispersive X-ray spectroscopy (EDS). Calcified lenses showed decrease in *ortho*-positronium (*o*-Ps) lifetime and free volume hole size of the lens material suggesting diffusion of Ca^{2+} into these cavities. The change in optical property viz. refractive index of these calcified lenses were measured and correlated with positron results. To find a better correlation, a series of worn spoilt PHEMA lenses of the same power with mainly calcium deposits, were similarly characterized using PLS and refractive index. These results correlate well with the free volume of the material. For hydrophilic lenses this correlation is reported for the first time.

1 Introduction

Spoliation of hydrophilic soft contact lenses has been extensively investigated over the past three decades. Under the influence of a complex array of causative factors, the lens materials allow deposition of proteins, lipids, and mineral components of the tear film, leading to deposits that may differ greatly in their morphology and composition [1]. Deposition of calcium salts is a common and significant factor in the spoliation of hydrophilic contact lenses. Calcium deposits have been found and reported in a variety of hydrophilic contact lenses and intraocular lenses [2, 3 and references therein]. The path way for these varied deposits to occur, are the open spaces or voids present in the lens system. Polymer scientists use the nomenclature for these open spaces as free volume holes or cells. The free volume holes evolve due to the molecular architecture of the polymer system and are of nanometer size. Chirila et al. [4] have demonstrated the propensity of heterogeneous poly(2-hydroxy ethyl methacrylate) (PHEMA) hydrogels to calcify by simple incubation in a metastable calcium phosphate solution, in the absence of any organic and biological components. It follows that the onset of calcification in biomaterials is independent of the physiological microenvironment and biological factors but mainly depends on the microstructure, in particular the free volume content of the materials. It is known that calcium or other deposits like lipids, protein are associated with the loss of optical transparency of these lens materials. The particular optical property of interest viz. the refractive index what we are concerned with lens materials is related to the polarizability of the material and therefore understanding the calcification process at the molecular level and how it influences this optical property becomes foremost important in the design and application of soft contact lens materials. Though there are a number of studies on the spoliation in soft lens hydrogels [1–3 and references there in], we found no attempt has been made to connect the open spaces or free volume cells present in these biomaterials which facilitate diffusion of essential fluids or molecules like water, oxygen, etc. also helps deposit formation which results to change in its optical property viz. refractive index.

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In the present work, we have made an attempt in this direction. Though this may not be a conclusive study, this provides an incentive for further research on this aspect. For this, we have carried out an experiment similar to that of Chirila et al. [5] employing a simple mechanism of calcification in abiotic aqueous solutions for soft contact lens materials namely PHEMA. Since our interest is to connect changes in free volume hole sizes and their numbers following calcification, to the optical property viz. the refractive index of the contact lens material, our studies are directed to measure the free volume fractions and the refractive index of the lens system upon calcification. So we have used in this study two new and unworn PHEMA lenses of two different companies and eight worn (deposited-spoilt) PHEMA lenses. To characterize free volume parameter, we have used positron annihilation spectroscopy (PLS) since it is one of the most sophisticated tool available for determining directly the average free volume size and their relative number density (concentration) in polymers [2, 6–10]. This technique has proved to be very useful in studies like sorption of water [9], glucose [10] and sodium chloride [11] in contact lens polymers, miscibility properties of blends [12], structural characterization of gels [13], etc. To evaluate the changes in optical property of the calcified lenses, refractive index measurements have been carried out using the conventional method of Brewster's angle. To supplement these results, we have used energy dispersive X-ray spectroscopy (EDS) using LEICA S 440I scanning electron microscope equipped with an Oxford EDX attachment to ascertain the presence of calcium deposits through elemental analysis.

2 Materials and methods

2.1 Sample details

For calcification experiment, two new and unworn continuous wear contact lenses of two different companies were procured from commercial sources. One is Soflens (Polymacon) by Bausch & Lomb eye care Pte. Ltd. and another is Super Soft by Silklens Pte. Ltd. The monomer is PHEMA in both the lenses and also they are of the same power (–4.75). We have also collected a series of worn (used-spoilt) PHEMA lenses (Bausch & Lomb eye care Pte. Ltd.), all of which prescribed for the same power (–4.75). Positron lifetime and refractive index measurements were carried out for these spoilt lenses.

2.2 Calcification experiment

For calcification, as described in Ref. [5], solutions of $CaCl_2$ (2.57×10^{-3} mol L^{-1}) and Na_3PO_4 (1.54×10^{-3} mol L^{-1}) were separately prepared. After adjustment of the pH to 8 with 0.1 N HCl in each of these solutions, equal volumes of each were mixed to result in a metastable calcifying medium with a ratio $[Ca^{2+}]/[PO_4^{3-}] = 1.67$ (as in hydroxyapatite) and pH 7.3. The above-mentioned unworn two PHEMA lenses were immersed in vials containing calcifying media and incubated in a shaker at 150 cycles/min for 2 weeks. When examined after 2 weeks, both lenses presented deposits in the form of white spots which could be clearly seen. The EDS scans were taken for these two lenses before and after calcification experiment. Positron lifetime and refractive index measurements were carried out for these lenses before and after calcification.

2.3 Positron lifetime measurements (PLS)

Before we describe the positron lifetime data acquisition, we briefly outline the positron method. The basis of PLS involves injection of positrons from a radioactive source (namely Na-22) into the material under study in which they thermalized and annihilate with the electrons of the medium. A positron can annihilate from different states in a medium. In molecular media like polymers, it can form a bound state depending on the relative spin of the positron and the electron. The *para*-positronium (*p*-Ps) with spins antiparallel has a lifetime of 125 ps and it annihilates with the emission of two γ photons. The *ortho*-positronium (*o*-Ps), with parallel spins has a longer lifetime and annihilates in free space into three γ photons with a lifetime of 140 ns. In polymers, *o*-Ps annihilates predominantly via a fast channel, called pick-off quenching, in which the positron of *o*-Ps annihilates with an outside electron having opposite spin by two γ photon emission. Through this its lifetime gets reduced to a few nanoseconds and therefore *o*-Ps pick-off lifetime is a measurable parameter which depends on the overlap of the Ps wave function with the wave function of the electrons of the medium. The *o*-Ps gets localized in free volume holes or cavities like positrons localize in defects before annihilation. So, its lifetime is a measure of the free volume cavity size and *o*-Ps intensity is a measure of relative number of such cavities. The formation of *o*-Ps and its yield in polymers or biopolymers is determined by the positron lifetime measurement, attributing the long-lived component to the *o*-Ps decay, which provides information on the free volume holes in the polymer matrix [6].

Positron lifetime measurements were carried out using a standard fast–fast coincidence system with conically shaped BaF_2 scintillators, coupled to photomultiplier tubes of type XP2020/Q with quartz window as detectors. The coincidence lifetime spectrometer has a time resolution of 220 ps. The details of the experiment can be found elsewhere [6, 12]. Typical spectrum accumulation time was 2 h with a 17 μCi Na^{22} positron source, which provided good counting statistics with more than 10^6 counts under each spectrum. The lifetime spectra so acquired were analyzed into three lifetime components using PATFIT-88 computer program [14], resulting in better χ^2 values and standard deviations.

2.4 Energy dispersive X-ray spectroscopic (EDS) measurements

To identify the elemental composition of the calcified lenses (Soflens and Silklens), approximately 1 mm^3 of each lens, taken from dense white spot region was air dried before subjected to EDS measurements. Their virgin samples were also subjected to EDS study in the same way for comparison. The EDS measurements for the samples were done using the LEICA S 440I scanning electron microscope equipped with an Oxford EDX attachment.

2.5 Refractive index measurements

The refractive indices of the new PHEMA lenses (Polymacon & Super Soft lens) were measured before and after calcification, by Brewster's angle method. Helium–Neon red laser light of wavelength 632.8 nm was used as the source. Several trials of measurements were carried with an accuracy of 0.001 and the average values are reported in Table 1. A similar method was followed in measuring the refractive indices of worn spoilt lenses and the results reported in Table 2.

3 Results and discussion

3.1 EDS results

From the EDS chemical analysis of Polymacon lens material, the formation of calcium (2.03%) (Fig. 1b) could be clearly seen. The silicon in both untreated (Fig. 1) and treated (Fig. 2) is the impurity which is a common observation. In the calcified Polymacon (Fig. 2), the traces of Na and Cl may be attributed to the calcifying medium containing these ions. The low intensity of phosphorus indicates that a small amount of calcium is present in the form of hydroxyapatite. A similar observation was made even in the case of Super Soft lens. Here also untreated Super Soft lens showed no calcium trace and the calcinated Super Soft lens indicated slightly less calcium content (1.30% of Ca) compared to Polymacon.

3.2 PLS results

All the measured positron lifetime spectra were resolved into three lifetime components τ_1, τ_2, and τ_3 with intensities I_1, I_2, and I_3, respectively. Generally, the attribution of these lifetime components is as follows: The shortest lifetime component τ_1 with intensity I_1 is attributed to *p*-Ps and free positron annihilations. The intermediate lifetime component τ_2 with intensity I_2 is usually considered as due to annihilation of positrons trapped at the defects present in the crystalline regions or at the crystalline–amorphous interface regions of the medium. The longest-lived component τ_3 with intensity I_3 is due to pick-off annihilation of the *o*-Ps in the free volume sites present mainly in the amorphous regions of the polymer matrix. A simple relation developed by Nakanishi et al. [7] relates *o*-Ps lifetime τ_3 to the free volume hole size, which is based on the quantum mechanical model of Tao [15] and Eldrup et al. [16]. In this model, positronium atom is assumed to be localized in a spherical potential well having an infinite potential barrier of radius R_0 with an electron layer in the region $R < r < R_0$. As per this, the relation between τ_3 and the free volume hole or cavity radius R is given by

$$(\tau_3)^{-1} = 2\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right] \text{n s}^{-1} \tag{1}$$

where $R_0 = R + \delta R$ and δR is a fitting parameter. By fitting Eq. 1 with τ_3 values for known hole sizes in porous materials like zeolites and other molecular media, a value of $\delta R = 0.1657$ nm was obtained. It has been verified that this value of δR also holds good for the present lifetime value for the present lens materials. Hence, with this value of δR, the free volume radius R has been calculated from

Table 1 Positron and refractive index results of Polymacon (Soflens) and Super Soft lens before and after calcification

Contact lens sample		o-Ps lifetime τ_3, (ns)	o-Ps intensity, I_3 (%)	Free volume hole radius, R (nm)	Free volume hole size, $V_f \times 10^{-3}$ (nm^3)	Fractional free volume, F_v (%)	Refractive index, n
Polymacon (B & L)	Untreated	1.98	13.9	0.283	95.2	2.43	1.430
	Calcified	1.85	6.7	0.270	83.2	1.00	1.465
Super Soft (Silklens)	Untreated	1.96	9.8	0.281	93.2	1.64	1.434
	Calcified	1.88	7.6	0.273	85.8	1.17	1.460

Table 2 Positron and refractive index results of worn spoilt PHEMA lenses

Lens no.	o-Ps lifetime, τ_3 (ns)	o-Ps intensity, I_3 (%)	Free volume hole radius, R (nm)	Free volume hole size, $V_f \times 10^{-3}$ (nm^3)	Fractional free volume, F_v (%)	Refractive index, n
1(New)	1.98	13.9	0.283	95.2	2.38	1.430
2	1.96	10.0	0.281	93.2	1.68	1.435
3	1.93	9.9	0.279	90.4	1.61	1.443
4	1.92	10.8	0.278	89.5	1.74	1.445
5	1.91	10.4	0.277	88.5	1.66	1.448
6	1.91	9.9	0.277	88.5	1.58	1.448
7	1.91	10.2	0.277	88.5	1.62	1.448
8	1.90	10.8	0.276	87.7	1.70	1.450
9	1.89	12.0	0.275	86.8	1.87	1.453

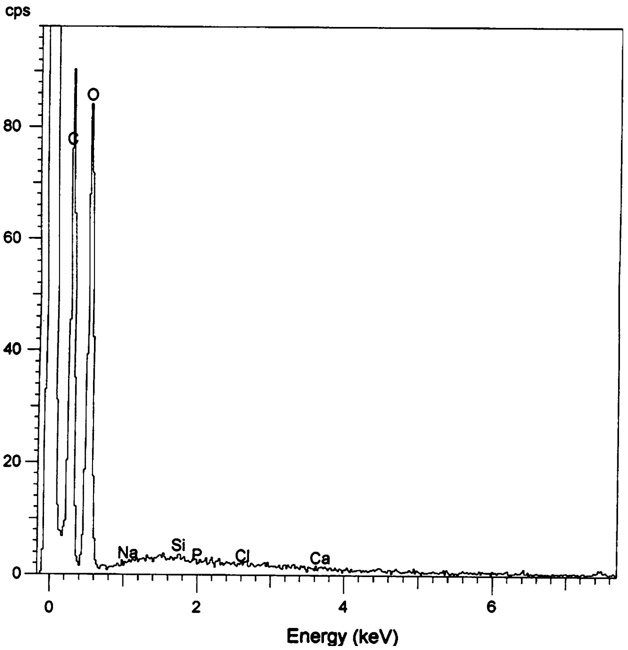

Fig. 1 EDS plot of new unworn virgin Polymacon. calcium peak is absent

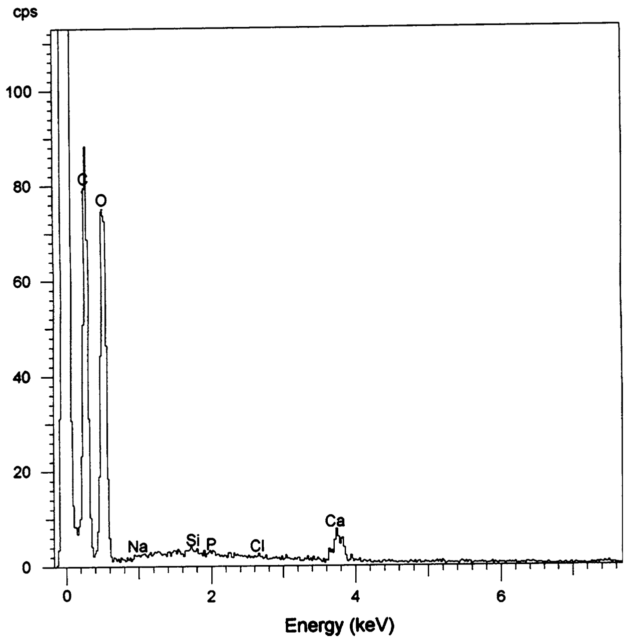

Fig. 2 EDS plot of calcified Polymacon. Calcium peak is present

Eq. 1, and the average size of the free volume holes V_f is evaluated as

$$V_f = \frac{4}{3}\pi R^3 \tag{2}$$

The fractional free volume or the free volume content (F_v) can then be estimated as

$$F_v = CV_f I_3 \tag{3}$$

where C is a constant whose value is taken as 1.8 nm^{-3} and V_f and I_3 are the parameters described above. The free volume data so derived is tabulated in Table 1.

From the Table 1, we observe that *o*-Ps lifetime τ_3 decreases after calcification and hence the average free volume hole size V_f from untreated to that of treated lenses. This suggests that the diffused calcium seems to be localized in the free volume cavities present in the lens material since PLS indicates changes mainly in the bulk of the system [2]. The Ca^{2+} ion, which has an atomic radius of ~0.1 nm can very well fit into the free volume cavities of the lenses having larger radius (Table 1). The Ca^{2+} ions, once they localize themselves in free volume holes, seem to repel positrons following their like charge and thus reduce the *o*-Ps formation probability, suggesting a decrease in *o*-Ps intensity (I_3). This is what we observe after calcification (Table 1) [2]. The difference in calcium content of Super Soft lens (1.30%) and Polymacon (2.03%) is very well reflected in all the positron parameters. For example, the average free volume hole size in Super Soft lens decreased by only 7.4 × 10^{-3} nm^3 in case of Silklens while in that of Polymacon, it is reduced by 12 × 10^{-3} nm^3, corresponding to *o*-Ps lifetime decrease of 80 ps in Super Soft lens and 130 ps in Polymacon. The decrease in *o*-Ps intensity, which is a measure of free volume hole number density, is about 2.2% in Super Soft lens but it is 7.2% in Polymacon. Though the monomer PHEMA is the same in both the lenses, the deposit formation depends on the method of preparation of the lens (evolution of free volume) and even these small changes in the microstructure are well reflected in positron data, suggesting its versatility and sensitivity.

3.3 Refractive index results

Now, let us consider the changes in refractive index as we see from Table 1. We see an increase in refractive index (n) in both the calcified lenses compared to their respective virgin (untreated) lenses. On the other hand, the change in τ_3 is exactly opposite to change in refractive index. In a recent study on sodium chloride [11] diffusion in fluorosilicone acrylate (FP92) a rigid gas permeable lens, we observe a similar change, i.e., as τ_3 decreases refractive index increases. This provides the base to connect the optical property to molecular orientation and molecular architecture to the free volume of the lens material. The possible interpretation to this is as follows: as the calcium gets into the free volume cavities of the lens material, this brings about orientational change of the molecules or group of molecules at the site of adhesion. That is to say the polarizability of the medium gets altered which in turn changes the refractive index of the material according to Lorenz–Lorentz equation. This change in polarizability is indicated by the change in *o*-Ps lifetime since free volume changes due to change in molecular orientation. It is a known fact that polarizability is the relative tendency of the electron cloud of an atom or a molecule to be distorted from its normal shape by an external field, which may be caused by the presence of nearby ion or a dipole. In other words, polarizability, which depends on particle orientation, shape and size, is a measure of the response of the electron density distribution to nearby ions or dipoles. It is well established that PLS is the best and sensitive probe of electron density distribution in a system of study [6] and even a very small change in polarizability gets reflected in positron parameters.

Therefore we propose that in the absence of theoretical models to connect free volume which is the result of molecular orientation and architecture of the system and the refractive index, the most important optical property of the lens material, the experimental data could be used to find empirical correlation between these two important parameters.

To strengthen our hypothesis, we chose to collect a series of worn (used-spoilt) PHEMA lenses and carried out Positron and refractive index measurements, the results of which are tabulated in Table 2. We observed discrete white spots in all these lenses which could be calcium deposit which is major factor for spoliation of all these lenses. Other deposits like sodium, lipid, protein and even glucose if worn by a diabetic are possible in these lenses.

The variation of refractive index n and the *o*-Ps lifetime τ_3 in the spoilt lenses is plotted and shown in Fig. 3. Now by using Lorenz–Lorentz equation, the molar refraction defined through this equation can be calculated from the measured n values [17–19],

$$\left(\frac{n^2-1}{n^2+2}\right)\frac{M_0}{\rho}=\frac{N_\mathrm{A}\alpha}{3\varepsilon_0}=R_\mathrm{L} \tag{4}$$

where M_0 is the molecular weight of the polymer repeat unit, ρ the density, N_A the Avogadro's number, ε_0 the permittivity of free space and α is the polarizability. The parameter R_L is a direct measure of polarizability of the molecules. To connect this to the measured *o*-Ps lifetime τ_3 (Table 2), we make use of the relation for the cross-section for *o*-Ps quenching $\langle\sigma v\rangle_\mathrm{av}$ which depends on τ_3 as shown below.

The *o*-Ps annihilation rate is given by [20]

$$\lambda_3=(\tau_3)^{-1}=N\langle\sigma v\rangle_\mathrm{av} \tag{5}$$

$N = (\rho N_\mathrm{A})/M_0$, is the number of molecules per unit volume, where ρ is the density, M_0 the molecular weight and N_A, Avogadro's number. σ is the cross-section for pick-off quenching and v is the velocity of *o*-Ps atom. $\langle\sigma v\rangle_\mathrm{av}$ denotes the mean value obtained by averaging over the velocity distribution of the *o*-Ps atoms relative to the molecules of the medium in which it annihilates.

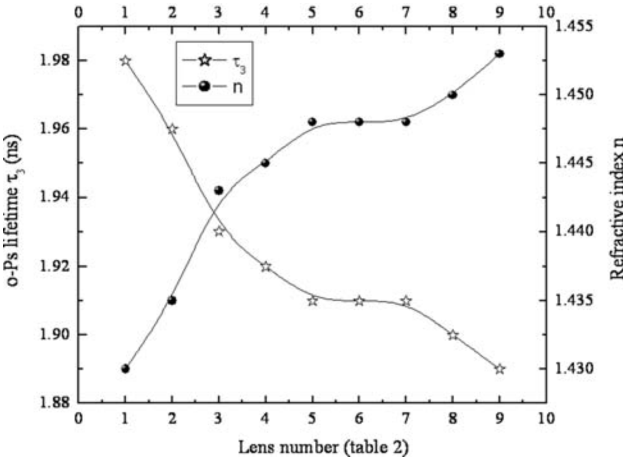

Fig. 3 Variation of refractive index n and *o*-Ps lifetime τ_3 for spoilt lenses (solid line is to guide the eye)

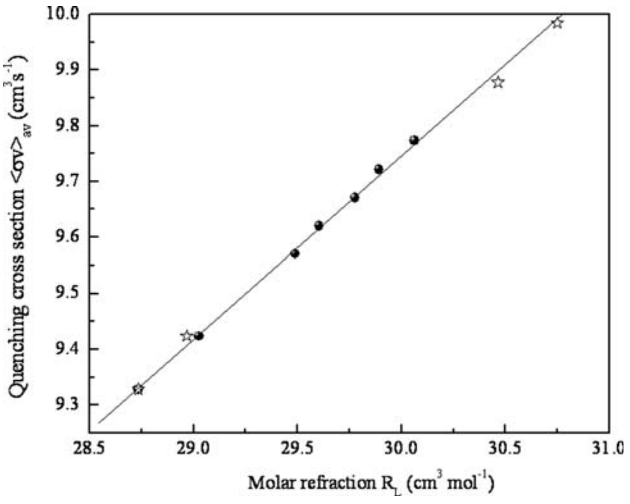

Fig. 4 Variation of quenching cross-section $<\sigma v>_{av}$ as a function of molar refraction R_L (solid line is linear regression fit). Closed circles, worn spoilt lens readings; open stars, new unworn virgin and calcified lenses

$$\langle \sigma v \rangle_{av} = \left(\frac{M_0}{\rho N_A} \right) \left(\frac{1}{\tau_3} \right) \text{cm}^3\,\text{s}^{-1} \tag{6}$$

$\langle \sigma v \rangle_{av}$ for different values of τ_3 are then calculated and is plotted against R_L and shown in Fig. (4). Evidently $\langle \sigma v \rangle_{av}$ varies linearly with R_L and first-order linear regression describes the data very well:

$$\langle \sigma v \rangle_{av} = 0.3342 R_L - 0.2786 \quad (R^2 = 0.99; \text{ and shown as solid line in Fig. 2}) \tag{7}$$

Using Eq. 7, we have calculated refractive indices of unworn Polymacon and Super Soft lens (before and after calcification), using measured τ_3 values. These calculated values are in very good agreement with the measured values and they are shown as open squares in Fig. (4). Therefore a direct correlation between polarizability and the free volume of soft lens material is found from this study. By this we conclude that free volume measurements do indicate small changes in polarizability of the material particularly contact lenses and thereby the changes in n.

4 Conclusions

Measured *o*-Ps lifetime τ_3 decreases in calcified PHEMA lenses suggesting that the diffused calcium ions are localized in the free volume cells present in the lens material. These ions repel positrons following their like charge and thus reduce the *o*-Ps formation probability, i.e., I_3 decreases from 13.9% to 6.7%. Similar changes in lifetime and intensity are observed in case of eight spoilt PHEMA lenses. A direct correlation between refractive index and the free volume of soft lens material is found from this study. Also free volume measurements do indicate the small changes in polarizability of the material particularly contact lenses and thereby the changes in n. Based on this we conclude in conjunction with our earlier study on glucose sorption in RGP contact lens, that lens spoliation from different specie changes the molecular orientation and hence microstructural architecture of the material that affects its optical transparency. Few more studies of this kind would provide means to improve the making of lens materials.

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