Environmental stress cracking of low molecular weight high density polyethylene

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Stress intensity factor (K) — crack speed ($\dot{a}$) relationships have been obtained for environmental stress cracking (*ESC*) of specimens of a high density polyethylene having different thermal treatments. Also, scanning electron microscope examination of *ESC* fracture surfaces has been carried out and correlation between K and the fracture surface appearance has been established. It appears that at low values of K the failure takes place by interlamellar crack propagation; as K increases the mechanism undergoes a transition to void formation and growth, with voids beginning to appear within the spherulites. At high K the failure is entirely by void formation and growth.

INTRODUCTION

Marshall *et al.*[1,2] have demonstrated that linear elastic fracture mechanics can be used to study the environmental stress cracking (*ESC*) of polyethylene. They showed that a unique correlation exists between stress intensity factor (K) and crack speed ($\dot{a}$) in *ESC* tests using notched specimens of low and high density polyethylenes. They also suggested that K-$\dot{a}$ relations be used to compare *ESC* resistances of these materials. In subsequent papers Williams and Marshall[3], then Williams[4], obtained theoretical relationships between K and $\dot{a}$ during different stages of crack propagation. They suggested that failure occurred in three stages with increasing K and $\dot{a}$. The first stage is relaxation controlled, the second flow controlled and finally at high speed and K there should exist a stage where the fluid does not effect the failure as it cannot flow fast enough to keep up with the crack tip.

Although fracture mechanics is useful for characterization of fracture phenomena, it is only when its results are combined with a study of fracture surfaces that much information can be obtained on fracture mechanisms. *ESC* fracture surfaces have been studied by a number of workers most of whom have observed a voided, fibrillar structure[5-7]. Interlamellar failure has however been seen in low stress, slow crack speed conditions[8]. These two results could be reconciled if there is a transition from interlamellar failure at low K and low crack speed to failure by void formation and growth at higher K and crack speeds. The implicit assumption here being that, as K controls crack speed, it will also control fracture surface appearance.

Here the results of the *ESC* studies of a high density polyethylene having difficult thermal treatments are presented. The purpose of this paper is twofold — to obtain the K-$\dot{a}$ relationships for the different thermal treatments and to attempt to establish a correlation between K and the fracture surface appearance.

MATERIALS AND TEST METHODS

The material used was a linear HDPE, GA7260 (melt flow index: 18) supplied by Hoechst Australia Pty Ltd. Specimens were cut from compression moulded sheets of thickness 1.5 mm which had the following thermal treatments:

(a) Fast cooled to room temperature from 180°C (quenched);

(b) Quenched then annealed at 85±1°C for 20 hours followed by furnace cooling;

(c) Quenched then annealed at 115±1°C for 20 hours followed by furnace cooling;

(d) Slow cooled (furnace cooled) to room temperature from 180°C.

The average spherulite size and density of the specimens for these different thermal treatments are shown in *Table 1*. Slow cooling resulted in the largest spherulite size as well as the highest density. The spherulites in all materials were found to be banded. In differential scanning calorimetry (d.s.c.) studies all the specimens showed a broad single isotherm. Unnotched tensile tests in air revealed that the specimens had little or no work-hardening characteristics.

The *ESC* tests were carried out at 24.5±0.5°C, under dead weight tensile load. The *ESC* agent used was a 10% (v/v) solution of the detergent Igepal Co-630 in water. Single edge notched (*SEN*) specimens were used for the majority of the tests although double edge notched specimens (*DEN*) were used occasionally. In all the

Table 1 Average spherulite size and density values of HDPE

Thermal treatment	Average spherulite size (μm)	Density (g cm^{-3})
Quenched	30	0.957
Quenched, annealed 85°C	30	0.960
Quenched, annealed 115°C	30	0.966
Slow-cooled	50	0.970

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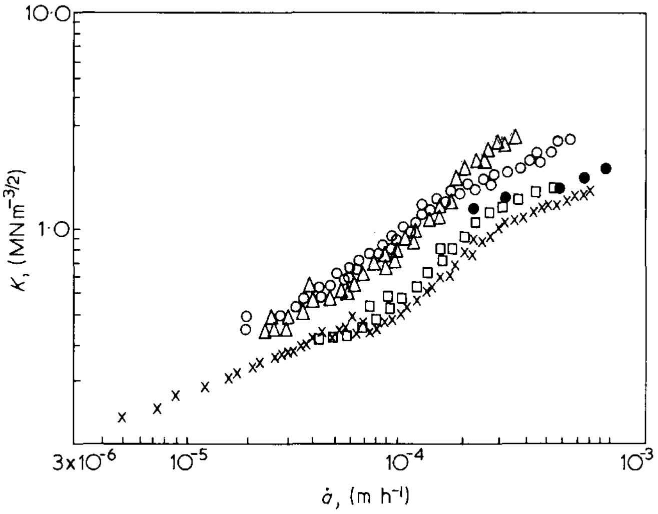

Figure 1 K–$\dot{a}$ relationships of specimens of HDPE with different thermal treatments. O — slow cooled; △ — annealed at 115°C; □ — annealed at 85°C; X — quenched, all tested in detergent; ● — 85°C annealed material tested in air

specimens a sharp razor cut was made at the notch tips giving an initial crack length of approximately 5 mm. During crack propagation the crack length was monitored by a travelling microscope in-built with the dead weight load apparatus and having an accuracy of 0.02 mm. The fracture surfaces were sputter-coated with gold then studied in a Cambridge S4-10 scanning electron microscope. In all micrographs the crack propagation was from left to right.

RESULTS AND DISCUSSION

Fracture mechanics results

During environmental stress crack propagation at constant load, the crack speed increased monotonically with time in a manner similar to that observed by Marshall *et al.*[2] in high melt flow index materials. K–a relationships for specimens of all thermal treatments are shown in *Figure 1*, also shown in this figure are a few points obtained from an 85°C annealed material tested in air.

From this figure one can see that the quenched specimens have similar crack propagation characteristics to those annealed at 85°C. The slow cooled and 115°C annealed specimens were also similar to each other but more resistant to crack propagation at all crack speeds than the former pair of materials. These results are in agreement with data obtained by Isaksen *et al.*[9] and Schotland *et al.*[10] using other methods. As the result of annealing is to shift the curves fairly uniformly it is perhaps not surprising that other test methods give similar results. Schotland *et al.*[10] ascribed the increase in *ESC* resistance on annealing to a decrease in stress on the tie molecules. At the temperature concerned, 115°C, lamellar thickening has started so that might indeed be the case. It is worth noting, in this context, that low density polyethylene in general shows a decrease in *ESC* resistance on annealing[11].

The K–$\dot{a}$ relationships shown in *Figure 1* exhibit some evidence of three different gradients and therefore could be divided into three regions as suggested by the theory of Williams and Marshall[3]. The quenched specimens and specimens annealed at 85°C show the first change in gradient at a crack speed of about 10^{-4} m h^{-1}. This can be compared with the transition crack speed of 2×10^{-4} m h^{-1} for an HDPE in detergent, as reported by Williams and Marshall[3]. However, the gradient in the intermediate crack speed region, is between 0.8–0.9 whereas Williams and Marshall predicted a gradient of 0.5 in the region which they considered to be flow-controlled. Williams[4] has recently suggested that flow controlled failure should occur at constant velocity, independent of K and this phenomenon has in fact been observed by the present authors in low density polyethylene[12]. It is clear that the current results on a low molecular weight high density polyethylene fall somewhere between the two predictions. Williams and Marshall[3] suggested that in general, in the case of *ESC* failure of polyethylene, the third region would be absent. The failure in that region would be similar to that in air, which in the case of polyethylene is expected to be by necking and cold drawing. In the present case, a third region is seen as this low molecular weight material shows brittle failure in air[13]. A few air failure points are shown on *Figure 1*, demonstrating the equivalence of air and *ESC* failure in this region.

STUDY OF FRACTURE SURFACES: CORRELATION BETWEEN *K* AND FRACTURE SURFACE APPEARANCE

The first *ESC* fracture surface studied was that of the quenched specimen in which the initial K was very low, i.e. 0.1 MNm$^{-3/2}$. The fracture surface was apparently brittle at low K values with spherulite bands visible in *SEM* examination of both the fracture surfaces and two-stage replicas of the fracture surfaces. The importance of the latter observation was that it showed the existence of the bands on a surface that had experienced no electron radiation damage. This work has already been published[8] and *Figure 2*, which is taken from that publication, is of a fracture surface corresponding to $K = 0.16$ MNn$^{-3/2}$. The

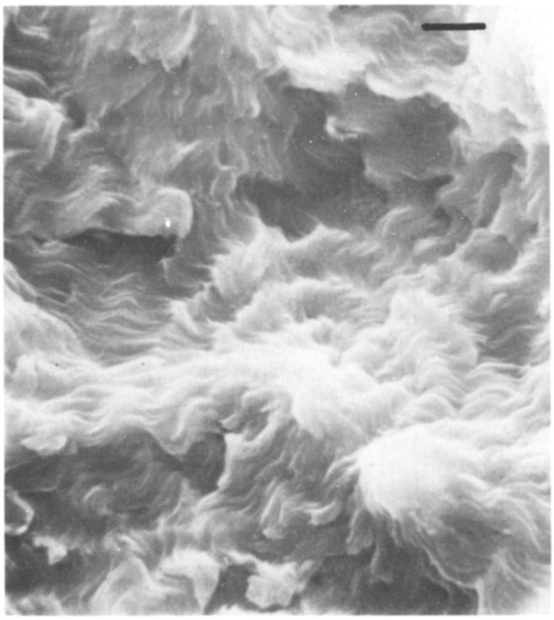

Figure 2 Fracture surface showing a banded texture. The electron beam makes an angle of 60° with the specimen surface. K = 0.16 MNm$^{3/2}$. Scale: 5 μm

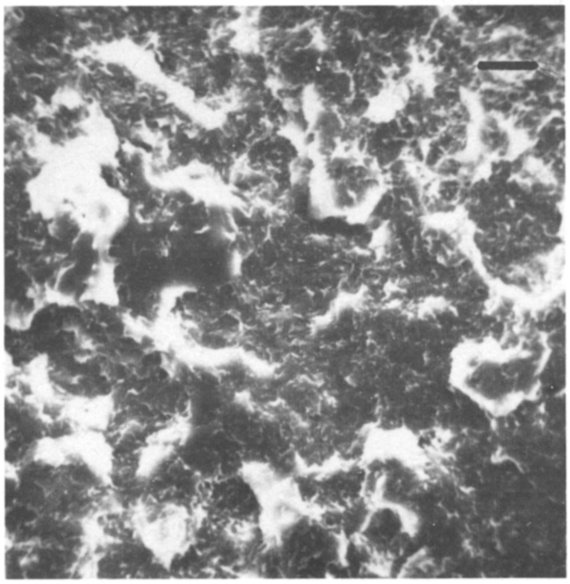

Figure 3 Fracture surface at $K = 0.43$ MNm$^{3/2}$ shown after very little irradiation. Scale: 20 μm

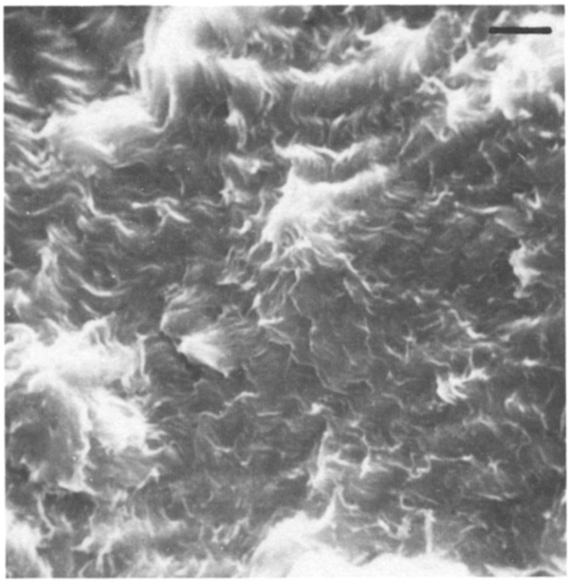

Figure 4 Central section of *Figure 3* after 40 min. irradiation showing final development of banded contrast. Scale: 5 μm

existence of spherulite bands and conical spherulite sections was considered as evidence of interlamellar failure for K values less than 0.4 MNm$^{-3/2}$.

To examine whether a transition exists between interlamellar and void growth failure, as suggested in the introduction, two tests were made on quenched material using one DEN specimen and one SEN specimen. The test on the DEN specimen was carried out in three steps. Firstly, with an initial K of 0.3 MNm$^{-3/2}$ the crack was allowed to propagate under constant load until K reached 0.4 MNm$^{-3/2}$. K was then increased abruptly to 0.9 MNm$^{-3/2}$ and crack propagation allowed to continue for about 0.3 mm. Finally K was decreased to 0.4 MNm$^{-3/2}$ and crack propagation allowed to continue at constant load across all the specimen.

In the SEN specimen an initial K of 0.35 MNm$^{-3/2}$ was used and the crack propagation was allowed to continue until a K value of 1.5 MNm$^{-3/2}$ was reached. The load was then reduced abruptly to lower the K value to 0.3 MNm$^{-3/2}$ and crack propagation continued across the specimen. The purpose of the sudden increase and decrease of K was to examine whether fracture surface appearance was controlled entirely by current values of K or if memory effects were present. As results from the two specimens were entirely equivalent they will be considered together. The fracture surfaces where K increases steadily at constant load will be presented first.

Figures 3 and *4* show one region of the fracture surface ($K = 0.43$ MNm$^{-3/2}$) in which the effect of irradiation on development of the band contrast is clearly illustrated. *Figure 3* is taken with very little irradiation; the specimen was then irradiated in the beam for 40 min before *Figure 4* was taken.

Grubb and Keller[14] have demonstrated that a banded surface topography can be caused or enhanced by the effect of electron radiation in the microscope which creates distortions as it breaks up the lamellar crystallites. The depth of this damage must be controlled by the penetration depth of electrons within the polyethylene. The maximum penetration of 20 keV electrons into solid polyethylene can be estimated to be 7 μm with a maximum dose at depths of approximately 2.5 μm[15]. If there exists a certain amount of mechanical surface damage, caused by the *ESC* failure, which has a depth significantly less than the penetration depth of the electrons, then one would not expect bands to be visible on initial observation. On prolonged irradiation, that material within the penetration depth which has not suffered mechanical damage will distort, thereby carrying the surface with it. A banded texture will hence appear. It seems likely therefore that *Figures 3* and *4* show a situation where the mechanical surface damage layer which consists of yielded and voided material, is considerably thinner than the penetration depth of electrons into polyethylene.

Figure 5 presents a fracture surface for $K = 0.56$ MNm$^{-3/2}$ after considerable irradiation. The banded nature is still seen although quite a few voids have

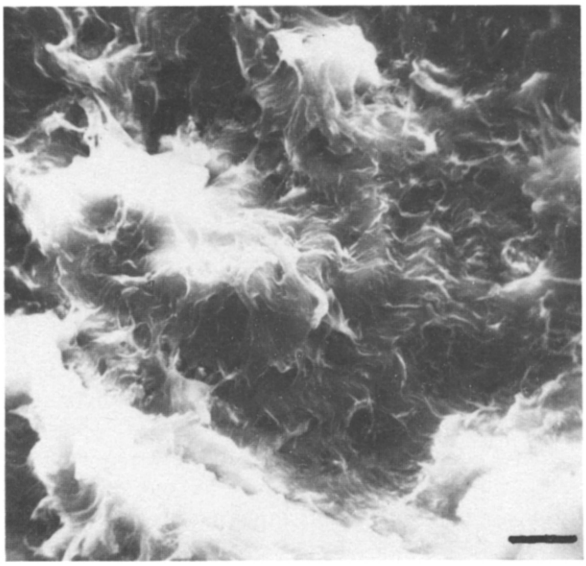

Figure 5 Fracture surface after considerable irradiation at $K = 0.56$ MNm$^{-3/2}$. Scale: 5 μm

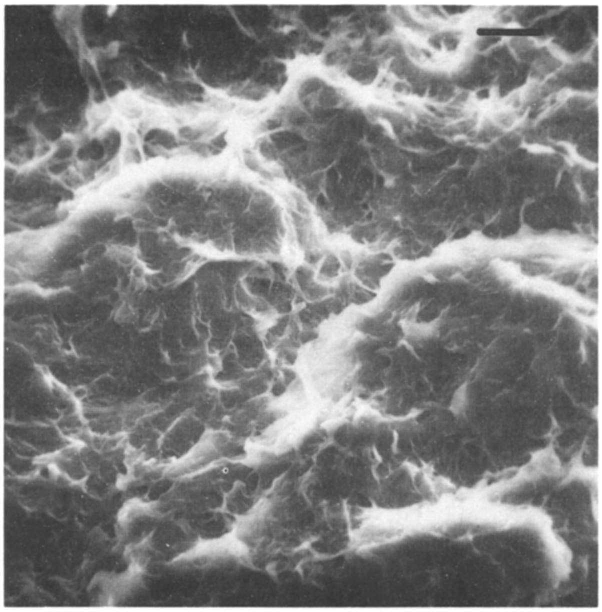

Figure 6 As Fig. 5, $K = 0.70\ \mathrm{MNm}^{-3/2}$. Scale: 10 μm

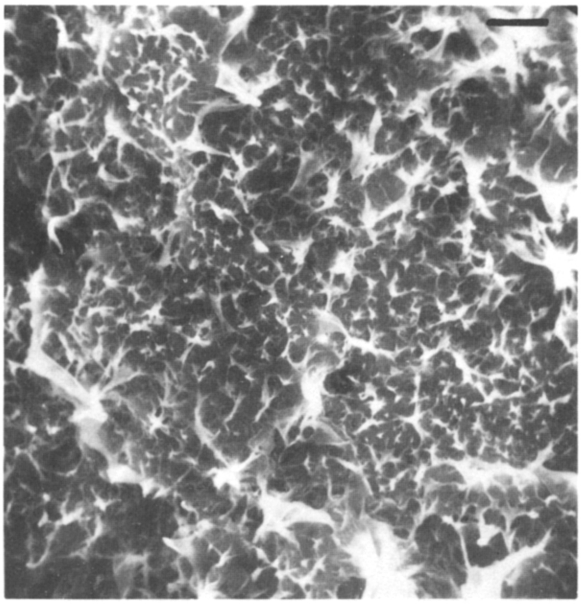

Figure 7 As Fig. 6, $K = 0.84\ \mathrm{MNm}^{-3/2}$. Scale: 10 μm

appeared in the spherulite. A similar fracture surface at $K = 0.70\ \mathrm{MNm}^{-3/2}$ is shown in *Figure 6*. In this figure, the banded texture within the spherulites has been destroyed, the spherulite boundaries are partially fibrillated and voids have spread almost throughout the spherulites. By *Figure 7* ($K = 0.84\ \mathrm{MNm}^{-3/2}$) the spherulite boundaries are totally fibrillated and the texture totally voided and fibrillar.

It is interesting to observe in the above figures that once the voids are visible within the spherulites, they grow very quickly with increasing K. When the entire spherulite becomes voided its boundary and centre in particular are drawn into fibrils which subsequently fail by necking, this giving a voided and fibrillated appearance of the fracture surface. The voided and fibrillated *ESC* fracture surfaces reported in the literature resemble *Figure 7* (and also *Figure 9*).

It is possible to estimate the stress across the damage zone from a knowledge of the K value at which the bands cease to be visible ($0.6\ \mathrm{MNm}^{-3/2}$). As the maximum dose is at a depth of 2.5 μm in solid polyethylene it seems likely that by the time the mechanical damage has effected 4 μm of solid material, bands will no longer be visible after irradiation. The specimen was in fact lightly coated with gold which will decrease the penetration depth to some extent but as the gold coating was very thin, the effect was probably not large. If this material failed at an extension ratio of approximately 3 then the crack opening displacement $\delta \simeq 16\ \mu$m. The strain energy release rate G is related to the stress across the damage zone or craze, σ_c, by

$$G = \delta\sigma_c$$

$$G = \frac{K^2}{E}$$

$$\therefore\ \sigma_c = \frac{K^2}{\delta E}$$

The tensile modulus (E) of this material was $1.1 \times 10^9\ \mathrm{N\ m}^{-2}$ so $\sigma_c \simeq 20$ MPa, a value that is close to the yield stress of this polyethylene. The numerical values are clearly very approximate but this calculation does demonstrate that this interpretation of loss of banded texture is plausible.

Coming now to the effect of sudden changes in K, *Figure 8* shows the fracture surface (with little irradiation) when the K value was reduced abruptly from $0.9\ \mathrm{MNm}^{-3/2}$ to $0.4\ \mathrm{MNm}^{-3/2}$. In this figure, the region in the left is clearly voided ($K = 0.9\ \mathrm{MNm}^{-3/2}$) whereas the region on the right ($K = 0.4\ \mathrm{MNm}^{-3/2}$) is similar to that shown in *Figure 3*. A part of the voided region of *Figure 3* has been shown at a higher magnification, after prolonged irradiation, in *Figure 9* which shows the voids very clearly. It can be seen from *Figure 8* that an abrupt change in the magnitude of K causes an equivalent rapid change in the fracture surface appearance. Similar observations were

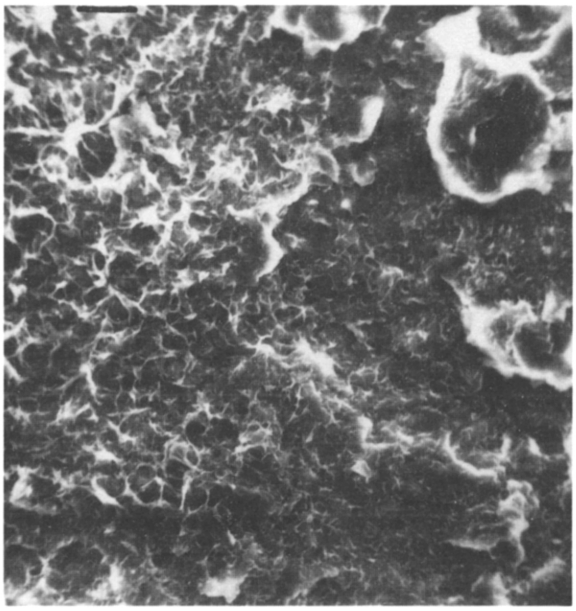

Figure 8 The change in fracture surface appearance is shown when K was reduced abruptly from 0.9 to $0.4\ \mathrm{MNm}^{-3/2}$. Scale: 20 μm

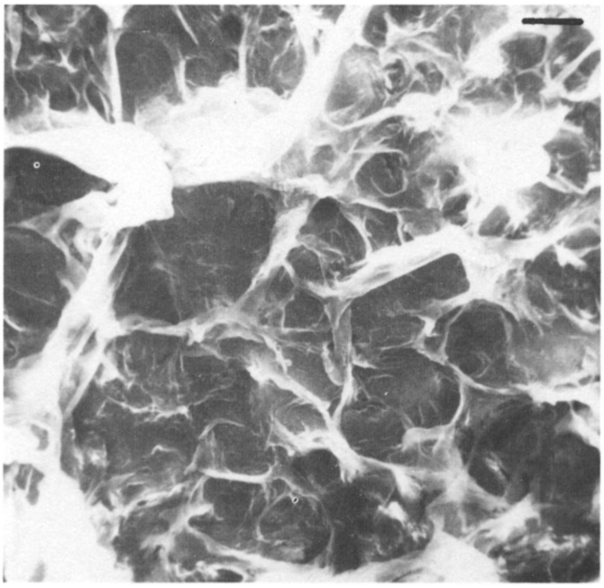

Figure 9 Part of the left hand side of *Figure 8* shown at higher magnification. Scale: 5 μm

made at other points where K was changed abruptly. There is therefore no evidence of a memory effect on the fracture surface existing over a significant distance.

CONCLUSION

The *ESC* resistance of a high density polyethylene with four different heat treatments has been measured using a fracture mechanics approach. The stress crack resistance of a quenched material was found to increase with annealing at 85°C and 115°C. The slow cooled materials were also found to show better *ESC* resistance than the quenched material. The shape of the K–$\dot{a}$ relationship was similar to that suggested by Williams and Marshall[3].

The fracture surfaces were found to show a transition from a banded appearance at low K, which was interpreted as an interlamellar failure, to a voided and fibrillated surface at high K. The banded contrast at moderate K values was shown to be caused by electron radiation damage to material which had not suffered mechanical damage in failure. The transition K, which was in the flow controlled region of failure, was shown to occur when the surface damage on failure was comparable with the electron penetration depth. For K values above this, there was insufficient undamaged material within the electron penetration depth for a banded contrast to form.

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