Susceptibility of Electronic Insulating Polyimides to Microbial Degradation

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SYNOPSIS

We used electrochemical impedance spectroscopy (EIS) to investigate microbial degradation of polyimides used as insulators in electronic packaging. The microbial inoculum was a fungal consortium isolated from degraded polyimides. Microorganisms grew on these polymers yielding distinctive EIS spectra indicative of failure. Degradation appeared to occur in a number of steps. Two distinctive stages in the decline of film resistance were observed in the inoculated EIS cells within 17 and 72 days after inoculation. The early stage of resistance decrease may be related to the ingress of water molecules and ionic species into the polymeric materials, whereas the second stage probably resulted from partial degradation of the polymers by fungal growth on the polymer film. The active fungal consortium was comprised of *Aspergillus versicolor, Cladosporium cladosporioides,* and a *Chaetomium* species. All of these fungi are common environmental contaminants. The relationship between changes of impedance spectra and microbial degradation of the coatings was supported by scanning electron microscopic observations of fungi on the surface of the inoculated polyimides. Our data indicate that the insulating polyimides used in electronic applications are susceptible to fungal degradation under appropriate environmental conditions, particularly in the presence of moisture. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyimides are an important class of electronic packaging materials used in insulating layers of integrated circuits in computers.[1] They are uniquely suited as interlayer dielectrics because of their high stability, processibility, and low dielectric constants.[2] These dielectric properties of polyimides are ideal for high-speed signal propagation and low interconnect capacitance, which require less power dissipation by output drivers. However, the polyimides in these systems are in contact with airborne microorganisms and their surfaces condense moisture, providing an opportunity for the development of microbial biofilms and consequent biodeterioration.

Polyimides have exceptional chemical, mechanical, and thermal stability,[3] but they respond to moisture, resulting in changes in their dielectric properties.[1] Even a very small change in transport or storage properties in a multilayer insulator may cause variations in the dielectric characteristics of underlying devices. In addition to moisture adsorption into the polymeric matrix of polyimides, indoor air contamination by microorganisms, particularly fungi, has been reported to be a common problem during processing and in service.[4]

Fungi have been found to be capable of colonization of surfaces of magnetic tapes,[5] building materials,[6,7] glass and carbon fibers,[8-12] graphite sheets,[8] and fiber-reinforced polymeric composites.[4,8,10-12] Earlier data from our laboratory have suggested that failure of polyimides may be a result of the susceptibility of the materials to microbial attack.[8,9,13-15] However, the role of microorganisms in the process of polyimide degradation was not verified. The objective of the study reported in this paper was to

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demonstrate degradation of polyimides by common fungi under controlled laboratory conditions.

EXPERIMENTAL

Electrochemical Impedance Spectroscopy (EIS)

Polyimides used in this study were Kapton HN (pyromellitic dianhydride and 4,4′-diaminodiphenyl ether) film (E. I. Du Pont Co., Wilmington, DE). The Kapton polyimides had a molecular weight(M_w) of 2.5×10^5 relative to polystyrene standards without further corrections, and a dielectric constant of 2.9 under conditions of 50% relative humidity and 1 kHz.

EIS cells were constructed by gluing a round piece of Kapton HN polyimide onto a 316 stainless steel coupon (50 × 50 mm) by a conductive silver epoxy (SPI Instrumental, West Chester, PA). On the polyimide film, a 30-mm-long acrylic tube (I.D., 34.9 mm; O.D. 38.1 mm) was attached to the polymer–stainless steel coupon by a mixture of Amercoat 90 resin (Ameron, Protective Coatings Group, Brea, CA) and Epon 828 resin (Shell Chemical Co., Houston, TX) in a ratio of 4 : 1. A schematic diagram of the EIS cell used in our study is shown in Figure 1. After curing, the internal and external surfaces of the constructed EIS cells were sterilized with 70% ethanol and dried at room temperature in a laminar-flow sterile hood.

Our EIS analytic system consists of a Schlumberger 1250 frequency response analyzer combined with a Schlumberger 1286 electrochemical interface (Schlumberger Technologies, Instruments Division, Billerica, MA). Z-plot software (Scribner Associates, Inc., Charlottesville, VA) was used to manipulate the system. During data acquisition, samples were potentiostatically held at their open circuit potential (OCP), and a sinusoidal perturbation of 20 to 50 mV was applied to the system. The impedance response was measured over a range of frequencies from 65 kHz to 1 mHz and spectra were recorded as a function of immersion time at ambient temperature and pressure. OCPs were monitored versus a saturated calomel electrode as a reference electrode of the trielectrode system. Platinum mesh was used in the EIS cell as a counter-electrode, and the EIS cell as a working electrode. In all experiments, surface areas of the working electrode were 38.3 cm^2. Both Bode magnitude and phase angle plots as well as Nyquist complex plane plots were used to provide information collectively on increases in porosity, local defects, and delamination.

Initially, a volume of 15 mL of sterile 0.2*M* NaCl solution was added into the acrylic tube of the working electrode, followed by 1.0 mL of a minimum salt solution. The salt solution consisted of (g per liter): K_2HPO_4, 0.8 g; KH_2PO_4, 0.2 g; $CaSO_4 \cdot 2H_2O$, 0.05 g; $MgSO_4 \cdot 7H_2O$, 0.5 g; $FeSO_4 \cdot 7H_2O$, 0.01 g; and $(NH_4)_2SO_4$, 1.0 g. The measurement of the impedance responses was made immediately after a short-time equilibration of the system. The uniformity of all prepared EIS cells was evaluated to determine the validity of using them in subsequent monitoring and to assign them to different treatments. The EIS cells used as working electrodes were divided into two groups. One set of the prepared EIS cells (four) was inoculated with 100 μL of a fungal consortium that was maintained on a malt extract medium (Difco Lab., Detroit, MI). The consortium was obtained by an enrichment process on degraded polyimides. Another set of EIS cells was kept sterile throughout the study by the addition of 100 μL 0.1% sodium azide to the 0.2*M* NaCl solution. At weekly or biweekly intervals, impedance responses of all EIS cells were determined. The tri-electrode system was housed in a sterile laminar-flow hood. Aseptic procedures were used throughout the determination to avoid contamination and cross-contamination of the EIS cells. At the end of the study the polymer films from inoculated and sterile EIS cells were prepared for examination by scanning electron microscopy (SEM).

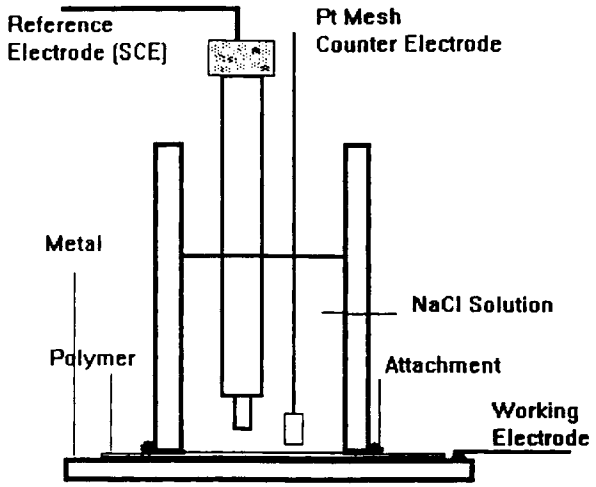

Figure 1 Schematic illustration of an electrochemical impedance spectroscopic cell containing a polyimide film used in our study.

SEM Sample Preparation

Polyimide film samples from the inoculated and sterile EIS cells were treated with 3% glutaraldehyde buffered with 0.2*M* sodium cacodylate overnight.

The solution was previously filtered through a 0.2-μm-pore-size polycarbonate membrane filter (Gelman Science, Ann Arbor, MI). Film samples were washed with 0.2*M* Na cacodylate three times, fixed in 1% osmium tetroxide with 0.1*M* Na cacodylate, and rinsed with 0.2*M* Na cacodylate and deionized water three times for each treatment. The samples were dehydrated by immersing in an ethanol–distilled water series of 40, 60, 70, and 80%, and 85, 90, 95, and 100% ethanol. Samples were stored in 100%

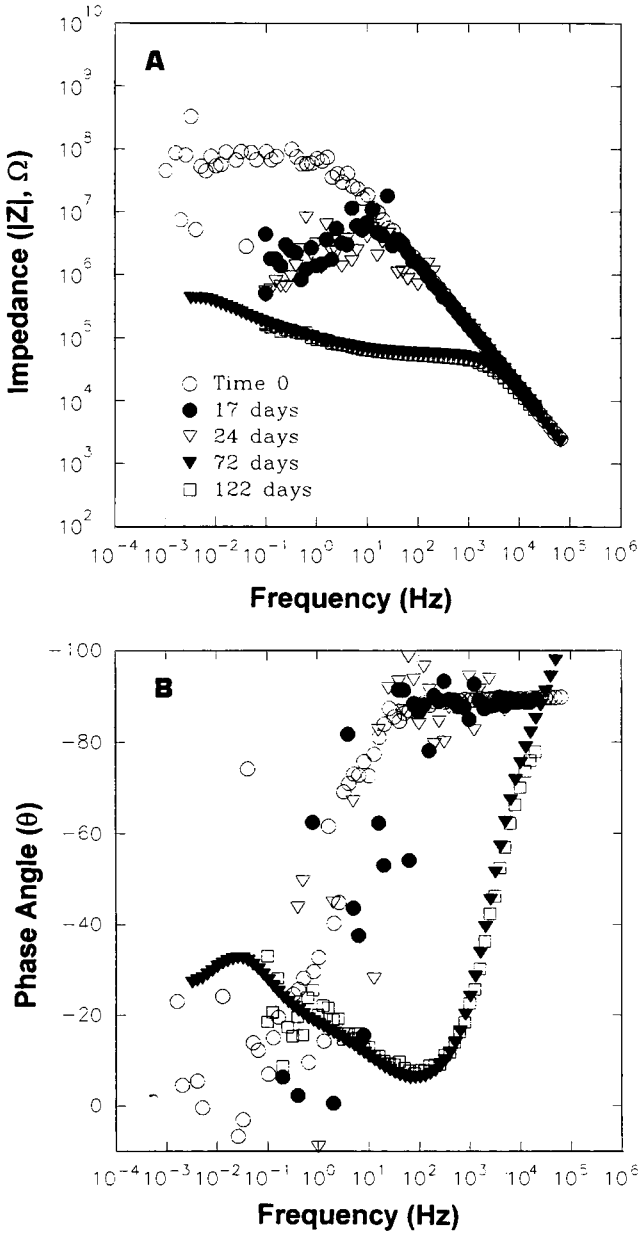

Figure 2 Bode magnitude (a) and phase angle (b) plots of polyimides inoculated with a fungal consortium incubated at ambient conditions.

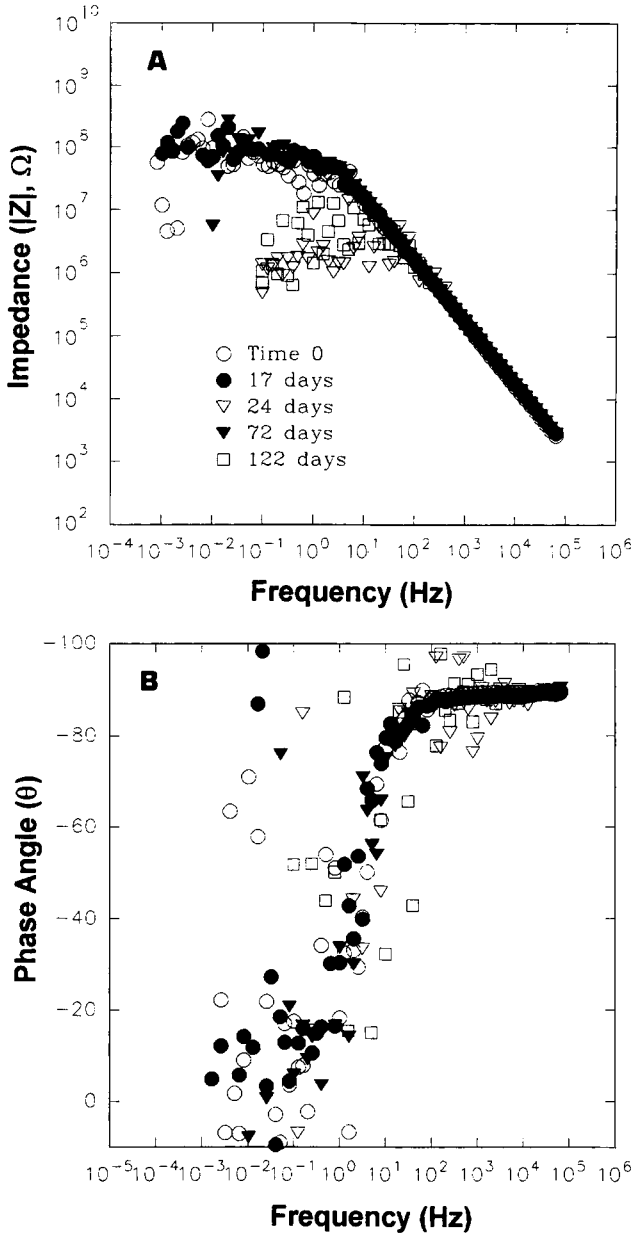

Figure 3 Bode magnitude (a) and phase angle (b) plots of sterile polyimides.

ethanol and airtight sealed glass vials before being critical-point-dried in liquid CO_2 (Smdri PVT-3B, Tousimis Research Co., Rockville, MD). Following drying, they were immediately coated with gold–palladium and viewed under an AMR 1000 scanning electron microscope.

RESULTS AND DISCUSSION

Impedance spectroscopy is the least destructive and most informative technique of electrochemical

analysis available for monitoring interfacial phenomena of polymeric coatings.[16–20] This technique has also been used effectively in the detection of microbial-induced degradation of polymeric protective coatings,[15] and fiber-reinforced polymeric composites.[10,12,21]

In the current study, degradation of polyimides was monitored in the inoculated and sterile EIS cells containing an 0.2*M* NaCl solution for 122 days of incubation at ambient temperature. Polyimides were fixed on a conductive stainless steel coupon in order to enhance current transfer crossing the polymer barrier (Fig. 1). No apparent difference in electrochemical responses between the inoculated and the sterile cells was observed at the initiation of the experiment, indicating the uniformity and excellent resistivity of the polyimide films [Figs. 2(a) and 3(a)]. However, a decrease of impedance in the lower-frequency region (10 to 10^{-2} Hz) was detected in the inoculated EIS cells after 17 days and in the sterile cells after 24 days. This initial decrease of pore resistance in both the inoculated and the sterile EIS cells was due to the adsorption of moisture and ionic species into the polymer matrix resulting in a decrease of the film resistivity. Inoculation of fungi enhanced this transportation process, probably as a result of fungal penetration into the polymer. However, this process was not as clearly identified in the Bode phase angle plots [Figs. 2(b) and 3(b)] as in the Bode magnitude plots [Figs. 2(a) and 3(a)], suggesting that the polymer was not being degraded in this first stage.

The second stage of decline in impedance, observed in the inoculated cells but not in the sterile control cells [Figs. 2(a) and 3(a)], signified a further decrease in capacivity of the polymer film. Impedance magnitude was decreased from 10^8 at time zero to below 10^5 in the inoculated EIS cells within 72 days. During the same period of incubation, spectra of the sterile cells did not change significantly. This second phase of decline was also reflected in the Bode phase angle plots, in which a second time constant was resolved, indicating the existence of at least one localized pore in the polymer. The presence of only one time constant in the

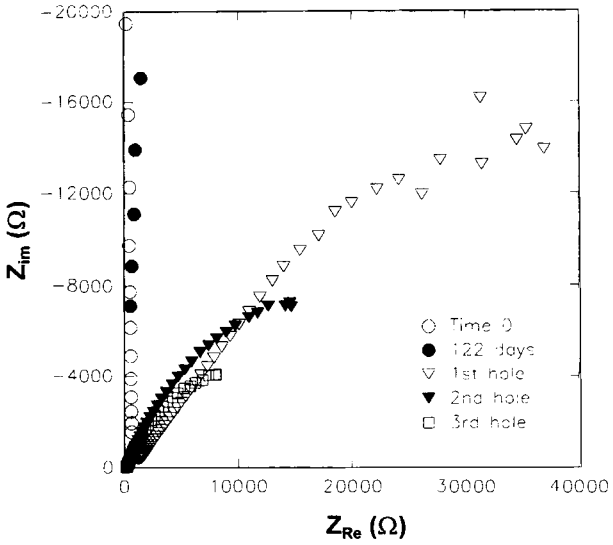

Figure 5 Nyquist complex plane plots from a sterile EIS cell that was intact after 122 days' exposure to sterile conditions and physically drilled with three needle-sized holes.

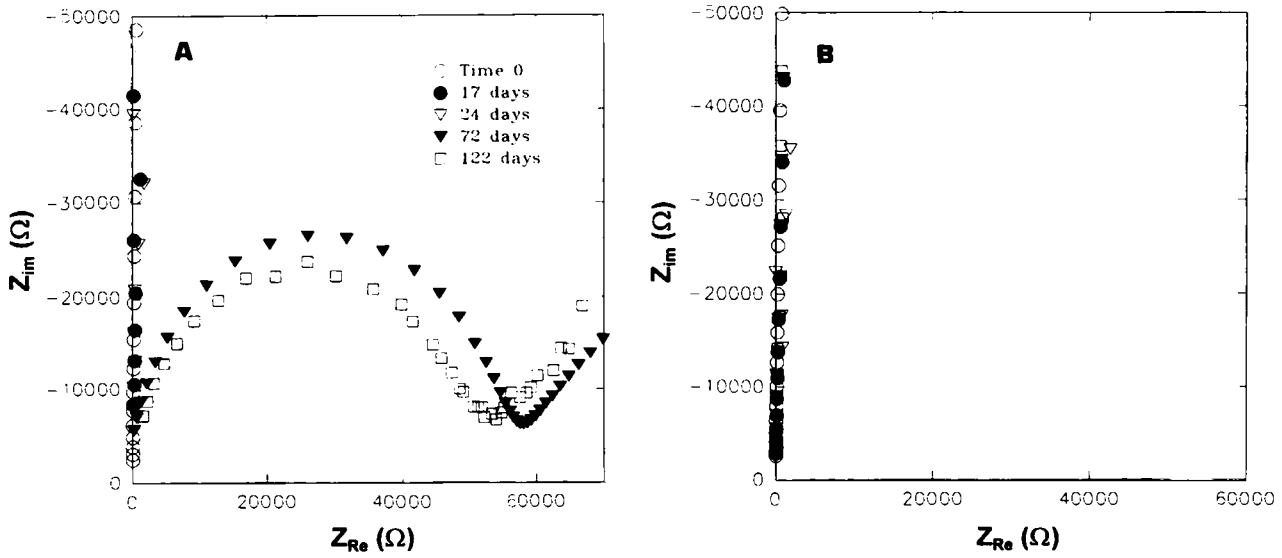

Figure 4 Nyquist complex plane plots from (a) inoculated EIS cells and (b) sterile cells.

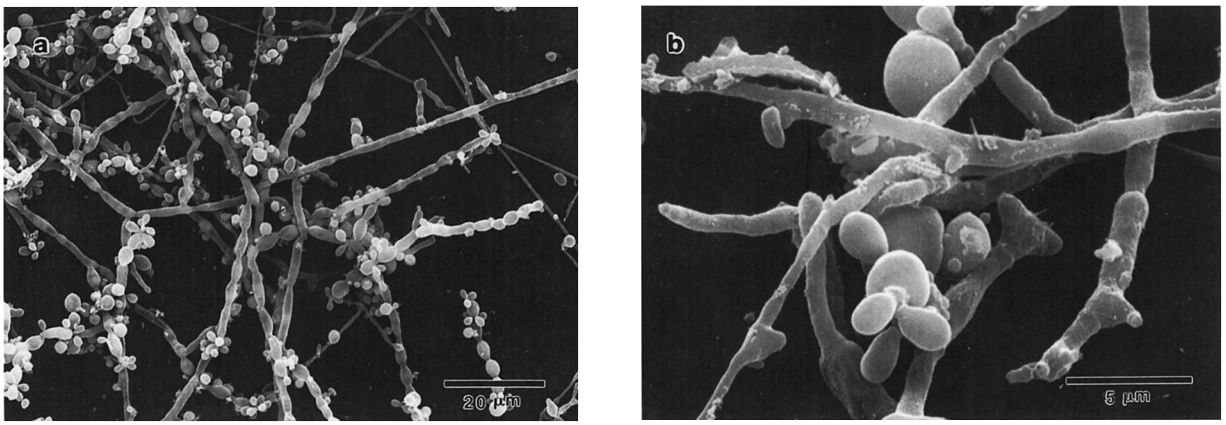

Figure 6 SEM micrographs of deteriorated polyimides from an inoculated EIS cell showing fungi growing on the polymer film.

sterile cells over the whole period of incubation supported the fact that the polymer was still intact. A high impedance value generally indicates that a coating is not defective.[22]

The Nyquist complex plane plots of the EIS cells contaminated with fungi clearly differed from those of the sterile EIS cells in that the semicircles were observed over the time of incubation in the former, specifically after 72 days [Fig. 4(a,b)]. The appearance of the semicircles coincides with the second time constant observed in the Bode phase angle plot, and also the second decline of impedance in the Bode magnitude plots of the cells containing fungi. However, similar results were not observed with our sterile EIS cells. Results of this study also showed significant semicircular compression from 72 days to 122 days, indicating the relationship between the semicircle compression and the severity of deterioration of the polymers.

The relationship between the decrease of pore resistance and polymer degradation in the presence of fungi was further demonstrated by drilling a series of needle-sized holes in the polymeric film that had previously been held in sterile conditions for 122 days and shown to be intact from its EIS spectra [Fig. 5(a,b)]. After each hole was drilled, electrochemical data from the damaged EIS cells were collected and analyzed for Bode magnitude and phase angle plots. When one needle-sized hole was created in the polymer, pore resistance decreased drastically. In response to the increased number of holes in the polymer, impedance spectra showed successive declines, but the difference between the intact and damaged film was much greater than that between the films with different numbers of holes. The effect of drilled holes in the polymer was also shown in the phase angle plots in which a second time constant was resolved in the saddle-shaped curves, indicating severity of damage of the polymer film. The damage by drilling was also reflected in the Nyquist complex plane plots, where the appearance and compression of the semicircles could be seen only after drilling. As the number of holes in a polymer increased, the radius of a semicircle tended to decrease (Fig. 5). Because of the physical nature of penetration, phase angle plots before and after drilling deviated greatly. These data provide insights into the nature and extent of the film biodeterioration after exposure to fungal contamination. As expected, the degree of damage by fungal activity was less severe than that by drilling, however continuous growth of the fungi would result in severe deterioration of the polymer, with disastrous consequences for the electronics.

Following our impedance studies, polyimide films from the inoculated and sterile EIS cells exposed to fungi for 122 days were examined by SEM in order to observe growth of fungi. SEM micrographs showing fungal colonization on polyimide surfaces from the inoculated cells are shown in Figure 6. In contrast, SEM micrographs of the sterile EIS cell polymer showed no fungal colonization (Fig. 7). The fungi were responsible for the deterioration of coating electrochemical properties as demonstrated by EIS. The species of fungi, *Aspergillus versicolor, Cladosporium cladosporioides,* and a *Chaetomium* species, were isolated and identified from a sample of the polyimide surface. All of these fungi are common in air and on surfaces.[4,8–15] Similar microorganisms have been isolated from electronic components, including magnetic disks.[5]

In conclusion, microbial degradation of the dielectric properties of polyimide insulators has been detected by analysis with EIS. Our data support the

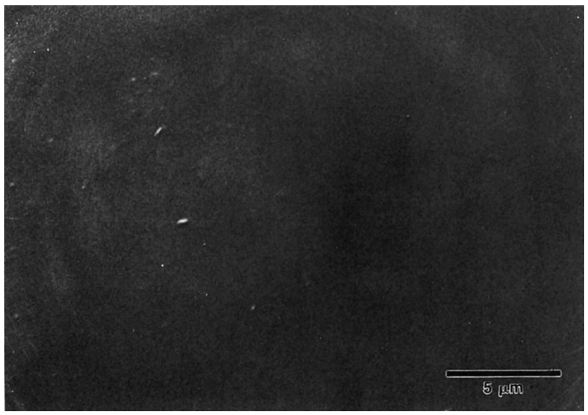

Figure 7 SEM micrograph of intact polyimides from sterile cells after 122 days of incubation.

view that electronic packaging polyimides are susceptible to attack by common airborne fungal species when the polyimides are exposed to moisture and atmospheric contamination.

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