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The influence of hydrogen on the deformation and fracture of the near surface region of solids: proposed origin of the Rebinder–Westwood effect

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Results are presented which show the embrittling effect of hydrogen-bearing environments on the near surface region of solids. This effect was indicated by shifts to higher amplitude of the acoustic emission amplitude distributions obtained during low-speed drilling, by the drilling rate, and by scanning electron microscopy. The extent of embrittlement in liquid environments was found to depend on the availability of the hydrogen, which depends on its bonding in the liquid (covalent, partially ionized, ion paired in media of low dielectric constant, etc). The time dependence of this effect is consistent with the permeation of hydrogen in the near surface region. It is proposed that the hydrogen effect on the deformation and fracture of solids is a universal phenomenon affecting the near surface region of metals, ceramics, glasses, semiconductors, ionic crystals, minerals, and rocks (organic solids may be exceptions) and that this embrittlement by hydrogen is one of the origins of the Rebinder–Westwood chemo-mechanical effect.

1. Introduction

The Rebinder–Westwood environmental effect on mechanical behaviour is exhibited in such diverse materials as minerals [1], ionic and ceramic crystals [2–4], glasses and polycrystalline materials [5–13], rocks [12], and metals [14, 15]. The properties which have been changed as a result of the various chemical environments are the microhardness, Vickers and pendulum hardness, indentation creep, anelastic behaviour, elasticity, ductility, brittleness, and drilling and machining rates. These effects are classed as chemo-mechanical. There are two other classes of Rebinder effects, electromechanical and opto-mechanical, which were reviewed elsewhere [12]. A useful contribution to understanding these effects was made by Westwood and MacMillan [12], on recognizing the significance of the existence of a maximum in hardness of materials associated with the zero in the surface charge (zeta potential) produced by ions adsorbed from solution environments. Subsequently, the present author [13] found a minimum drilling rate for Pyrex glass in liquid environments where the dielectric constant and/or the electrolyte concentration resulted in a predominance of paired ion aggregates. This condition also corresponds to the zero zeta potential [13].

It has since been postulated [16] that (1) ion-pair formation reduces the free hydrogen-ion content of the liquid environment, and (2) the embrittling effects of hydrogen are responsible for the Rebinder–Westwood effects. It was shown for the first time that glass is embrittled by gaseous hydrogen [16]. It is suggested in the present paper that (1) the list of materials which are embrittled by hydrogen is quite extensive, (2) the Rebinder–Westwood effects of liquids are the same as those for gaseous hydrogen (modified by factors which affect the availability of hydrogen in the liquids, such as ion-pair formation, dissolved water, and the hydrogen content of the environ-

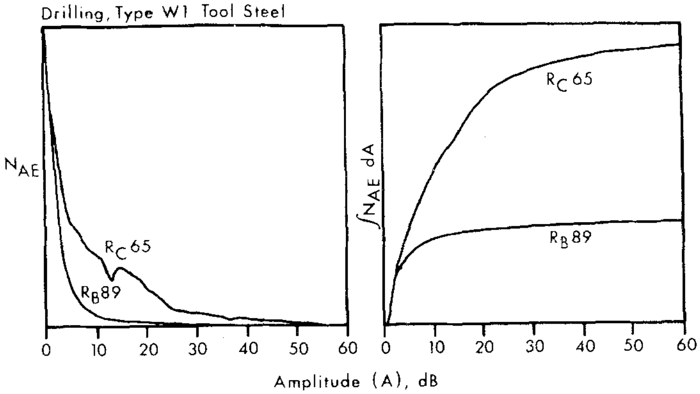

Figure 1 The drilling in air of a furnace-cooled W1 tool steel (hardness R_B89) produces an acoustic emission amplitude distribution which is typical of ductile materials. The distribution is shifted to higher amplitudes for the fully hardened steel (hardness R_C65). The total number of acoustic emission events (ΣN_{AE}) for each N_{AE} versus A curve is indicated on a relative scale by the final value of the integral.

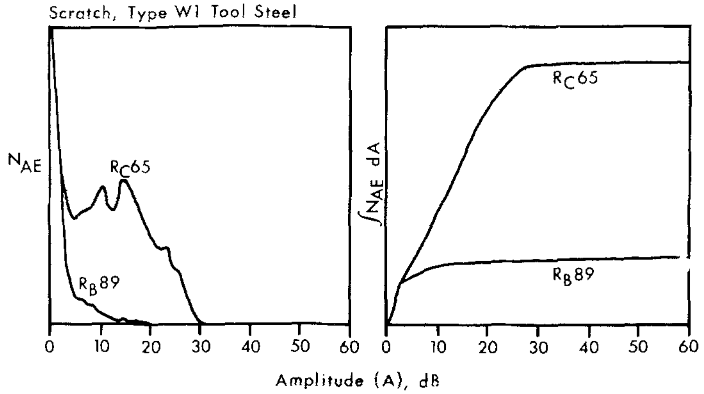

Figure 2 Scratching the surface in air of a W1 tool steel in the furnace-cooled (hardness R_B89) and the fully hardened (hardness R_C65) conditions produces acoustic emission amplitude distributions which are significantly different. The total number of acoustic emission events (ΣN_{AE}) for each N_{AE} versus A curve is indicated on a relative scale by the final value of the integral.

ment molecules), (3) catalytic cracking of hydrogen from hydrocarbons at freshly machined solid surfaces may be a precursor of embrittlement, and (4) the use of these concepts in industrial applications may have significant economic consequences (especially in the case of silicon).

2. Experimental details

The material studies included type W1 tool steel, Ferrovac E iron, furnace-cooled 440C and 1080 steels, aluminium, annealed tungsten, nickel, molybdenum, Pyrex and soda-lime glasses, fused silica, calcite, fluorite, quartz, alumina, sapphire, TiC, TiB_2, ZrC, and B_4C. Samples 2.54 cm diameter and 0.32 cm thick were ultrasonically cleaned in trichloroethylene and acetone and then drilled in air, under various liquids, or in ultrahigh vacuum (10^{-10} Torr) using a spherical ended (2 mm radius) diamond studded bit rotated at 10 rpm under a 1500 g load. It should be noted that drilling at 10 rpm may be more closely related to wear or abrasion tests than to conventional drilling at high speeds. The low bit velocity was chosen to preclude complications arising from localized heating. Scratch tests were performed in air using a Vickers diamond indenter under a 1500 g load with a cross-head speed of 3.2 mm min^{-1}. The acoustic emissions accompanying the fracture of the samples during drilling or scratching were filtered and monitored using equipment described previously [13]. Acoustic emission amplitudes were measured over the range from 0 to 68 dB. Twenty or more acoustic emission amplitude distribution curves were averaged using a digital computer (Nicolet model 1072). The integrations of these curves were performed using the same instrument.

The heat-treatments of the type W1 tool steel were performed following standard metallurgical procedures. Phosphorus-doped single crystal silicon wafers covering the resistivity range from 0.0039 to 870 Ω cm were obtained from Crysteco, Inc, and Dow Corning Corporation. The silicon samples were drilled perpendicular to the (1 1 1) plane.

3. Results and discussion

The effect of changing the sample hardness on the acoustic emission amplitude distribution is shown in Fig. 1 for the drilling and in Fig. 2 for the scratching of a tool steel in air. Although a significant portion of the curve is shifted to higher

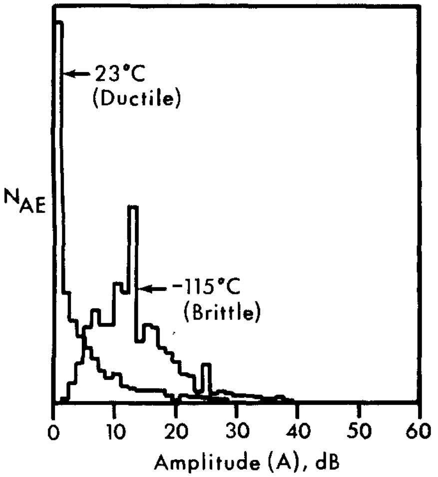

Figure 3 The drilling of Ferrovac E iron at 23° C produces an acoustic emission amplitude distribution which is typical of ductile materials. Drilling the same sample at $-115°$ C (well below its ductile-to-brittle transition temperature of about $-73°$ C) produces a peaked acoustic emission distribution at higher amplitudes which is typical of brittle materials.

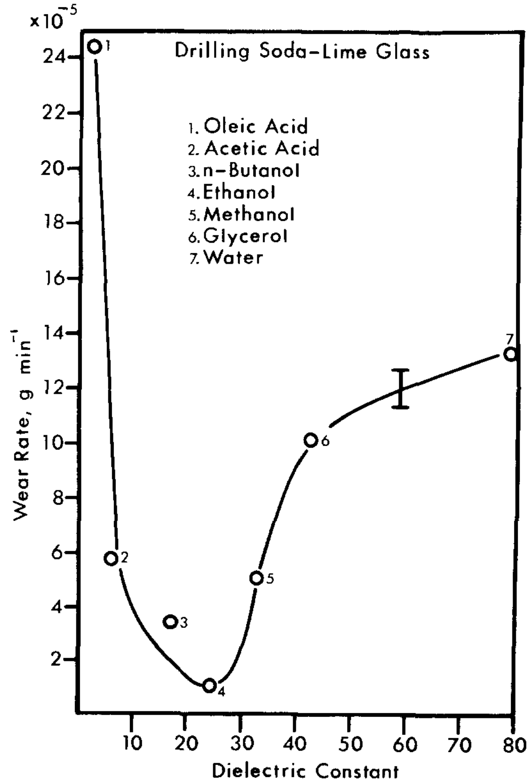

Figure 4 Drilling soda-lime glass under various liquids results in a minimum wear rate for liquids of dielectric constant between 20 and 30 where paired ion aggregates are the predominant species in solution. The pairing of hydrogen ions with other ions in solution reduces the availability of hydrogen for embrittling the glass. The error bar is the average deviation for all the datum points.

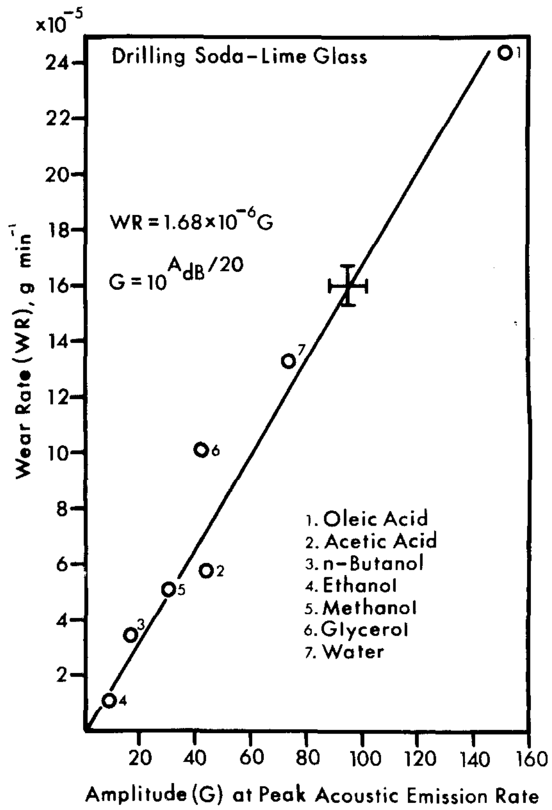

Figure 5 Drilling soda-lime glass under the same liquids as for Fig. 4 produces peaked acoustic emission amplitude distributions (N_{AE} versus A). The wear rate is linearly related to the amplitude at the peak when the amplitude (A) is converted from dB to gain (G) as indicated in the second equation. The error bars on the straight line fit are the average deviations for all the datum points.

amplitudes for the hard sample, the low amplitude tail remains. This tailing portion of the curve, or all of the curve for the softer material (far left, Figs. 1 and 2), has a shape that is characteristic of all of the ductile materials studied (furnace-cooled 440C and 1080 steels, austenitic stainless steels, iron, aluminium, annealed tungsten, nickel, and molybdenum). The effect of changing from a ductile to a brittle condition in the same sample (Ferrovac E iron) without changing structure or composition was shown (Fig. 3) by drilling above and below the ductile-to-brittle transition temperature (about $-73°$ C) *in vacuo* (10^{-10} Torr, to avoid ice, condensation, or oxidation). The distinct peak at higher amplitudes was found to be a characteristic curve shape for the fracture of all of the brittle materials studied (Pyrex and soda-lime glasses, fused silica, calcite, fluorite, natural and synthetic quartz, alumina, sapphire, TiC, TiB_2, ZrC, and B_4C). The two types of characteristic curves may find utility in the rapid assignment of the fracture mode for composite materials. For instance, under the above drilling/grinding conditions, a ductile type curve was found for a cemented carbide (Kennametal K701, WC + 15 wt % Cr, Co binder). This result indicates that material failure occurred in the ductile binder phase rather than in the tungsten carbide particles.

The Rebinder–Westwood chemo-mechanical effect is exhibited in the drilling rates for soda-lime glass under various liquids (Fig. 4). These data are very similar to those previously published for the drilling of Pyrex glass [13] in that a minimum wear rate occurred for drilling under fluids of dielectric constant between 20 and 30. According to the theories of ionic association of Bjerrum [17], Harned and Owen [18], and Fuoss and Kraus [19], there is a maximum tendency for the pairing of ions in this dielectric constant range. Therefore, a reduction in the availability of hydrogen ions for embrittlement of the glass would be expected in liquids which have dielectric constants between 20 and 30. A linear relation between the amplitude at peak N_{AE} versus A is shown in Fig. 5 for the drilling of soda-lime glass under the same fluids as for Fig. 4. Progressively increasing amplitudes (A) for peak acoustic emission (N_{AE}) (Fig. 5) are interpreted as progressively increasing brittleness associated with increasing availability of hydrogen ions for embrittlement. This interpretation is consistent with the data in Fig. 4 since the predominance of ionized species would increase to the left or to the right of the minimum. The results in Figs. 4 and 5 also appear to be consistent with those of Westwood and Mills [20] in that they found a minimum grinding rate associated with a zero zeta potential and a maximum hardness (the present drilling at 10 rpm may be more closely associated with grinding than with conventional drilling at high speeds where pronounced local heating may occur).

If the Rebinder–Westwood chemo-mechanical effect is due to hydrogen, a pronounced time-dependent embrittlement of the near surface layer should be observed for the drilling of glass on exposure to hydrogen in an ultrahigh vacuum system where other adsorbates may be scrupulously excluded. Such an effect was observed and recently reported [16]. Furthermore, if the phenomena observed in this well-controlled hydrogen environment are the same as those which

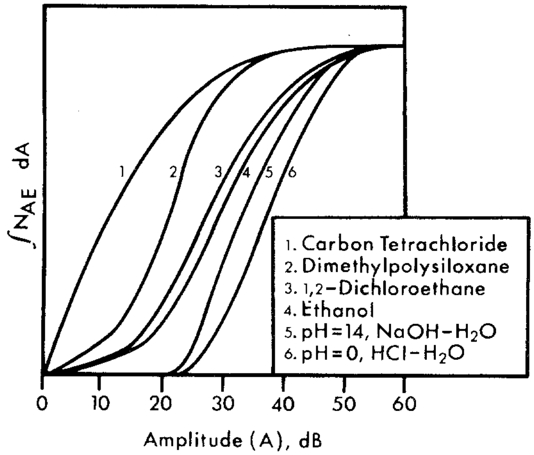

Figure 6 Drilling soda-lime glass under various liquids produces peaked acoustic emission amplitude distributions. The integrals of these peaks, which were normalized to the same final value, are plotted to avoid overlapping of the curves. The availability of hydrogen for embrittling the glass increases in the indicated order.

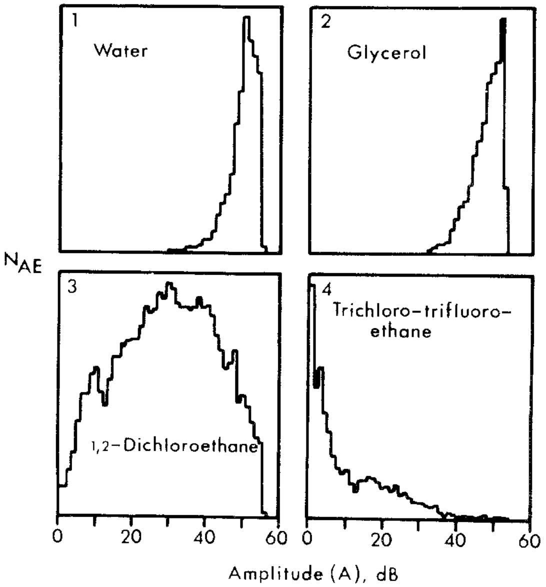

Figure 7 The acoustic emission amplitude distribution obtained during the drilling of the (111) plane of silicon is shifted to lower amplitudes as the availability of hydrogen for embrittling the silicon is decreased in the order 1 through 4.

occur in liquid environments, a progressive increase in the amplitude at which peaks in the acoustic emission amplitude distribution occur should be observed as the availability of hydrogen is increased in the drilling fluids. Fig. 6 shows such a trend over a wide amplitude range for the drilling of soda-lime glass (the integrals of the acoustic emission peaks are plotted in Fig. 6 to avoid confusion from overlapping peaks). The amplitude order of curves 4, 5 and 6 is readily understood in terms of the availability of ionizable hydrogen. Curves 2 and 3 fall to the left of curves 4, 5 and 6 since hydrogen is made available for embrittlement of the glass only by catalytic cracking of covalent bonds in liquids 2 and 3 at the freshly machined surfaces (thus the availability of embrittling hydrogen is less than for the spontaneously ionizable cases). Although liquids 2 and 3 both contain covalently bound hydrogen, the high viscosity of the silicone oil (liquid 2) may result in slower diffusion of reactants and reaction products to and from the glass surface (thus curve 2 falls to the left of curve 3). Curve 1 occurs at the lowest amplitude (and approaches that obtained in ultrahigh vacuum) since the liquid molecules contain no hydrogen for embrittlement of the glass. A similar trend is shown in Fig. 7 for the drilling of silicon. The hydrogen-dependent change in amplitude distribution for silicon (about 50 dB) is the largest we have observed. Since the hydrogen is covalently bound in many of the liquids studied, it is proposed that catalytic cracking occurs at the freshly fractured surfaces to make hydrogen available for embrittlement of the solid.

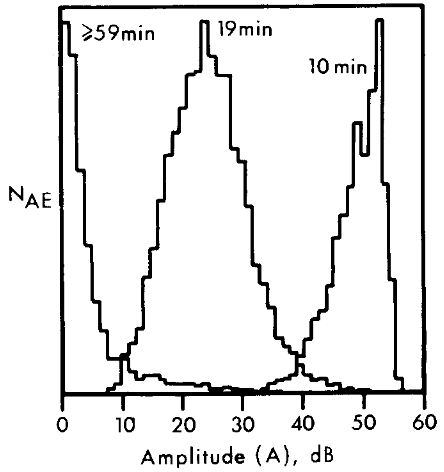

Figure 8 The time-dependent decrease in amplitude of the acoustic emission amplitude distribution obtained during the drilling of the (111) plane of silicon under an aprotic liquid (CCl_4) is interpreted as a decrease in brittleness (and an increase in ductility) as a result of a decrease in the hydrogen content of the near surface region. The initial condition was exposure to air (an aqueous environment).

It should be noted that the change in peak location from the high amplitudes in aqueous environment (after exposure to air) to lower amplitudes during drilling under fluids containing less hydrogen, requires between 7 and 59 min, depending on the extent of the change (Fig. 8). This time dependence is consistent with the estimated hydrogen permeation rates in silicon at room temperature [21]. It is also consistent with

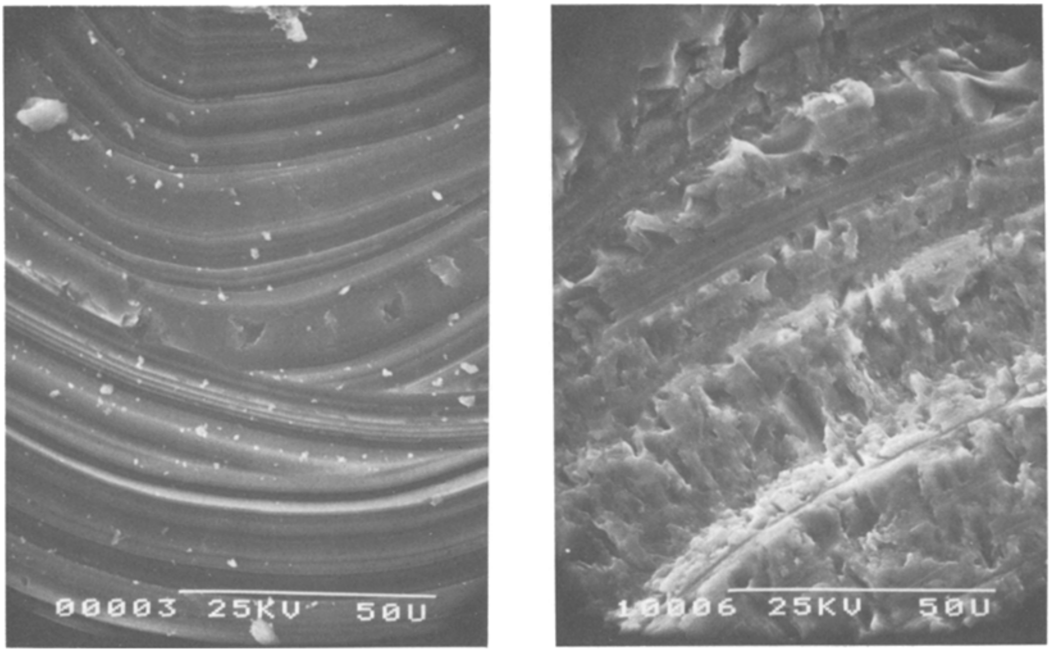

Figure 9 Scanning electron microscope photographs of the surface of a silicon sample showing the ductile fracture (left) when drilled under an aprotic liquid (CCl_4) and the brittle fracture (right) when drilled under a hydrogen-bearing liquid (H_2O).

the results obtained in the ultrahigh vacuum system [16]. Fig. 9 shows that drilling silicon under CCl_4, an aprotic liquid, produces primarily ductile fracture in the near surface layer (ductile plowing in smooth grooves which follow the drill rotation) while primarily brittle fracture (with some ductile plowing) occurs under water, a source of hydrogen, for the same surface. This behaviour was independent of the dopant level in the silicon over the range from 0.0039 to 870 Ω cm resistivity. The dramatic differences shown in Fig. 9 indicate that considerable economic benefit may be derived by cutting or grinding silicon in aprotic liquids in the semiconductor industry where greater freedom from mechanical defects is of importance.

4. Conclusions

The results presented indicate that the embrittling effect of hydrogen is one of the origins of the environment-dependence of the deformation and fracture of the near-surface region of solids (the Rebinder–Westwood effect). It was indicated that the results for drilling solids under hydrogen-bearing liquids were the same as those for drilling in a well-controlled gaseous hydrogen environment except that the availability of the hydrogen in the liquid case depends on its bonding (covalent, partially ionized, or bound as ion aggregates). The time dependence of the chemo-mechanical effect is consistent with a hydrogen permeation process. It was shown that the wear rate during the low-speed drilling of soda-lime glass in linearly related to the amplitude at the peak acoustic emission rate (which is a function of the energy released during fracture and is environment-dependent). It should be noted that an increase in the drilling speed may have opposing and unpredictable effects: (1) material removal may occur at rates higher than those of hydrogen permeation, (2) hydrogen permeation rates may be increased by local heating, (3) local heating may cause changes in the dielectric constant of the liquid environment thus affecting the availability of hydrogen ions for embrittlement of the solid, (4) the local temperature rise may differ with solids of different thermal conductivity and with liquids of different heat capacities and wetting capabilities, (5) chemical interactions between hydrogen and the solid may be changed by local heating, and (6) the intrinsic properties of the solid may be different at higher temperatures and higher strain-rates.

Although silicon exhibits one of the largest observed hydrogen-dependent changes in mechanical properties, we have now observed similar effects in many quite different materials (Pyrex glass [13, 16], soda-lime glass and silicon [present work], fused silica, quartz, polycrystalline alumina, calcite, fluorite, sierra white granite, Texas pink granite, hot-pressed B_4C, hot-pressed TiB_2 and type 02 tool steel [22], 440C stainless steel [15, 22], and 1080 steel [22]. We propose that this embrittlement by hydrogen is a universal effect (organic solids may be exceptions) which would be expected to affect other materials and other forms of wear in addition to low-speed drilling (such as high-speed drilling, erosion, grinding, polishing, comminution, machining, and cutting).

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