

Relationship between fracture toughness and temperature in epoxy coatings^{*)}

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Abstract: The fracture toughness K_{IC} of nine kinds of epoxy coating specimens was tested in the temperature range from 20 to -40 °C, and the influence of temperature on K_{IC} was discussed. The results showed that K_{IC} decreases sharply in unmodified systems but increases for some specimens with 20–50 portions of rubber impact modifier. The elastic modulus test indicated that K_{IC} is closely related with the modulus. Scanning Electron Microscopy images showed that the introduction of impact modifier to epoxy can enlarge the ductile deformation of the fracture surface. As a result, the addition of rubber modifier is a suitable path to improve the anti-cracking performance of epoxy coatings at low temperature due to an increase of fracture toughness and reduction of elastic modulus, which thus can reduce the thermal stress in the process of cooling.

Keyword: epoxy resin, fracture toughness.

Odporność powłok epoksydowych na kruche pękanie w funkcji temperatury

Streszczenie: Zbadano odporność na kruche pękanie (K_{IC}) dziewięciu rodzajów powłok epoksydowych w zakresie temperatury -40–20 °C. Wyniki badań wskazują, że wartość K_{IC} powłok epoksydowych bez udziału modyfikatora (polimeru uretanowego DESMOCAP 11) zmniejsza się gwałtownie wraz z obniżeniem temperatury. Dodatek modyfikatora, w ilości 20–50 g/100 g żywicy, zwiększa odporność powłok na kruche pękanie. Na podstawie analizy SEM stwierdzono, że wprowadzenie do żywicy epoksydowej modyfikatora DESMOCAP 11 powoduje zmniejszenie deformacji plastycznej powierzchni powłoki podanej uderzeniu. Wykazano też, że obecność modyfikatora powoduje zmniejszenie wartości modułu Younga i wpływa korzystnie na odporność powłok epoksydowych na naprężenie termiczne związane z procesem chłodzenia.

Słowa kluczowe: żywica epoksydowa, kruche pękanie.

In recent years, epoxy resin coatings have emerged as a general method for concrete surface repair and reinforcement in hydropower engineering buildings due to their excellent mechanical performance, adhesive reliability and longterm water tolerance. To achieve the protection purpose for concrete from damage such as corrosion, carbonization, erosion and abrasion, *etc.*, the thickness of the coating layer is usually about 2 mm in practical applications. An important issue are coating cracks caused by high inner stress, which are induced by temperature variations and the difference of linear expansion coefficients between the coating and concrete body. Therefore, for the safety of repair projects, the toughening treatment of the materials is crucial for epoxy coatings.

The main toughening methods for epoxy resins include rubber toughening, thermoplastic resin toughening, the addition of rigid inorganic nanoparticles or minute particle toughening. Rubber toughening was proposed at the end of the 1960s [1] and extensive studies have been made by many researchers. The typical character of rubber toughening is the increase of toughness at the cost of decreasing the modulus. In contrast, thermoplastic resin toughening overcomes this shortcoming and can not only increase the toughness but also maintain the mechanical properties [2, 3]. An amazing effect is observed on the basis of rigid inorganic nanoparticle toughening [4] but it does not play a role at low temperature as demonstrated by Deng S. [5] and Kwon S.C. [6]. The use of nanoclays in epoxy anticorrosive coatings was studied by Tomić M.D. *et al.* [7] and the results showed that nanoclays have a positive effect on the mechanical, thermal and especially barrier and anticorrosive performances of the epoxy coating. However, the effect on fracture toughness of the clay nanolayers was not discussed.

The toughness of epoxy coatings under low temperature conditions has practical significance for coating app-

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lications in hydropower engineering buildings because the cracks of a coating layer always occur at low temperature. This work specifically selects an active rubber impact modifier to toughen the epoxy coating and symmetrically studies the relationship between fracture toughness and the temperature of the epoxy resin coating.

TOUGHENING DESIGN AND TOUGHNESS EVALUATION METHODOLOGY

Toughness in low-temperature conditions are the focus in this work. S. Deng and S.C. Kwon's studies showed that the toughening effect of rigid inorganic particles is not obvious at low temperatures. Analysis on the toughening mechanism of thermoplastic resins shows that the bearing capability to microcrack and shear deformations of the epoxy matrix is closely related to toughness, and so the toughening effect of thermoplastic resin is remarkable for high crosslinking-density epoxy resin systems [8]. In the case of rubber toughening, to the contrary, the toughening result is remarkable for the epoxy resin systems with relatively lower crosslinking density as the rubber particle cavitation and the formation of a plastic zone in the matrix are the main toughening mechanism [9].

For applications in hydropower engineering buildings, the coatings are expected to have adequate mechanical properties and low modulus while at the same time lead to low inner stress. In this paper, an active rubber is selected to toughen the epoxy coatings, which has a good anti-cracking property to meet the demands.

There are many methods to measure the toughness of materials, such as Sharp impact, Izod impact, fracture toughness K_{IC} (i.e. the critical-stress-intensity factor) and J-integral, etc. The K_{IC} and J-integral are based on fracture mechanics and there are good correlations between them and cracking. The K_{IC} was selected to measure the toughness of epoxy resin coatings in this paper since the test process has become the standard for polymers.

EXPERIMENTAL PART

Materials

– Epoxy resin (bisphenol A diglycidyl ether CYD-128) with an epoxy equivalent of about 190 is used in this study.

– The impact modifier is an active rubber (DESMO-CAP 11) purchased from Bayer Ltd.

– Three kinds of modified amines (A, B and C) as curing agents are used to find the best properties of the coatings. They are modified aliphatic polyamine (CYDHD593) – A, polyamidoamine (V140) – B and their mixture in the proportion 1 to 1 – C. To tune the viscosity of the coating systems, a certain amount of reactive diluent is added.

Specimen preparation

Single-edge notched bend (SENB) specimens, obtained by casting and machining operations, were used in this study (Fig. 1). First, the curing agent was added to the mixture of epoxy resin, diluents and impact modifier with stirring for 5 min in a vacuum container. After mixing uniformly, the mixture was poured into a mold with

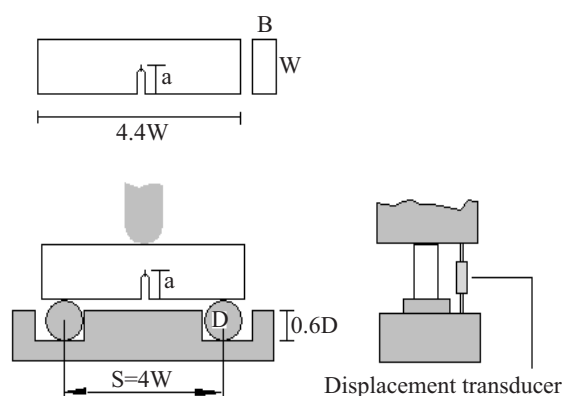


Fig. 1. Bending rig with transducer for SENB

the size of 10 mm × 25 mm × 280 mm. After 24 hours, the casting body was demounted and kept at room temperature for 14 days. Specimens with a size of 10 mm × 20 mm × 88 mm were finally obtained from the casting body by machining operations. Then, a 9.5 mm deep notch was sawed first, and a sufficiently sharp crack was generated by a new razor blade sliding across the notch root in one motion. The crack length was in the range of 9 mm to 11 mm, and was measured accurately after the test. Nine different formula coating systems and three specimens for each system were prepared for the test (see Table 1). The whole curing time of specimens before testing was 21 days.

Methods of testing

– The test method of fracture toughness K_{IC} was performed according to ASTM D 5045-99 using the SENB specimen. It should be specifically mentioned that the tests were conducted at four different temperatures; 20, 0, -20 and -40 °C, which covered the main temperature range for applications. Before testing, the specimens were placed at the corresponding test temperatures in a high low temperature test chamber for at least 4 hrs. A material testing machine with a temperature chamber, which can be set freely in the range of 100 ~ -70 °C, was used to ensure the tests were conducted under accurate temperature settings. A loading rate of 10 mm/min was used in all the tests, and the load values and the load-point displacements in the test process were recorded automatically.

– The dynamic mechanical thermal analysis curves were obtained by a DMTA instrument from Rheometric

Scientific Inc. Test specimens with a size of 50 mm × 6 mm × 2 mm were prepared by casting and machining. The casting process of the specimens was the same as for the SENB tests stated in the previous section. A 3 Hz scan rate and 3 K/min temperature rate were selected for the test.

– Photographs of the fracture surface of the broken SENB specimens were observed by a Hitachi S-4700 SEM (Scanning Electron Microscope).

– The Young's modulus of each epoxy system at different temperatures was tested according to ASTM D 638-08, and type I casting specimens were used. The specimens were cured and conditioned at 23 ± 2 °C and 50 ± 5 relative humidity for 21 days before testing. The testing apparatus was a type CMT5504 material testing machine made by MTS systems (China) Co., Ltd., and LVDT transducers were set at both sides of the specimen to obtain the change of gauge length. A 5 mm/min loading speed was selected for the test.

RESULTS AND DISCUSSION

Typical load-displacement curves are shown in Fig. 2. The behaviors of specimen 1# had the characteristics of a brittle fracture at all the test temperatures and specimens 6# and 8# showed a limited yield phenomenon at relative-

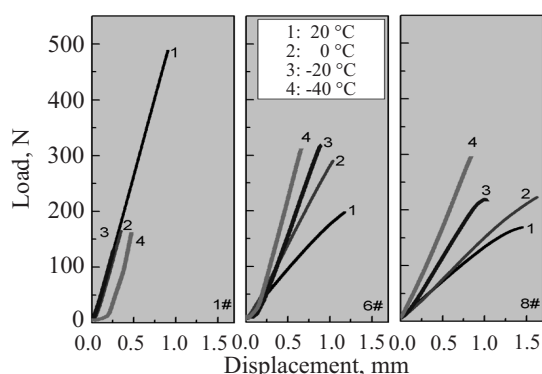


Fig. 2. Load versus load point displacement of specimens: a) 1#, b) 6#, c) 8#

ly higher temperatures and brittle fractures at lower temperatures. All the test results satisfied the valid testing requirement and the specimen size criteria mentioned in sections 9.1.1 and 7.1.2 of ASTM D 5045.

The calculation of K_{IC} was measured according to annex A1 of ASTM D 5045-99 and the results of 9 kinds of specimens at four different temperatures are listed in Table 1.

The results can be divided into three groups according to the variation of K_{IC} against temperature. For groups one and group two, there were clear decreases and increases, respectively, of K_{IC} with lower temperatures. However for group three, there were slight variations of K_{IC} as the temperature changed.

The influence of the hardener structure on toughness

In the modified resin systems (the numbers from 4# to 9#), the specimens with the same amount of modifier cured by hardener A have the highest toughness at lower temperatures and the minimum at room temperature. In the unmodified systems (the numbers from 1# to 3#), the toughness value of the specimen cured by hardener A is better than that cured by hardener B in the studied temperature range as shown in Table 1.

Hardener A is a kind of adduct formed by DETA (diethylenetriamine) and BGE (butyl glycidyl ether) and hardener B is a kind of adduct as well, formed by DETA and linoleic acid dimers. The hardeners are different in chain structure but similar in reaction group structure. Maybe the linear chain structure of hardener A is the main reason of the test results.

Toughness variation to temperature

The behaviors of specimen 1#, 6# and 8# are the focus in this study because their variable features are very typical, as shown in Fig. 3.

The fracture toughness K_{IC} of specimen 1# at room temperature is very high, but decreased sharply as the temperature lowered below 0 °C. Specimens 6# and 8# of

Table 1. Fracture toughness of prepared samples at different temperatures

Specimen	Impact modifier (g/100 g epoxy)	Kind of curing agent	T_g , °C	Young's modulus, GPa	K_{IC} , MPa·m ^{1/2}				Group
					20 °C	0 °C	-20 °C	-40 °C	
1#	0	A	68	3.18	3.19	1.06	0.85	1.12	1
2#	0	B	—	2.44	2.16	0.76	0.81	0.85	1
3#	0	C	—	1.99	1.97	1.87	1.14	1.16	1
4#	20	B	—	1.61	1.40	1.08	0.92	0.94	1
5#	20	C	69	1.53	1.62	1.59	1.70	1.88	3
6#	20	A	65	0.55	1.30	2.08	2.34	2.32	2
7#	50	C	76	0.91	1.31	1.23	1.26	1.67	3
8#	50	A	74	0.58	1.02	1.45	1.79	2.17	2
9#	50	B	—	0.59	1.37	1.64	1.22	1.14	3

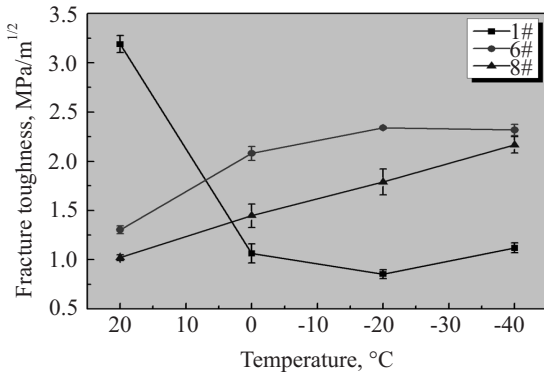


Fig. 3. Fracture toughness of specimens: 1#, 6#, 8# versus temperature

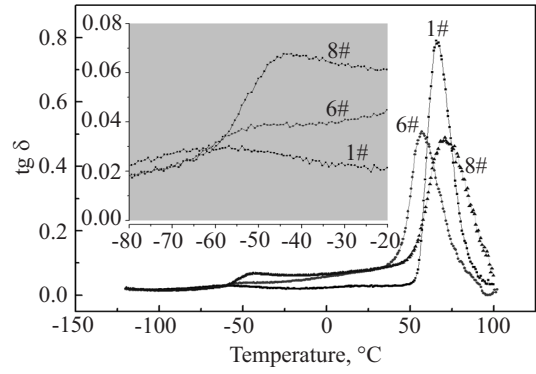


Fig. 4. DMTA curves of specimens: 1#, 6#, 8#

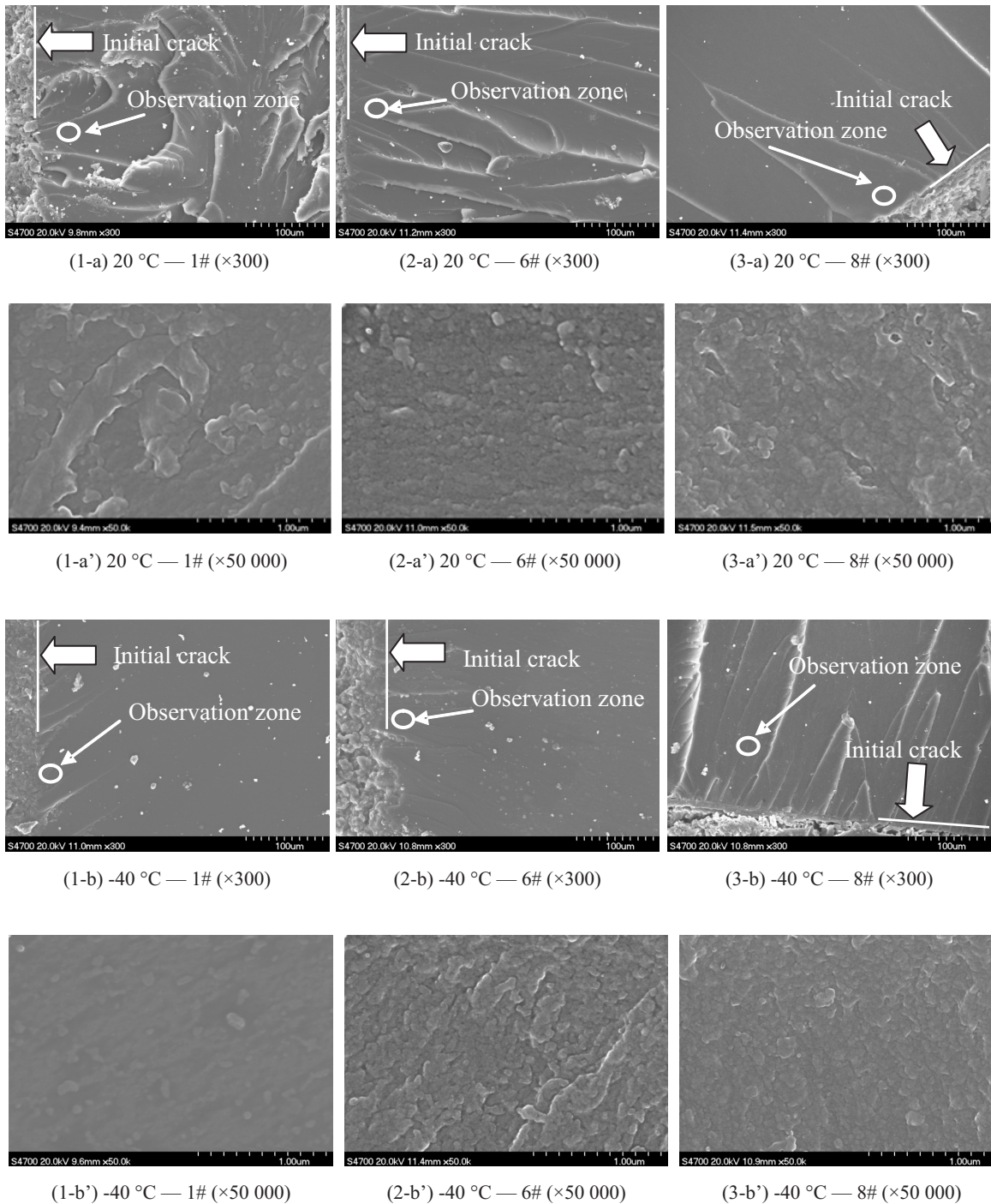


Fig. 5. SEM images of the fracture surfaces for different specimens

group two, whose fracture toughness increased at lower temperature, were the desired coating systems applied outdoors for anti-cracking. The K_{IC} of specimen 6# increased sharply when the temperature dropped from 20 °C to 0 °C, and then grew slowly as the temperature dropped further. The fracture toughness values of specimen 8# are lower than that of specimen 6# over the whole temperature range but it almost linearly increased as the temperature dropped.

Inner temperature stress is accumulated in the coating layer as the temperature is lowered. Accordingly, the cracking risk of the layer is higher. Therefore, specimen 6# is the preferred system for an anti-cracking coating layer.

The roles of the impact modifier to the fracture toughness of specimen 1#, 6# and 8# can be illustrated with the dynamic mechanical thermal analysis (DMTA) curves, as shown in Fig. 4.

All the α -transition peaks, corresponding to the glass transition, are in the range from 60 to 70 °C. The peak shape of specimen 1# is relatively tall and narrow, while the rest are lower and wider. Furthermore, there is a step in the curves of specimens 6# and 8# at about -60 °C. The steps, but not peaks, may be caused by the impact modifier, indicating that the compatibility between epoxy resin and the impact modifier is excellent. The higher fracture toughness values of specimen 6# and 8# at the lower temperature may be closely related to the steps.

Relationship between fracture toughness and morphology

SEM images of the fracture surface can give more information about the toughening mechanism. The micrograph of the crack tip regions of specimen 1#, 6# and 8# at two temperature points, 20 °C and -40 °C, are shown in Fig. 5.

As the non elastomer toughening system, specimen 1# exhibits a typical ductile fracture surface containing many river markings and deep furrows at room temperature. In contrast, a smooth surface is shown in the micrograph of the fractured section at -40 °C even at high magnification observed by SEM as can be seen from Fig. 5(1-a), 5(1-b) and 5(1-b'). The SEM photos of specimen 6# shows a similar trend in the fracture surface with lower temperatures [Fig. 5(2-a) and Fig. 5(2-b)] but a rough surface can be seen under high magnification observations. The images for specimen 8# show that there are more river markings contained in the fracture surface at low temperatures [Fig. 5(3-a) and Fig. 5(3-b)].

Relationship between fracture toughness and modulus

The value of fracture toughness K_{IC} is not only closely related to the morphology of the fracture surface but also to the modulus of the materials. The results of the Young's

modulus of each epoxy system at different temperatures are shown in Fig. 6. The modulus variations of specimen 6# and 8# are clear in the tested temperature range and that of specimen 1# is relatively small.

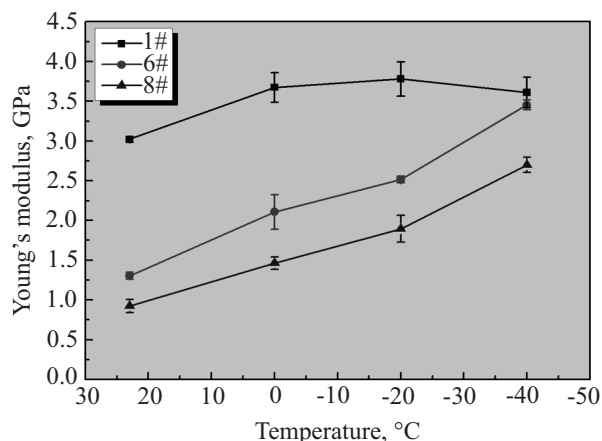


Fig. 6. Young's modulus of specimens: 1#, 6#, 8# at different temperatures

Ductile tearing and high modulus, according to energy absorbing mechanisms, will result in high toughness values. Specimen 1# shows a high toughness value at room temperature but greatly reduced values at low temperatures. At the same time, the morphology shows that the fracture surface turned to brittle tearing from ductile tearing as the temperature dropped and the modulus varied little in the process. In contrast, the large extensional deformation of the fracture surface and increase of modulus of specimen 8# lead to higher toughness values when the temperature dropped.

Regarding specimen 6#, the decrease of extensional deformation and the increase of modulus occurred simultaneously when the temperature dropped. The toughness values, under the combined actions of the two factors, showed an increasing trend with gradually reduced rates as the temperature dropped.

CONCLUSIONS

In this paper, the fracture toughness of nine kinds of rubber modified epoxy coating systems are tested at four temperatures, that is 20, 0, -20 and -40 °C. Moreover, the relationship between the toughness and temperature was discussed. The following conclusions can be made from these experiments:

- The toughness of the epoxy system cured by an amine curing agent is closely related to the test temperature. The wrong conclusion could be drawn from test results at room temperature only for coatings applied outdoors. It is necessary to study the relations between fracture toughness and the temperatures in which the coating is applied. For protection coatings for hydropower engi-

neering buildings, toughness at low temperature is especially significant.

– Rubber modifier changes the morphology of the fracture surface of the epoxy system at low temperature. The extensional deformation in the fracture surface will increase the dissipation of energy and result in higher values of fracture toughness.

– The values of fracture toughness are influenced greatly by the modulus of the material. The cooperation of morphology of fracture surface and modulus will lead to high toughness. When the toughening epoxy systems are kept in the ductile tearing station at low temperature, higher toughness is attributed to the modulus increase with cooling.

– The addition of rubber modifier is a suitable way to improve the anti-cracking performance of epoxy coatings at low temperature because of the increase of fracture toughness and the relative low modulus, which can decrease the thermal stress in the cooling process.

– The epoxy system of specimen 6# is a priority selection for protection coatings for concrete applied outdoors. The higher fracture toughness at lower temperatures will provide the epoxy coating with a better anti-cracking ability.

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