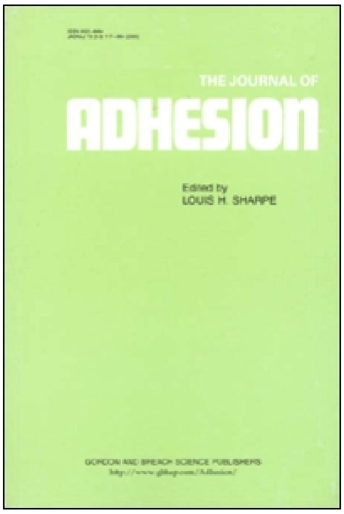

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Study of the Molecule-metal Oxide Interface using Inelastic Electron Tunneling Spectroscopy†

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Several examples in the application of inelastic electron tunneling spectroscopy (IETS) to study the molecular species which occur in adhesion, and in the corrosion and corrosion inhibition of aluminum in chlorinated hydrocarbons are reviewed. These examples illustrate some of the common aspects of the phenomena which occur at the metal oxide-organic interface in the areas of adhesion and corrosion. On a molecular level the concept of inhibition can be usefully applied to the areas of corrosion and adhesive failure.

INTRODUCTION

Information on the types of molecular species which exist at microscopic metal oxide–organic interfacial regions and the nature of their bonding to the oxide layer would be an important aid in the development of better theories for the mechanisms of adhesion and adhesive failure. Unfortunately, it is invariably difficult, and in many cases impossible, to obtain such information for several obvious reasons. One of the more important reasons is that the thickness of the interfacial region is on the order of 10 to 100 angstroms. Many of the experimental tools at our disposal cannot be used to "sample" such a thin region, and therefore do not possess the required sensitivity. For example,

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ultrasonic techniques play a very important role for investigation in a number of areas of adhesion, however, the characteristic wavelengths used are much too long to provide microscopic information at the bond line. Of those experimental tools which have the required sensitivity the number which can be used in *in situ* geometries are very limited in number and scope. Vacuum spectroscopies such as ESCA and Auger have given valuable information on surface species in a wide variety of investigations but are clearly not *in situ* probes. A program has been developed in our laboratory to study the molecular surface species which are formed on aluminum oxide when exposed to a variety of organics using inelastic electron tunneling spectroscopy (IETS). Although IETS is not an *in situ* tool it does provide information complementary to that obtained by other surface spectroscopies. In addition, it has several unique aspects—the most notable of which is its extreme sensitivity. A monolayer, or fraction thereof, can be easily detected using electronic modulation techniques. The great majority of IETS studies use aluminum/lead electrodes. The aluminum oxide surface can be formed in several ways, such as growing in either oxygen or air at ambient or at elevated temperatures, electrochemically, or in a low pressure oxygen discharge. The oxide can then be exposed or reacted with various organics. Although the oxide film formed by these techniques will not be identical to those often encountered in adhesive studies, there is evidence that many of the essential features of the oxide films are the same—at least with respect to the types of surface chemical species which are formed.

IETS involves the measurement of the electric current I associated with electrons which tunnel through an oxide film having an adsorbed molecular layer on its surface. Electrons which inelastically tunnel through the oxide excite the characteristic vibrations of the adsorbed molecules. Graphs of the second derivative d^2I/dV^2 versus the bias voltage V display large peaks centered at the voltage $V_m = h\nu_m/e$, where h is Planck's constant, e the electronic charge, and ν_m a molecular vibrational frequency. These graphs show peaks that can be associated with the presence of both infrared and Raman-like modes. The spectra can be used to identify molecular species on the oxide layer, estimate molecular orientation, and detect chemisorption bonding to the oxide layer.

During the past few years the potential of IETS as a diagnostic tool has begun to be realized. Since the technique is sensitive to the vibrations of molecules in close proximity to an oxide surface, it provides critically needed information to a large class of problems associated with molecular surface interactions on metallic oxide surfaces. Reported applications include studies of molecular adsorption,[1] identification of radiation damage of biological molecules,[2] molecular kinetics,[3] studies of catalytic particles,[4] thin polymer films,[5] corrosion,[6,7] corrosion inhibition,[8] and adhesion.[9]

The goal of this paper is to review the basic experimental and theoretical features of IETS as a spectroscopic tool and to discuss applications relevant to adhesion. The topics discussed include those on the general features of IETS and its application to studies of the molecular surface species associated with adhesion, corrosion and corrosion inhibition on aluminum oxide which have been made in our laboratory. The topics of corrosion and corrosion inhibition are very relevant to the topic of adhesion since one of the more important failure mechanisms for adhesively bonded structures is by chemical degradation at the bondline. This mechanism can be viewed as a corrosion process. Venables *et al.*[10] have shown that changes in the morphology of aluminum oxide is responsible for a large class of adhesive failures. This work strongly suggests that inhibition of the chemical activity associated with this process could extend bondlife considerably. Results on the comparison of experimental and calculated IETS peak intensities are also presented since this method shows promise of providing information on the type and orientation of inhibitor surface species.

GENERAL FEATURES OF IETS

There are several reviews of the general features of IETS.[11-13] Techniques used in our laboratory which are relevant to the results presented later are included in this section. The tunnel junctions employed were formed by deposition of about 1000 angstroms of aluminum on a glass or ceramic substrate. An oxide of approximately 20 angstroms was grown by glow discharge. The oxide forms a barrier to current flow. A dilute solution containing the molecular species to be studied was placed in contact with the oxide and the excess removed by spinning. A lead film was then deposited over this dopant which acted as a protective coating and was the second electrode during measurement of the spectra. Fortunately, this electrode does not perturb greatly the vibrational frequencies of the adsorbed molecules.

If a variable bias V is applied across the junction terminals the electrons can tunnel by an elastic mechanism without loss of energy, or by an inelastic process in which energy is lost. If the tunneling electron interacts with a molecule adsorbed on the oxide and excites one of the characteristic vibrational modes of the molecule, then the energy lost by the tunneling electron is $h\nu_m$. The threshold bias for such an inelastic tunneling event is $eV_{\text{threshold}} = h\nu_m$. Figure 1 shows a schematic for the cross section of a junction and the elastic and inelastic tunneling processes which can occur.

At a threshold voltage there is an abrupt change in the slope of the current–voltage characteristic of the tunnel junction. The detection of this effect can be greatly enhanced by using electronic modulation methods. The appearance of

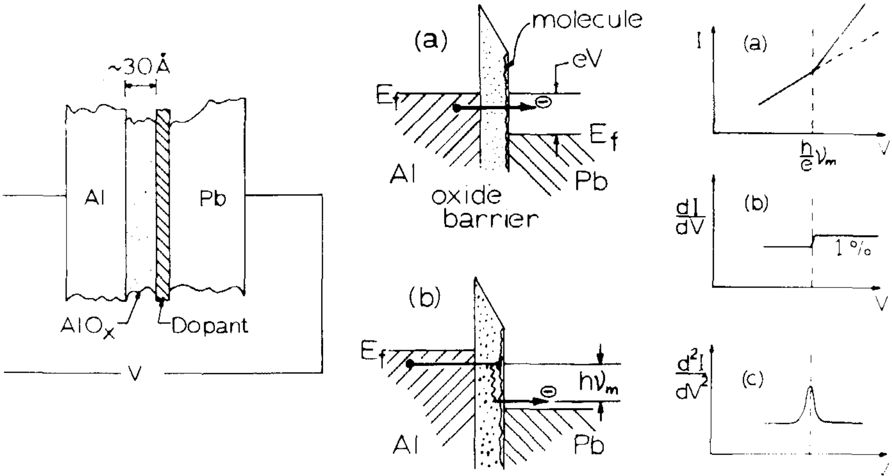


FIGURE 1 Schematics which illustrate the cross-section of a tunnel junction, the elastic and inelastic tunneling processes, and current–voltage features near the threshold voltage associated with the onset of inelastic tunneling for a mode.

d^2I/dV^2 (or d^2V/dI^2) *versus* V curves are very similar to optical spectra in that peaks in the IETS spectra correspond to the location of Raman and infrared active vibrational modes. Figure 1 shows the relevant features in the I, dI/dV and d^2I/dV^2 *versus* V curves associated with the threshold voltage. Figure 2 shows an IETS spectrum of benzoic acid taken in our laboratory. It illustrates the spectral range ($\sim$400 to 4000 cm^{-1}) and resolution which can be obtained. Typically the resolution in IETS is about 10 cm^{-1} for FWHM (full-width-at-half-maximum). Two major contributions to this width are those due to electronic modulation and finite temperature effects. Some reduction can be obtained by cooling the junctions to near 1°K. Inhomogenities in the substrate, the close proximity of two or more vibration modes for an adsorbed species, or the presence of several different surface species can cause the observed FWHM of certain peaks to be considerably more than 10 cm^{-1}. The fact that such a large signal-to-noise ratio could be obtained for approximately one monolayer coverage of benzoic acid demonstrates the sensitivity. IETS can be used to identify various interface molecular species by comparing the location of peaks in the d^2I/dV^2 *versus* V curves with available infrared and Raman spectra. There exists an orientational dependence of the intensity of vibrational modes which is observed by IETS. When the oscillating molecular dipole is oriented parallel to the oxide surface, the corresponding IETS intensity will be weak.[14] The intensity is expected to be large when the molecular dipole is perpendicular to the oxide surface due to strong excitation of "infrared" like modes.

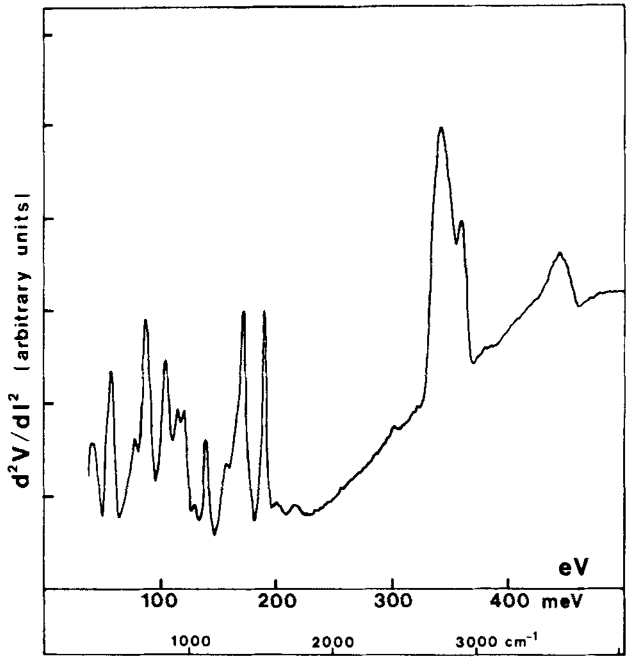


FIGURE 2 An IETS spectrum of benzoic acid adsorbed on aluminum oxide measured in our laboratory. The coverage is approximately one monolayer. The high signal-to-noise ratio indicates the sensitivity of IETS to adsorbed surface species.

To obtain spectra in our laboratory the junctions are placed on a Dewar insert and cooled to 4.2°K. A d.c. bias across the junction is swept slowly from 30 to 500 millivolts using the ramp output of a 2048 channel electronic signal averager. An a.c. modulation signal of 1000 Hz and about 2.0 millivolts (rms) is applied continuously. The amplitude of the second harmonic signal d^2V/dI^2 generated by the tunnel junction is recorded by the signal averager or a laboratory computer as a function of the applied voltage V. Peaks in this signal locate the energies of the vibrational modes as read from the measured bias voltage (energy) scale. The fact that measurements are made at 4.2°K rather than 300°K does not change the observed frequencies by any perceptible amount.

APPLICATIONS TO ADHESION AND CORROSION

It is reasonable to expect that information gained on surface species and the nature of the substrate-molecular bonding in one surface related phenomenon might have application to other areas which are also surface sensitive. Although there are obvious differences, it appears that this relationship does exist between adhesion and the areas of corrosion and corrosion inhibition. First, in the processes of adhesion, corrosion, and corrosion inhibition, thin chemisorbed surface layers are formed, all of which involve reactions between an oxide layer and a chemical molecular species. Hence, a study of the surface sites and mechanisms by which certain inhibitor molecules are chemisorbed to an oxide can have direct application to an investigation of bonding mechanisms by molecules which have groups with similar chemical features.

A second reason for this relationship is that the role played by the oxide, especially its mechanical integrity, is of paramount importance to both the inhibition of corrosion and the prevention of adhesive failure. The corrosion resistant properties of most metals are intimately connected with the formation and preservation of a passivating oxide layer. For aluminum this layer is approximately 20 angstroms thick. Thicker anodic films may be grown over this thin barrier layer, but they tend to be porous and therefore less protective against corrosion. Likewise, the surfaces of aluminum panels prepared for adhesive bonding have a thin, exposed oxide layer next to the metal, similar to the passivating oxide layer described, which is an integral part of thick films grown by one of the accepted methods (*e.g.*, FPL or PAA etches).[10]

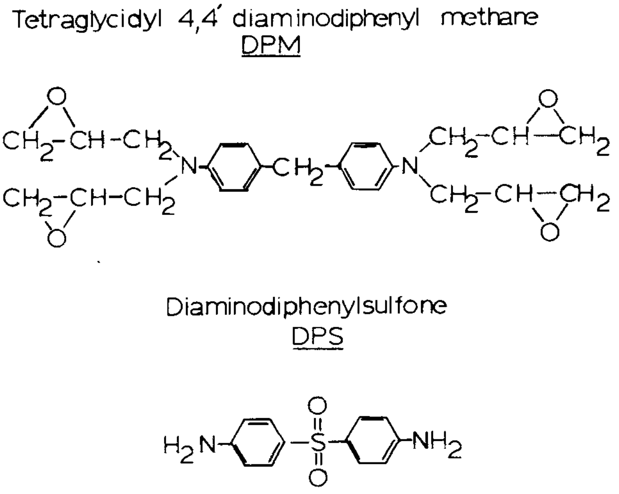
The remainder of this section is a brief discussion of work done in our laboratory on the applications of IETS to the study of adhesion, corrosion, and corrosion inhibition. A brief discussion is also included on comparisons of experimental and theoretical IETS peak intensities for formic acid. The goals of this latter work are to provide more specific information on the orientation of an adsorbed species relative to the oxide surface, and to allow a more quantative interpretation of IETS spectra.

Adhesion

Any tool or method which can be used to monitor the chemical state of an interface of the type encountered in adhesive bonding to aluminum would be of considerable benefit. For example, catalytic action at the bondline is recognized as a factor leading to a decrease in shear strength. Also, water at the interface is known to play a very important role in the failure mechanisms but to date there have been few good means of studying its effects. Since IETS data provide information on the vibrational frequencies of the first monolayer of adsorbed molecules, then to some limited extent, changes in the vibrational spectrum can be correlated with changes in the chemical state of the molecule/oxide interface.

In an effort to explore the potential of IETS for adhesive studies we have carried out IETS experiments on the components of the commercial adhesive, Hercules 3501.[9] Since much of this work has been reported earlier only a brief summary is given here. This epoxy system consists primarily of two molecular components; diamino diphenyl sulfone (DPS) and tetraglycidycl 4,4′ diamino diphenyl methane (DPM) which are shown schematically in Figure 3. IETS spectra of the individual components DPS and DPM, a deuterated sample of DPM, and of the epoxy mixture adsorbed on aluminum oxide were obtained and the vibrational modes and frequencies assigned by comparison with computer calculations and existing optical spectra. Some evidence for an aging effect was observed for the adsorbed DPS. This effect appeared as a dramatic change in the low frequency vibrational modes and may be associated with the formation of hydrogen bonds or the polymerization of the DPS. One of the primary difficulties encountered in these studies was that of obtaining junctions in the appropriate resistance range (50–500 ohms) which had good spectral resolution. This fact is undoubtedly related, in part, to the lack of purity of the components, and possibly to some polymerization which may have occurred in the DPM component prior to the doping process. The polymerization could cause the tunneling barrier to be non-uniform in thickness, which greatly reduces the signal-to-noise ratio.

Magno and Adler[5] have used IETS to study the molecular structure of barriers formed on aluminum and magnesium in glow discharge of ethylene and benzene. Such studies seem appropriate for the study of thin polymer films.



Tetraglycidyl 4,4′ diaminodiphenyl methane

DPM

Diaminodiphenylsulfone

DPS

FIGURE 3 Schematics of the two molecular components of the Hercules 3501 epoxy system.

Corrosion

IETS has been used in our laboratory to determine the molecular species which occur on an aluminum oxide surface during metallic corrosion by several chlorinated hydrocarbons. The chlorine radical is a particularly aggressive species. Results for carbon tetrachloride and trichloroethylene are given.

IETS spectra were obtained for spectroscopically pure CCl_4 adsorbed on aluminum oxide, and the observed vibrational modes were assigned by comparison with infrared and Raman frequencies for species which could reasonably be present.[6] In particular, we used the free radical reaction sequence proposed by Stern and Uhlig[15] as a guide. The reaction was shown to be,

$$2Al + 6CCl_4 \rightarrow 3C_2Cl_6 + 2AlCl_3, \qquad (1)$$

with the production of aluminum chloride and hexachloroethane. The corrosion rates for the liquid and vapor phases were similar. For this reaction Stern and Uhlig proposed a free radical mechanism with several intermediate steps which contained intermediate and final species such as $\cdot Cl$, $\cdot Cl_3$, AlCl, $AlCl_2$, $AlCl_3$ and C_2Cl_6. The reaction is initiated with homolytic cleavage of the C–Cl bond to produce the free radicals $\cdot Cl$ and $\cdot CCl_3$. Production of aluminum chloride $AlCl_3$ allows the subsequent formation of the complex $CCl_3^+[AlCl_4]^-$. The IETS data showed modes which could be associated with the molecular species CCl_4, AlCl, $AlCl_2$, $AlCl_3$, and C_2Cl_6. The fact that no modes were observed which would reflect oxygen–carbon bonding, and the presence of a large number of aluminum–chlorine modes suggest that the corrosion mechanism is by reaction of the solvent with exposed aluminum atoms. These exposed sites could occur at oxygen vacancies and other imperfections such as grain boundaries. IETS is one of the few techniques which has the required sensitivity to detect intermediate species.

Similar IETS studies on metallic corrosion by trichloroethylene have also been made.[7] The results indicated that the corrosive attack occurs by a two-step mechanism which could account for the fact that the corrosion rate of aluminum by trichloroethylene is lower than that of carbon tetrachloride which occurs by direct chemical attack. In the first step, trichloroethylene reacts with the aluminum oxide surface as follows:

$$AlOH + CHCl{=}CCl_2 \rightarrow AlOCH{=}CCl_2 + HCl \qquad (2)$$

The $AlOCH{=}CCl_2$ species has an enolate type bond. This intermediate surface product can react with hydrogen (*e.g.*, from the surface) to yield,

$$AlOCH{=}CCl_2 + 4\cdot H \rightarrow AlOCH_2{-}CH_3 + 2\cdot Cl; \qquad (3)$$

by successive removal of ·Cl radicals from the $AlOCH{=}CCl_2$ product. The extent to which this reaction proceeds is not known; therefore, the ratio of aluminum ethoxide species to species with Cl instead of H is not known.

It should be noted that Archer[16] has postulated that the product shown in Eqn. (2) could also undergo a reaction with trichloroethylene to form a dimer as follows:

$$AlOCH{=}CCl_2 + CHCl{=}CCl_2 \rightarrow CCl_2{=}CH{-}CCl{=}CCl_2 + AlO\cdot + \cdot H. \qquad (4)$$

A dimer of this type could leave the surface and not be observed by IETS, especially if the dimers were formed on surface sites which produced weak bonding. Such a reaction sequence is illustrated schematically in Figure 4a where the reaction of Eq. (4) occurs on Type II sites. The reaction in Eq. (3) is illustrated in Figure 4b as occurring at Type Ia sites which would bond more strongly to these species than do Type II sites. As noted above, the degree to which the reaction proceeds from the product to the final species, as illustrated in Figure 4b, could not be determined from the data. The final species is shown with complete hydrogenation. The formation of these species can precipitate

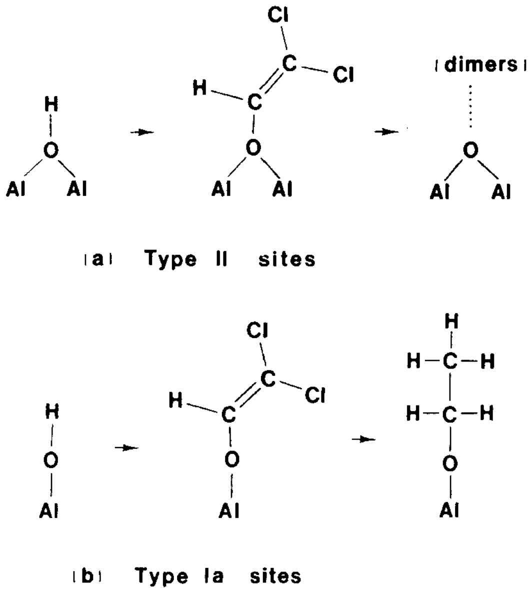


FIGURE 4 Schematics of the products formed by reaction of trichloroethylene with an aluminum oxide surface. In the sequence (a) the dimers formed at Type II sites may leave the surface. In (b) the sequence terminates with an aluminum ethoxide species. The degree of hydrogenation is not known.

aluminum corrosion by mechanisms in which the chlorine free radical reacts with exposed aluminum atoms at oxygen vacancies on the surface.

Corrosion inhibition

We have also determined the molecular species formed on aluminum oxide exposed to the corrosion inhibitor formamide.[8] Small concentrations of formamide on the order of 0.005% are known to inhibit the corrosion of aluminum by carbon tetrachloride and trichloroethylene. IETS spectra were obtained for formamide and its deuteroderivatives, and for dilute solutions of formamide in carbon tetrachloride. The spectra showed that formamide in the presence of carbon tetrachloride was preferentially adsorbed on the aluminum oxide surface. Although there is some ambiguity as to the exact nature of the bonding it appears to be *via* the nitrogen bond. This type of bonding indicated that the formamide surface species were chemisorbed at oxygen vacancy sites which have exposed aluminum atoms. Such exposed sites are known to be prevalent on aluminum oxide, especially along grain boundaries. A model was developed to describe the interaction of the formamide molecule with the oxide surface and to show how the formation of the formamide surface species could inhibit the corrosion of aluminum by chlorinated hydrocarbons by reducing the availability of reaction sites. We have more recently determined the surface species associated with several inhibitors which are effective in reducing the corrosion rate of aluminum in hydrochloric acid. As mentioned earlier, information on the mechanisms, molecular species, and bonding sites for molecules which are effective in preserving the integrity of aluminum oxide in various media are of considerable importance to the study of adhesive failure.

Comparison of experimental and calculated IETS intensities

The experimental and calculated IETS peak intensities for several vibrational modes of formic acid adsorbed on aluminum oxide have been compared.[17] The ultimate goal of this work is to allow one to utilize in a quantitative manner the relative peak intensities (area under peaks) in an IETS spectrum so that information about the orientation of an adsorbed molecular species relative to the oxide surface can be obtained. Such information is important since it appears that the steric arrangement of certain adsorbed species is very important to the mechanisms by which they can inhibit the reaction of the oxide with corrosive media. Orientational effects could also play an important role in the mechanisms associated with adhesion promoters and with chemical treatments which help preserve the structural integrity of the oxide. The spectra indicated that the formic acid adsorbed as a formate ion. The peak intensities were calculated using a partial charge model developed by Kirtley, Scalapino and Hansma.[14] Comparison of intensity values for the C—O and C=O modes for two orientations of the formate ion—with the C—O bond perpendicular to, and parallel to, the oxide surface—indicated that the formate ion was oriented perpendicular to the oxide surface. The agreement was not good for C—H modes, as expected, due to charge distortion along the C—H bonds which could not be taken into account with the model used. Additional work is continuing in this area to determine the surface species and orientation of thiourea. Preliminary results indicate that the sulfur bonds to the oxide, and that the S=C bond is nearly perpendicular to the oxide layer.[18]

SUMMARY

The technique of IETS for study of the molecule–metal oxide interface has been presented, and several examples have been given from studies in our laboratory on adhesion, corrosion and corrosion inhibition. These examples have been used to illustrate some of the common aspects of adhesion and corrosion phenomena at the molecular level. Information and concepts gained in studies of the mechanisms whereby aluminum oxide surfaces are made more immune to corrosive attack can be relevant to studies of the mechanisms of adhesive failure arising from changes in aluminum oxide morphology due to chemical activity at the bondline. The concept of inhibition can be useful to both the areas of corrosion and adhesive failure.

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