Application of the Dynamic SIMS Technique to the Study of Silicone Release Coatings*

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SYNOPSIS

Secondary ion mass spectrometry (SIMS) depth profiling has been used to determine elemental compositions of cured silicone release coatings as well as the location of controlled release additives (CRAs) in the cured polymer matrix. The two CRAs examined were found to be uniformly distributed throughout the matrix with no apparent increase at either the air or adhesive interface. As CRAs are required for tight release, this suggests that a minimum concentration at the surface is necessary but this concentration is not greater than that found in the bulk.

INTRODUCTION

Silicone release coatings are used in the manufacture of release liners and backings for adhesive labels and tapes.[1] Typical laminate construction of an adhesive label system is shown in Figure 1. The essential components of a UV-curable silicone release liner invented at GE are an epoxy functionalized silicone fluid and a compatible diaryliodonium hexafluoroantimonate photocatalyst.[2] Optional components include a photosensitizer, a controlled-release additive (CRA), and a reactive diluent. Controlled release additives are added to provide tight release. Unfortunately, the mechanism of tight release to adhesives induced by these CRAs is poorly understood. Three roles for the CRA can be envisioned. First, the molecule may interact with both the adhesive and the matrix to form a physical linkage between them. Alternatively, the CRA may alter the polymer morphology, thereby producing a material with greater intrinsic adhesion. Incorporation of the CRA into the matrix may also cause an increase in the polymer surface free energy. Of course, the role may be a combination of the three effects.

In order to more clearly define the mechanistic aspects of release, we decided to determine the location of several CRA models in cured release coatings by using the SIMS depth profiling technique. One would assume that if strong physical attractions between the adhesive and release coatings were necessary, an appreciable concentration of the CRA or the polar groups of the CRA, which are of necessarily higher surface free energy, would be found at the interface. Further, depth profiling would determine whether a concentration gradient exists at the interface.

As an analytical technique, SIMS is unsurpassed in its ability to detect a wide range of elements (hydrogen to uranium) at high sensitivity (ppb to ppm atomic) and provide 3-dimensional mapping of elemental composition.[3] The interaction of a 5–20 keV ion beam with a surface removes or sputters species characteristic of that material, e.g., neutral and charged atoms and molecular fragments as well as electrons and photons. SIMS involves a mass spectrometric analysis of the positive and negative atomic and molecular fragments. By monitoring one or more of these secondary ions as material is removed, one may obtain an in-depth analysis of the sample. The key to the profiling capability of SIMS is its shallow sampling depth, ca. 5–50 Å.

Although SIMS has found widespread application in inorganic solid state and semiconductor research,[4] a relatively few number of papers have involved analysis of organic and biological materials.[5] In most

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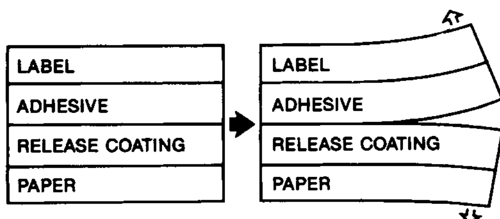


Figure 1 Typical laminate construction.

of these cases, static SIMS (low primary beam current density and energy) has been employed to detect molecular fragments from only the outermost monolayer(s) in order to obtain fingerprint mass spectra useful for characterizing the organic substrate. The lateral imaging capability of static SIMS has been recently demonstrated on organic surfaces by Briggs.[6] DiBenedetto and Scola used SIMS to depth profile an incompletely cured silane coating on glass.[7] Stein et al. used SIMS to determine the location of an adhesion promoter in a cured RTV matrix.[8] They found that the adhesion promoter was uniformly distributed throughout the matrix, with no preferential segregation at either the air or substrate interface.

We report SIMS in-depth profiling of two deuterated CRA models in a cured silicone release coating over distances of several micrometers. The advantages of using deuterium are twofold: (1) Deuterium at nominal *m/e* 2 is essentially free of any matrix interferences from the organic materials being studied; in fact, the limit of detection is governed by the natural isotopic abundance of deuterium found in the polymer. The relatively low secondary ion yield for H_2^- and the use of a mass-analyzed primary ion beam to reduce beam contaminants further aid in providing a high signal to noise ratio for deuterium detection. (2) As for many other labeling applications incorporating deuterium, little perturbation of the chemical system is expected by substituting deuterium for hydrogen. Hence, the rate of diffusion of a relatively large molecule with low deuterium content through a polymeric matrix will be the same as that of the hydrogen analogue.

RESULTS AND DISCUSSION

Model release coatings were prepared which incorporated either a premium release resin (UV9300), a deuterated CRA model or a combination of the two resins. SIMS test specimens were prepared by coating a glass slide with a thin film of the resin(s) or by spin coating the resin on top of a glass slide upon which had been placed an SBR adhesive, which was then cured and analyzed after approximately 1 week. A 300–500 Å gold overlayer was evaporated on the front face of the release coating to minimize charging of the sample surface region during ion bombardment (see Fig. 2).

A Cameca IMS-3f ion microscope was used to obtain depth profiles. Data were accumulated with a mass-analyzed primary beam of $^{16}O^-$ having an impact energy of 5.5 keV and a current density of ca. 3.5 mA/cm^2.

The intensities of negative secondary ions were measured. The pressure in the sample chamber during analysis was (2–3) $\times 10^{-8}$ torr. The primary beam was rastered over an area of $\sim 250 \times \sim 250$ μm with an analyzed area of 60 μm diameter as limited by the secondary ion optics. Sputtering rates of ca. 5 Å/s were obtained by ratioing the depth of each crater as measured by a profilometer to the total profile time. Analysis profiles ranged from 3 to 40 μm.

The depth profiles of C, H, Si, and D for a cured premium release coating (UV9300) which has not been enriched in deuterium are shown in Figure 3. It is apparent that the elemental composition re-

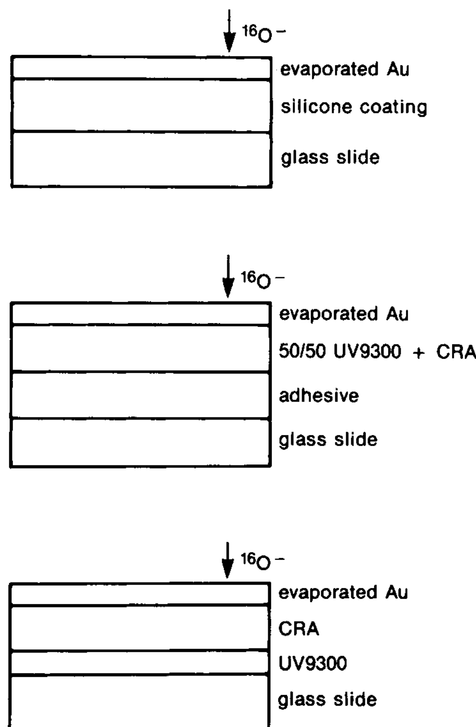


Figure 2 Depth profiles of release coatings: (A) depth profile of cured resin; (B) depth profile of cured blends on adhesive; (C) depth profile of layered resins.

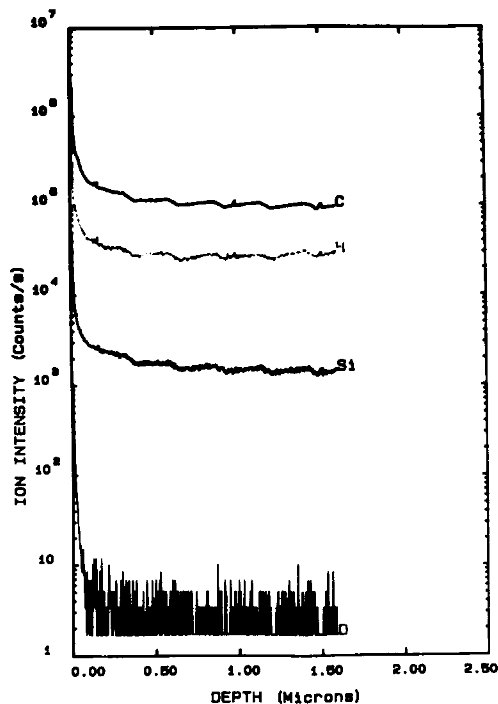


Figure 3 Depth profile of release resin with no CRA.

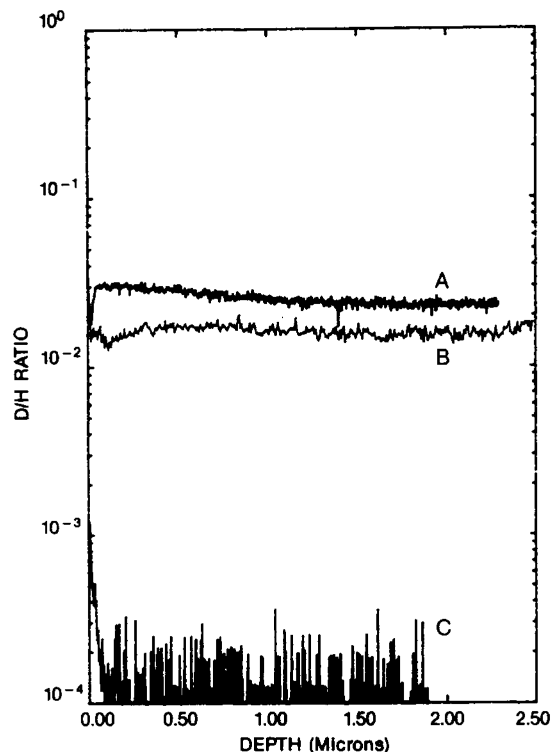


Figure 4 (A) 100% deuterated Model 1; (B) 50/50 blend Model 1/UV9300; (C) 100% UV9300.

mains constant throughout the profile. The observed D/H ratio, $\sim 1.5 \times 10^{-4}$, is equal to the ratio calculated based on the isotopic abundance of deuterium in hydrogen.

The elemental depth profile of a cured coating of deuterated CRA model (Model 1) prepared by reaction of $\frac{1}{2}$ of the epoxy groups in a silicone epoxy resin with deuterated benzoic acid is shown in Figure 4. Again the elemental composition remains constant as one profiles from the air interface into the release coating. The D/H ratio remains constant at 3×10^{-2}. The elemental composition of a 50/50 blend of UV9300 and deuterated Model 1 were also uniform throughout the depth profile. The D/H ratio of the blend is $\frac{1}{2}$ of that found in pure deuterated Model 1. Additionally, the D/H ratio of an 80/20 blend of Model 1 and UV9300 lies between that found for the 50/50 blend and pure Model 1. The results obtained by depth profiling films of a second model CRA, prepared by hydrosilylation with equimolar amounts of deuterated allylphenol and epoxy of a silicone hydride fluid (see experimental section) by itself or in blends with the premium release resin are analogous to those obtained with Model 1 (Fig. 5).

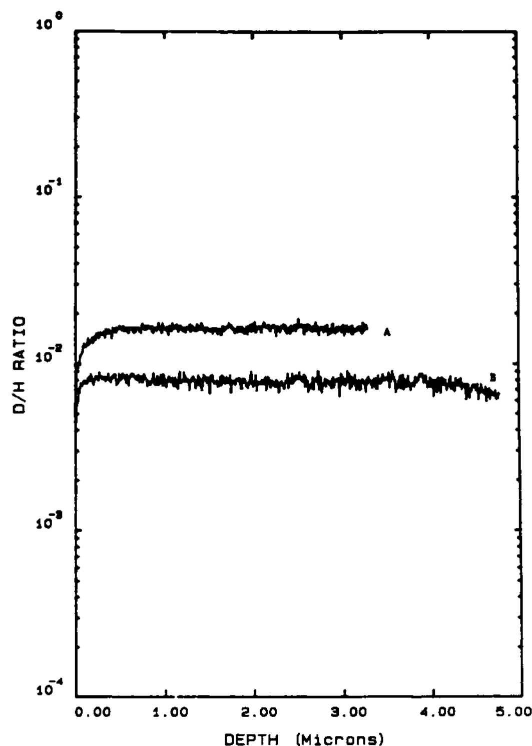


Figure 5 D/H ratios for: (A) 100% Model CRA 2; (B) 50/50 blend of UV9300/Model CRA 2.

Static SIMS experiments on UV9300, the deuterated Model 1 and a 50/50 blend of the two resins were also conducted. Static SIMS is an excellent

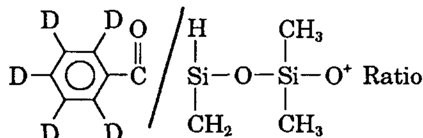
surface science technique for probing the elemental composition of the first few monolayers. A peak with m/e 110 was obtained with the deuterated benzoic acid derivatized resin and has been assigned to a C_6D_5CO fragment. This fragment is not present in the unlabeled epoxy resin, UV9300. This fragment is also present in a 50/50 blend of the two resins at a concentration exactly one half of that found in the deuterated Model 1. These data support our contention that the CRA is uniformly distributed throughout the matrix and does not segregate at the surface (see Table I).

In order to determine the elemental composition of the coating at an adhesive interface, a blend of UV9300 and deuterated Model 1 was spin coated onto a film of SBR adhesive on glass, cured, and then depth-profiled from the air interface, through the resin, and into the adhesive. Again no gradient is seen, indicating that neither the CRA nor its polar functionality preferentially segregate at the adhesive interface (Fig. 6).

Since the T_g of these coatings is well below room temperature, these results are not a consequence of limited skeletal flexibility. The depth profile of a coating prepared by first spin coating a 0.5 μm film of UV9300, curing followed by spin coating of a 1 μm film of deuterated Model 1 and curing did show a deuterium gradient over a 1.5 μm sampling depth indicating interpenetration of the two resins (Fig. 7).

Artifacts of the SIMS experiment may place limitations on the interpretation of these elemental depth profiles. Loss of resolution with increasing sputtering depth is certain. An optical micrograph is shown in Figure 8. Extensive beam damage of the crater is evident since cracking and rough topography are seen.

Table I Static SIMS of Silicone Release Coatings

Sample	 Ratio
UV9300	—
50/50 blend UV9300 and deuterated Model 1	0.11
Deuterated Model 1	0.23

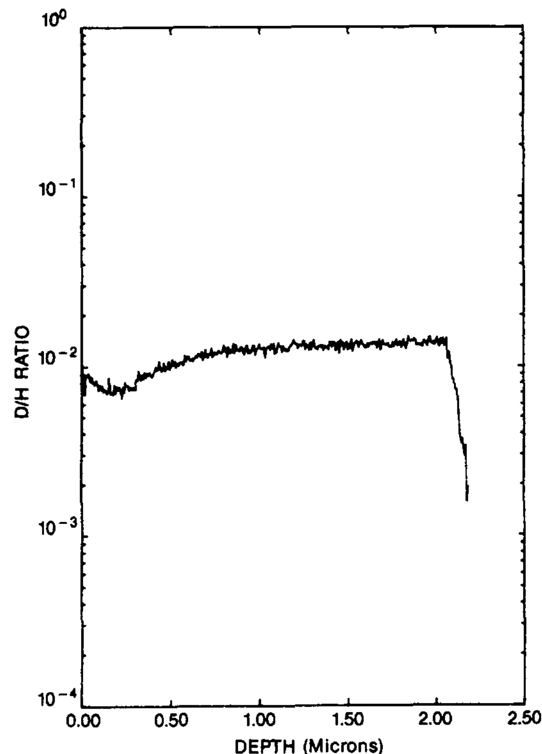


Figure 6 50/50 blend UV9300/Model CRA 1 on adhesive.

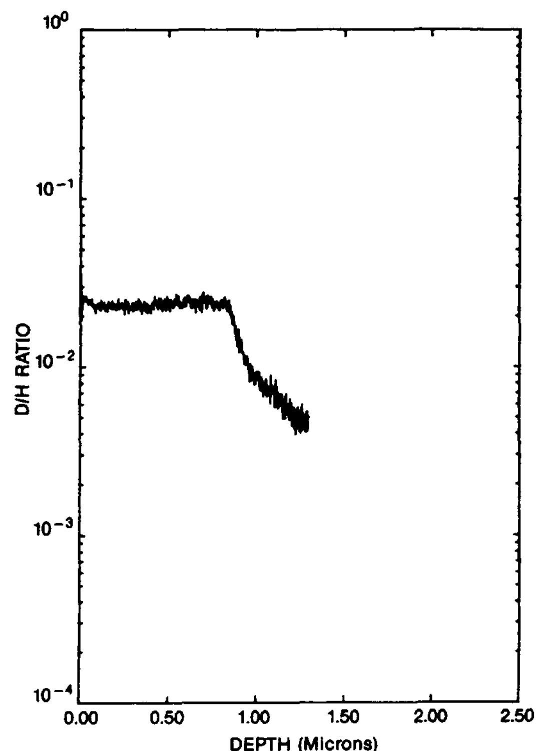


Figure 7 D/H ratio for deuterated Model CRA 1 on top of UV9000.

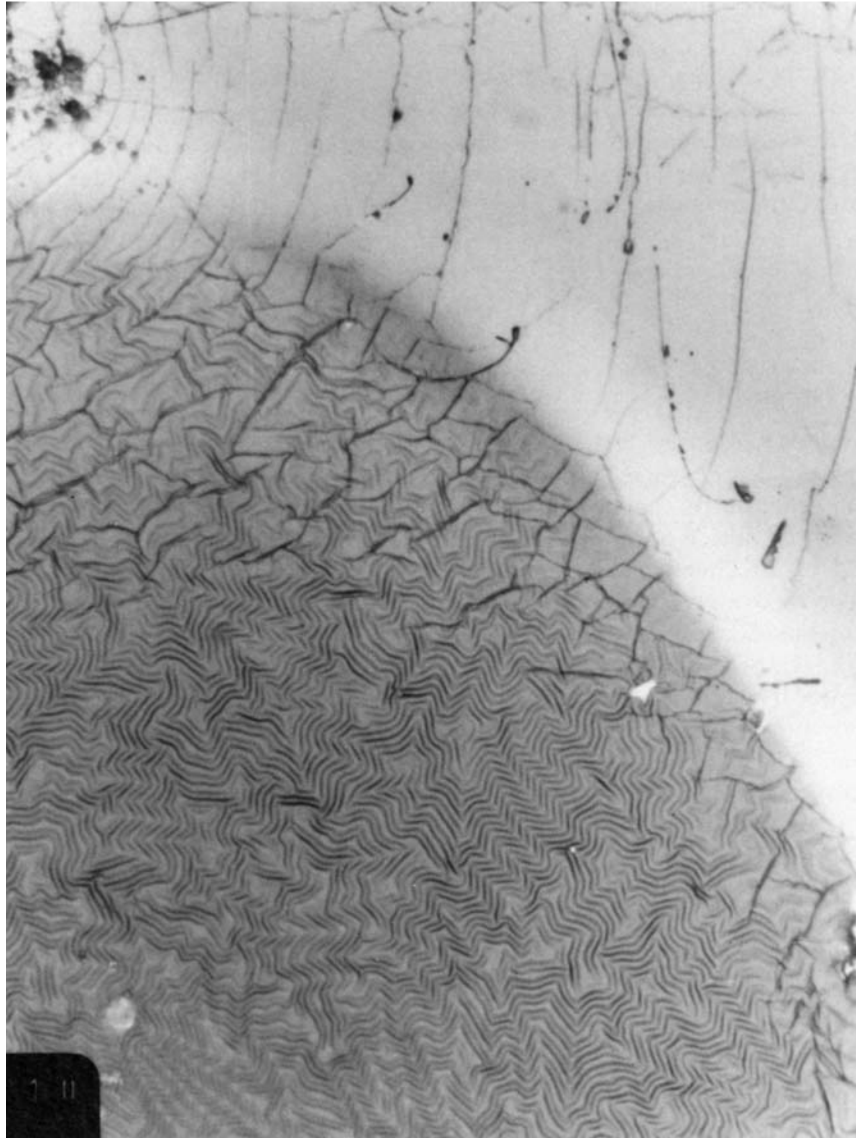


Figure 8 Optical micrograph of SIMS crater.

The results of small-spot ESCA of the crater and an unsputtered area are shown in Table II. The data in Table II indicate that the elemental composition of the two surfaces is different. In particular, there are two peaks for Si(2p) at the bottom of the crater whereas there is only one peak for siloxane backbone. Most likely, the second peak is associated with a more oxidized species such as SiO_2.

We have shown that CRAs are uniformly distributed throughout a coating and that the polar groups of high release resins do not preferentially migrate to the adhesive or air interfacial regions. These data complement results from pool data from the resins, which indicate that a minimum amount of CRA is necessary for tight release. We believe that coatings containing a tight release resin provide a lower interfacial tension with the adhesive. We are also currently investigating whether incorpo-

Table II Elemental Composition of Release Coatings Determined by ESCA Analysis

	Si(2p) (%)	C(1s) (%)	O(1s) (%)
Surface	26.3	50.8	23.0
BE (eV)	102.0	284.6 (97)	532.3
		286.0 (3)	
SIMS Crater	30.4	41.6	28.0
BE (eV)	102.1 (80)	284.6 (96)	532.4
	103.6 (20)	286.7 (4)	

ration of CRAs into release coatings alters the structure of the coating.

SIMS continues to be a valuable tool to employ when attempting to obtain elemental depth profiles of polymeric matrices. Continued effort must be maintained to determine how the ion beam–polymer interaction affects the interpretation of the analytical data obtained.

EXPERIMENTAL

Preparation of Deuterated Model 1

A 100-mL three-neck round-bottom flask equipped with stir bar, reflux condenser, thermometer, and pressure equalizing dropping funnel was charged with 60.0 g of a silicone hydride fluid (4.8% SiH), 30 mL toluene, and 0.2 mL drops of a Pt hydrosilylation catalyst. The mixture was heated to 65°C and 12.0 g vinylcyclohexeneoxide was added dropwise, maintaining the temperature below 70°C. The reaction was monitored by gas chromatography and infrared spectroscopy and was complete in 2 h. Then 0.5 g of hexene was added, followed by 0.03 g of mercaptobenzothiazole. Volatiles were removed under vacuum at 60°C. In order to prepare the deuterated resin, 11.11 g of the above resin, 1.0 g C_6D_5COOD (obtained from Aldrich Chemical Co.), and 5.56 mL of toluene were placed in a 100-mL flask equipped with stir bar, reflux condenser, and N_2 inlet and heated to 125°C for 24 h. The toluene was removed *in vacuo.*

Preparation of Deuterated Model 2

A 50 mL flask equipped with stir bar, reflux condenser, and N_2 inlet was charged with 5.0 g d_6 phenol (obtained from Aldrich Chemical Co.), 0.25 g Bu_4NBr, 10 g toluene, 10 g water, 2.8 g KOH, and 7 g allylbromide. The mixture was refluxed overnight after which GC analysis showed nearly complete consumption of phenol. The layers were separated, and the toluene layer was washed with several aliquots of water and the solvent removed *in vacuo.* The crude product was then refluxed overnight to effect conversion of allylphenylether to allylphenol. The deuterated allylphenol product was purified by column chromatography.

A three-neck flask equipped with stir bar, reflux condenser, and pressure equalizing dropping funnel was charged with 10 g silicone hydride fluid (4.8% SiH), 5 g toluene, and 0.2 mL Pt hydrosilation catalyst and heated to 70°C. Then 1.17 g d_4 allylphenol was added dropwise followed by 1.05 g vinylcyclohexeneoxide. The reaction was complete in 2 h. 0.10 g of hexene was added followed by 0.01 g dodecanethiol and 0.01 g tetramethylurea. The volatiles were removed at 120°C under vacuum.

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