

## An Investigation of the Distribution of Minor Components in Complex Polymeric Paint Formulations using ToF-SIMS Depth Profiling.

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### **Abstract:**

A series of complex polymeric paint formulations have been investigated by ToF-SIMS depth profiling. Employing a  $\text{Bi}_n^+$  analysis source and a Buckminster Fullerene ( $\text{C}_{60}$ ) etch source in the dual-beam mode of operation, depth profiles from poly(vinylidene difluoride) (PVdF), poly(urethane) (PU), polyester (PE) and epoxy based commercial coatings were obtained to determine the distribution of minor components included in the coating formulation.

The addition of small quantities of additives such as flow agents is known to induce significant changes in a paint's surface composition. Depth profiles were obtained from a PU primer formulation to which a  $^{35}\text{Cl}/^{37}\text{Cl}$  labelled flow agent had been added. The depth profiles show that the chlorine tagged component is confined to the surface region of the coating due to segregation of the flow agent to the air/coating surface. Depth profiles obtained from a PVdF topcoat formulation which included a hexamethoxymethyl melamine (HMMM) cross-linking agent demonstrate the

HMMM intensity is greater at the coating surface than in the bulk. The HMMM depth profile also reveals that the HMMM possesses a depletion zone between the coating bulk and the air/coating surface. Depth profiles obtained from both PE and epoxy primer formulations show that the concentration of inorganic particles included as pigments and anti-corrosion agents in the coatings is greater in the coating bulk than at the coating surface, demonstrating effective detection of these second phase particles, and that, as expected, they are properly dispersed in the organic phase. The results demonstrate that depth profiling of polymeric coatings, when employing a C<sub>60</sub> etch source, can be used to determine the distribution of minor components within cured coatings.

**Keywords:**

ToF-SIMS; polymeric coatings; depth profiling; C<sub>60</sub>.

**Running Headline:**

Distribution of Minor Components in Paints using ToF-SIMS Depth Profiling

## **Introduction:**

Today's coil coating formulations are a complex mix, typically consisting of some 15-20 different components. The bulk of the formulation comprises polymeric resins, pigments and solvents. However, many additives including pigment dispersants, flow-agents, corrosion inhibitors, cross-linking agents and matting agents can be added to the formulation to provide unique properties. Metal substrates such as galvanised steel and aluminium, protected by polymeric coil coatings, are used to manufacture a wide range of commercial and industrial products. Such products include architectural cladding, domestic appliances and caravans. Coil coatings are formulated such that they possess a wide range of diverse properties, and they must be able to withstand the deformation applied during the sheet forming processes without cracking or loss of coating-metal adhesion. Additionally, coil coatings are formulated so as to resist corrosion and photodegradation for 25 years or more. Because of these properties coil coatings are considered to be one of the most technologically advanced of all coatings/paint systems.

In this paper we investigate the distribution of minor components in a series of complex polymeric coating formulations including PVdF, polyester, polyurethane and epoxy coatings. SIMS depth profiling employing a  $C_{60}$  etch source was used to obtain the distribution of minor components within the coating formulations. Negative molecular ion, positive molecular ion and elemental ion depth profiles are presented to illustrate how this aim is achieved with  $C_{60}$  ToF-SIMS depth profiling.

## **Experimental:**

### Materials and Methods

The polymeric coating samples investigated here were prepared at Becker Industrial Coatings Ltd. The coatings used are based on commercial formulations. The samples provided were applied to aluminium panels using wire wound rods so as to achieve the correct film thickness. Full cure was attained by baking to the required peak metal temperature (where the peak metal temperature is the maximum temperature attained by the metal substrate just prior to extraction from the oven). The PVdF coating formulation contains a PVdF and plasticiser resin blended with acrylic copolymers to which a hexamethoxymethyl melamine cross linking agent was added. The PVdF coating employed in these studies was a clear coat formulation containing no pigments. The polyurethane coating formulation employed is based on a mixture of a blocked hexamethylene diisocyanate and an aromatic polyester resin to which was added a chlorine tagged acrylic flow agent. The polyurethane coating contained a yellow strontium chromate pigment. The epoxy primer coating is based on a high-molecular weight epoxy resin containing between 10 and 12 bisphenol-A moieties per molecule, cross linked with a urea-formaldehyde resin. The epoxy coating contained a yellow strontium chromate corrosion inhibitor pigment. The polyester coating is a standard polyester-melamine topcoat based on an isophthalate and neopentyl glycol backbone. The polyester coating contained a titanium dioxide pigment. For reasons of commercial confidentiality it is not possible to give complete formulations for the polymeric coatings employed in these studies.

## ToF-SIMS Analyses

ToF-SIMS analyses were carried out on an ION-TOF GmbH (Münster, Germany) TOF.SIMS 5 system. The instrument is equipped with a reflectron type analyser and microchannel plate detector. A  $\text{Bi}_n^+$  liquid metal ion source (LMIS) was employed for mass spectral data acquisition. SIMS spectra were acquired using the  $\text{Bi}_3^+$  cluster ion, data acquisition was performed by raster scanning the  $\text{Bi}_3^+$  primary ion beam over a  $100 \times 100 \mu\text{m}^2$  area. A 25 keV  $\text{Bi}_3^+$  primary ion beam delivering 0.3 pA of current was used, at a cycle time of 100  $\mu\text{s}$ . A  $\text{C}_{60}$  ion source was employed as the etch tool. The area analysed by the  $\text{Bi}_n^+$  LMIS was at the centre of the etch crater formed using the rastered  $\text{C}_{60}$  beam. The Buckminster Fullerene ions are produced by electron impact ionisation of a  $\text{C}_{60}$  vapour. The  $\text{C}_{60}$  source produces both singly and doubly charged  $\text{C}_{60}$  ions, only the  $\text{C}_{60}^+$  ion was used for etching in the depth profiling experiments described here. A 10 kV, 11 nA  $\text{C}_{60}^+$  primary ion beam with a fluence of  $1.5 \times 10^{14}$  ions  $\text{cm}^{-2}$  was employed, over an area of  $400 \times 400 \mu\text{m}^2$ , and an etch step of between 0.01 s and 0.1 s was used. The depth profiling analyses were performed in the ‘non-interlaced’ mode, that is, repeat cycles of mass data acquisition by the  $\text{Bi}_n^+$  LMIS, etch by the  $\text{C}_{60}$  source, followed by charge compensation using a low energy electron flood gun were employed. Estimation of the  $\text{C}_{60}$  etch rate for the PVdF based coating employed here (obtained using a surface profilometer), suggests an etch rate of  $\sim 3 \text{ nm s}^{-1}$  for the  $400 \times 400 \mu\text{m}^2$  etch area and instrumental conditions used in this work.

## Results and Discussion:

A range of polymeric materials including acrylics, polyesters, vinyls, polyurethanes, epoxies and fluorocarbons are employed in different coil coating formulations. In Figure 1 negative ion ToF-SIMS depth profiles ( $C_{60}$  etch step of 0.01 s) obtained from a poly(vinylidene difluoride) (PVdF)/acrylic copolymer based formulation are presented. In a previous publication <sup>(1)</sup> we demonstrated that a similar coating consisted of 3 distinct layers. A flow agent layer at the air/coating surface, an acrylic copolymer-rich sub-surface layer and a homogenous PVdF/acrylic bulk layer. In Figure 1 the  $F^-$ ,  $CF^-$  and  $C_5F_2^-$  fragments are derived from the PVdF resin component of the formulation whilst the  $C_4H_5O_2^-$  anion is diagnostic of poly(methyl methacrylate) (PMMA), the major constituent of the acrylic copolymer component of the formulation. The  $F^-$ ,  $CF^-$ ,  $C_5F_2^-$  and  $C_4H_5O_2^-$  depth profiles of Figure 1 have similar shapes to those previously reported indicating the distribution of the PVdF and acrylic copolymer in this coating is consistent with those described in our previous work <sup>(1)</sup>. However, in the coating of Figure 1 the flow agent was excluded but an additional component, a hexamethoxymethyl melamine (HMMM) cross linking agent, was included in the formulation. The  $C_3H_2N_2^-$  ion at  $m/z$  66 is diagnostic of HMMM <sup>(2)</sup> and the depth profile obtained from this ion in Figure 1 reveals the distribution of the HMMM cross linking agent within the coating. The HMMM constitutes < 1.5% by weight of the cured coating. The  $C_3H_2N_2^-$  depth profile in Figure 1 demonstrates the cross linker is in greatest concentration at the surface of the coating. The HMMM concentration then decreases with depth into the coating before reaching a stable concentration in the coating bulk (after ~1s acquisition time). It is also observed that the  $C_3H_2N_2^-$  depth profile exhibits a small depletion zone at ~0.8 s of acquisition time. Figure 1 clearly demonstrates that SIMS depth profiles can be obtained for minor organic components in complex polymeric coating formulations and the distribution of such components determined. The segregation of the acrylic resin to the surface is consistent with a front of PVdF/acrylic alloy cooling and pushing excess acrylic ahead of it. The increased melamine concentration will improve surface hardness. These results demonstrate the complexity of the dynamic processes that are ongoing during formation of the final polymeric coating system.

This complex set of processes involves solid PVdF dissolving into the acrylic resin solution at elevated temperatures, the cross linking and self condensation of the melamine with the resin and itself respectively, the evaporation of the solvents included in the formulation and finally the morphology changes that occur upon cooling.

In Figure 2 positive ion ToF-SIMS depth profiles ( $C_{60}$  etch step of 0.1 s) obtained from a polyester based coating formulation containing a  $TiO_2$  pigment are presented. The polyester component employed is phthalate based and the  $C_6H_5^+$  and  $C_7H_4O^+$  cations are diagnostic of the phthalate component of the polyester resin employed. It is observed in Figure 2 that the polyester component of the coating exhibits a concentration maximum at the air/coating surface and that the concentration of the polyester decreases with depth before reaching a stable concentration in the coating bulk (after ~50 s acquisition time). Conversely the  $Ti^+$ ,  $^{50}Ti^+$  and  $Ti_2O_2^+$  depth profiles in Figure 2 (derived from the  $TiO_2$  based pigment)<sup>(3)</sup> are at their lowest concentration at the air/coating surface. The titanium based depth profiles then show increasing concentration with depth before a stable concentration is reached in the coating bulk (after ~60s acquisition time). It is not normal for pigments to be detected at the surfaces of un-weathered coatings as there is normally a layer of flow aid at the immediate surface under which there is a layer of resin surrounding the  $TiO_2$  particles. It is perhaps unfair to describe  $TiO_2$  pigments as minor components in coil coatings as they may account for more than 20% by weight of the cured coating. However, due to the photocatalytic activity associated with  $TiO_2$ , these pigments are formulated with a  $TiO_2$  core surrounded by a silica/alumina layer. Furthermore,  $TiO_2$  is typically incorporated into coatings in the form of particles 200-300nm in diameter. Given the analysis depth of ToF-SIMS (~1 nm) SIMS mass spectra do not usually contain titanium from the pigment as the titanium is too deeply buried within the particle. However, Figure 2 would suggest that the  $C_{60}$  etch source is able to remove the outer silica/alumina shell of the particle thus permitting access to the  $TiO_2$  core allowing the distribution of the  $TiO_2$  pigment to be determined.

Elemental, negative ion depth profiles ( $C_{60}$  etch step of 0.1 s) for  $C^-$ ,  $O^-$  and  $Cl^-$ , obtained from a poly(urethane) based coil coating formulation, are shown in Figure 3. In this particular formulation an acrylic based flow agent tagged with chlorine was included in the formulation. The  $O^-$  and  $C^-$  depth profile of Figure 3 possess very stable intensities suggesting a stable concentration of these elements with depth. The  $^{35}Cl$  and  $^{37}Cl$  depth profiles in Figure 3 however demonstrate concentration changes with depth. The high surface concentration of the chlorine is expected due to the nature of flow agents segregating to the air/coating interface, ensuring a surface free energy that is everywhere the same with the consequence that flow defects are minimised. They function on the basis of marginal compatibility and low surface free energy. The fact that chlorine is detected throughout the bulk indicates that this particular flow aid is very compatible with the paint, but at the extremities the low surface free energy enhances the concentration of this component at the surface, resulting in a depletion layer just below the surface. It is uncertain whether or not the chlorine tagging has altered the polarity of the molecule to such an extent that the compatibility with this particular formulation has improved. If this is the case, then its effectiveness as a flow aid could be compromised.

Coil coatings are formulated so as to provide a variety of properties, in Figure 4 positive ion depth profiles ( $C_{60}$  etch step of 0.05 s) obtained from an epoxy based primer coating are presented. In the epoxy coating formulation investigated here a strontium chromate ( $SrCrO_4$ ) pigment has been included as a corrosion inhibitor. Such corrosion inhibitors typically work by transport of the  $Cr(VI)$  to the metal surface on exposure to water, where the  $Cr(VI)$  is reduced to  $Cr(III)$ . Thus strontium chromate operates as an anodic inhibitor. The epoxy of Figure 4 is based on bisphenol A and the  $C_6H_5^+$  and  $CH_3O^+$  depth profiles in Figure 4 emanate from this polymeric component of the coating <sup>(4)</sup>. The  $C_6H_5^+$  and  $CH_3O^+$  depth profiles of Figure 4 show the polymeric component of the coating is at its highest concentration at the air/coating surface and possesses a stable, if lower, concentration in the coating bulk. Included in Figure 4 are depth profiles obtained for the  $Cr^+$  and  $Sr^+$  ions from the corrosion inhibitor pigment included in the formulation. It was anticipated that



strontium and chromium being from an inorganic pigment in a polymeric coating would possess similar distributions and result in depth profiles possessing similar shapes to those observed for the TiO<sub>2</sub> pigment species in Figure 2. This is indeed the case for Sr<sup>+</sup> whose distribution clearly shows greater intensity in the bulk than at the coatings air/coating surface. However, the Cr<sup>+</sup> depth profile in Figure 4 is drastically different to that of Sr<sup>+</sup> with Cr<sup>+</sup> being at its highest intensity at the air/coating surface of the coating, indeed the intensity of chromium is some 10 times that of strontium at the air/coating surface. The Cr<sup>+</sup> intensity then falls with depth before reaching a stable but lower intensity in the coating bulk. The reason for this separation of Sr<sup>+</sup> and Cr<sup>+</sup> within the polymeric matrix of the coating is as yet unknown but may be associated with the ready movement of Cr(VI) in paint films. It is not normal for pigments (as in Figure 2) and corrosion inhibitors (as in Figure 4) to be detected by SIMS at the air/coating surface and to give non-zero initial intensities. This indicates that sample etching occurs prior to initial mass data acquisition, which makes possible the initial non-zero intensities observed in Figures 2 and 4 for pigments and corrosion inhibitors respectively. However, the depth profiles in Figure 4 clearly demonstrate that the distribution of inorganic pigments such as corrosion inhibitors can be determined using SIMS depth profiling employing appropriate analysis and etch sources. The dissociation of the strontium and chromium though begs a resolution to the question the fate of the counter-ions on coating application.

### **Conclusions:**

We have demonstrated that SIMS depth profiling, when using a C<sub>60</sub> etch source, can be used to obtain depth profiles from a variety of polymeric coatings. Furthermore, we show that the distribution of minor organic and inorganic components included in a coating formulation, such as cross linking agents, pigments, flow agents and corrosion inhibitors, can be determined employing SIMS depth profiling.

## **Acknowledgements;**

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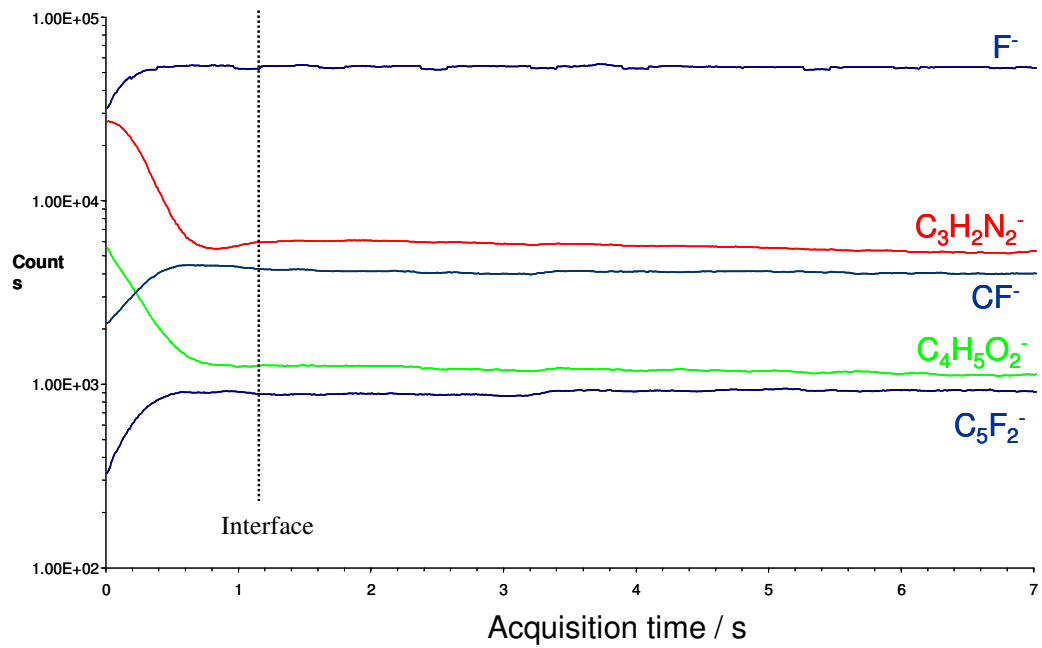


Figure 1. ToF-SIMS depth profiles obtained from the air/coating surface of a PVdF topcoat formulation to which an HMMM cross-linking agent was added.

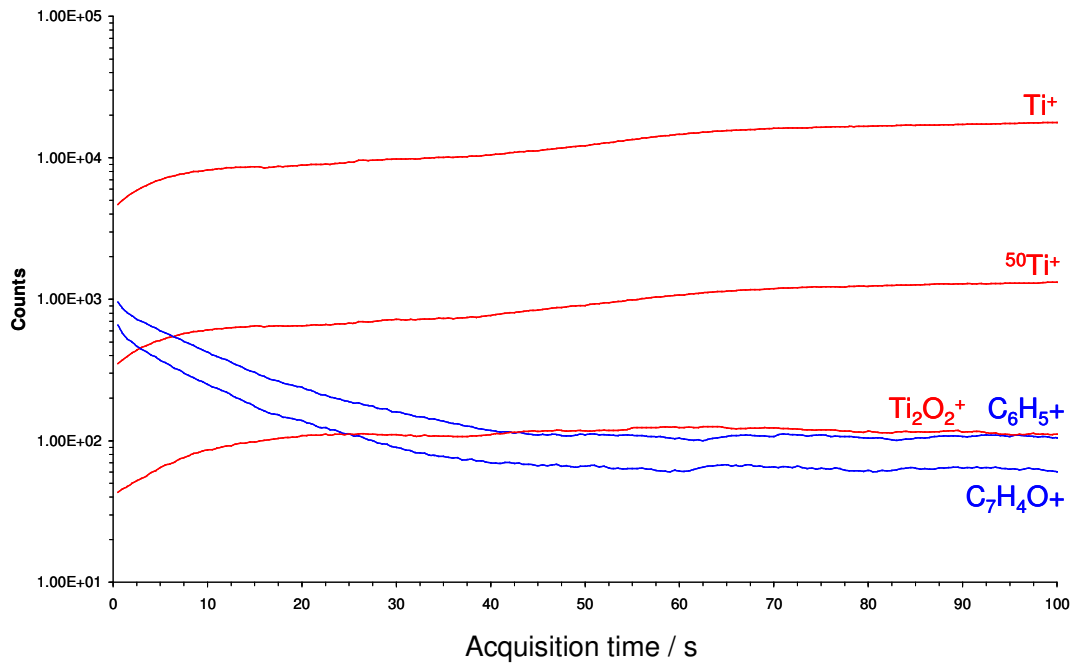


Figure 2. ToF-SIMS depth profiles obtained from the air/coating surface of a polyester formulation demonstrating the distribution of species derived from the inclusion of TiO<sub>2</sub> pigment in the formulation.

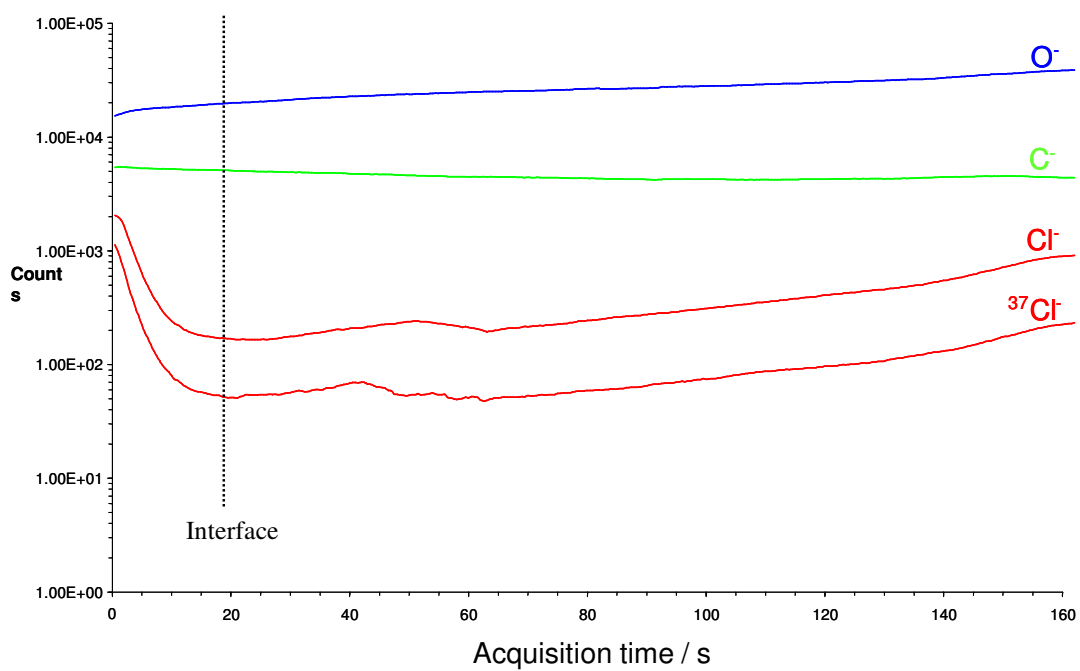


Figure 3. ToF-SIMS depth profiles obtained from the air/coating surface of a polyurethane formulation demonstrating the distribution of carbon, oxygen and chlorine ions derived from the inclusion of a chlorine tagged flow agent in the formulation.

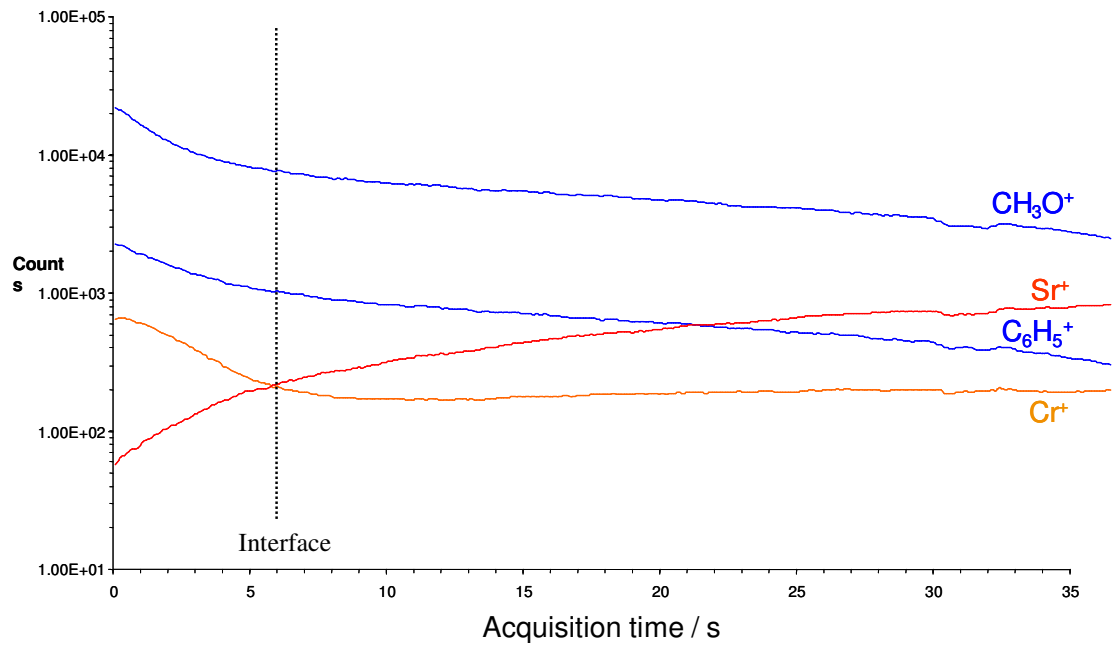


Figure 4. ToF-SIMS depth profiles obtained from the air/coating surface of an epoxy formulation demonstrating the distribution of Sr<sup>+</sup> and Cr<sup>+</sup> ions derived from the inclusion of a strontium chromate based corrosion inhibitor in the formulation.