University of Surrey
The Surface Analysis Laboratory

The Effect of Corona Discharge Treatment on a Commercial Polyester Coil Coating

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ECASIA '13

Cagliari, Sardinia Italy
13th – 18th October 2013

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Sandwich Panels

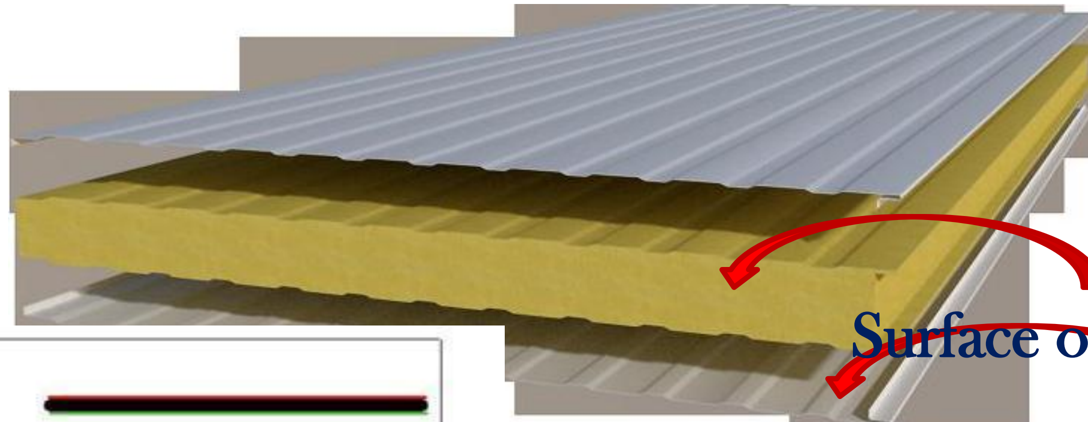
From Huntsman (2002)

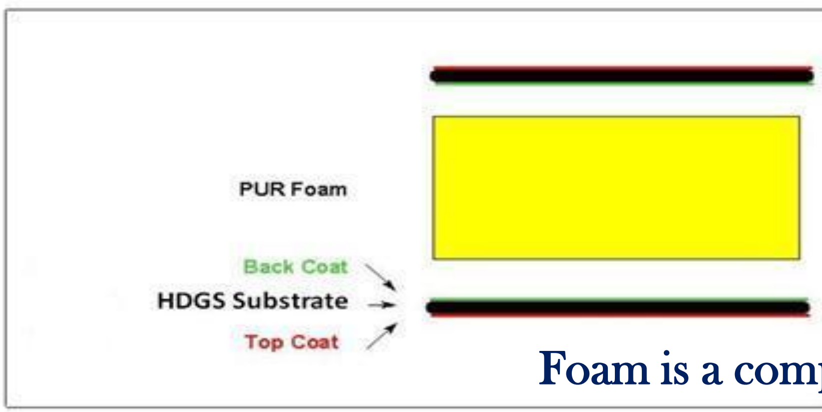
- **High insulation** properties coupled with **low relative thickness** due to significantly lower thermal conductivity
- **Efficient and fast manufacturing** with the **high-throughput** ability to foam onto coil stock in a **continuous lamination** process forming the finished product
- Potentially high levels of **quality** due to the ability to **manufacture** in a factory environment in an **automated process**
- **Low sandwich panel mass** due to **low density** of the **foam,** reduces the **structural requirements** and thus **costs** for the frame supports in the building
- **Faster building** erection times with **pre-formed components**

Many **millions** of **square metres** of **coil coated stock** used in this application

The Production Process

From ArcelorMittal (2011)

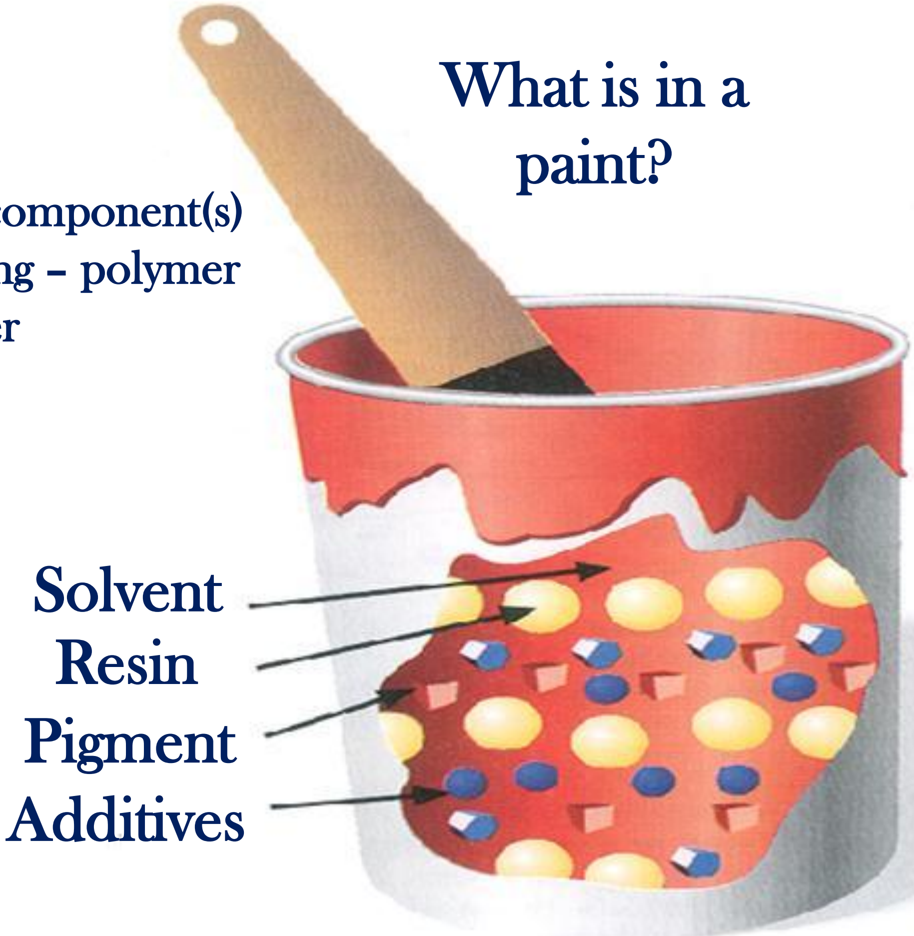




Foam is a complex commercial formulation consisting of many components but in current work we are interested in the effect of corona discharge treatments on the back coat of the coil coated stick: i.e. the surface to which the foam adheres when the sandwich panel is manufactured

Coil Coatings

What is in a paint?



Resin

Polymeric component(s) of the coating – polymer + crosslinker

Solvents

Dissolves the polymeric and other constituents
Evaporates on curing

Additives (including the following)

Anti-corrosive pigments
Flame retardants
Fillers
Surfactants
Flow control aids
UV protective agents

Pigment

Inorganic and/or organic pigments
Principally rutile TiO_2 – for current coating

Adhesion Enhancement

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Corona discharge treatment (CDT) improves performance

It occurs in an in-line process seconds before the application of the polyurethane foam

To understand the nature of the chemistry and also establish the consistency of the sample surface untreated samples of galvanised steel coated with 7µm of a commercial formulation of polyester/melamine/epoxy back-coat were first examined by XPS

Uniformity Test 1

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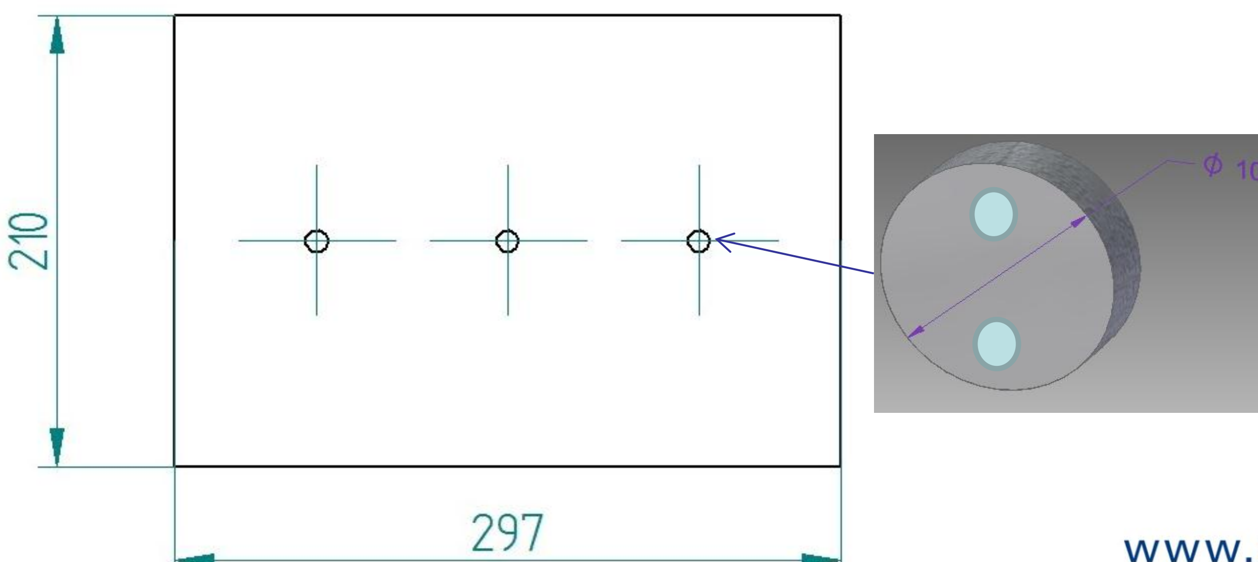
Samples were taken from:

- 3 Regions ca. 5cm apart
- 2 Sampling points per region ca. 5mm apart
- (6 analyses total)

A ThermoScientific Theta Probe spectrometer was utilised with a 400μm radius spot size

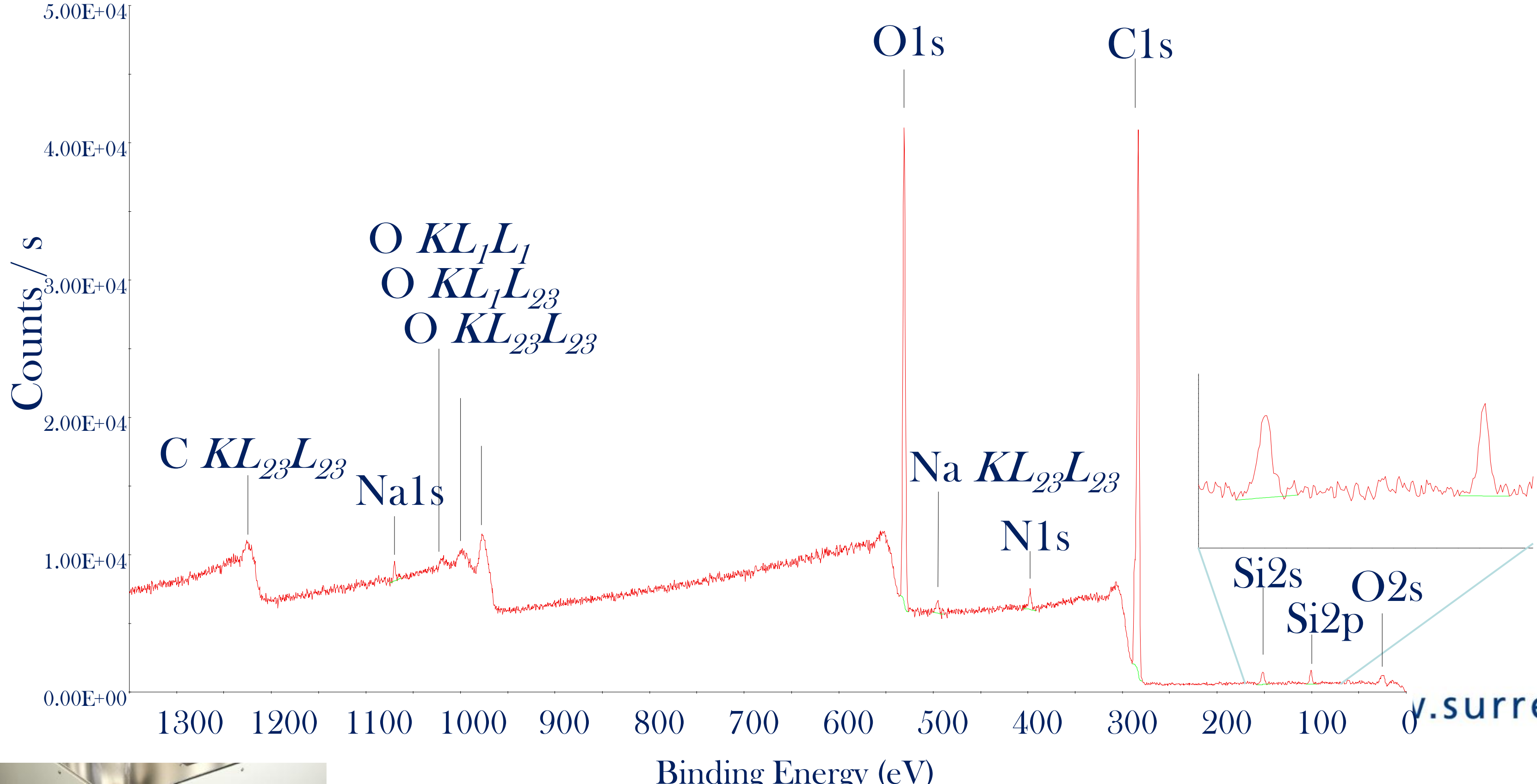


Unless stated all dimensions in mm

Uniformity Test 1

Sample	C	O	N	Si	Na	Zn
Overall Mean (6 analyses)	72.7	23.0	2.1	1.9	0.3	0.1
Overall Standard Deviation	0.7	0.5	0.2	0.2	0.1	0.0
Maxima	74.0	23.5	2.4	2.1	0.4	0.1
Minima	71.7	22.1	1.8	1.6	0.2	0.0
Range	2.3	1.4	0.6	0.5	0.2	0.1

- Variation of surface chemistry over backcoated coil is small
  - Single point analyses are valid
- Silicon also noted in significant quantity



CDT Conditions

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It is well known that CDT leads to oxygenation of polyolefinic films, in these thermoplastics relaxation and hydrophobic recovery by re-orientation can occur rapidly, this can alter the surface chemistry

Surface chemistry of back coated stock evaluated using three different energy levels represented by changes in the current of CDT – Corona 50 identified as the closest to typical production conditions

- Time dependant study of water contact angle suggests no significant change within 72 hours of treatment with this thermosetting coil coating

Identifier designation	Current (mA)	Treatment level
Corona 30	20	Undertreated
Corona 50	170	Optimum level
Corona 70	320	Overtreated

(θ°)	2 hour	72 hours
Control	77.7	76.5
Corona 30	77.4	76.8
Corona 50	54.8	55.2
Corona 70	57.9	56.7

Surface Free Energy Data

	Total energy (mJm^{-2})	Polar component (mJm^{-2})	Dispersive component (mJm^{-2})
Control	36.4	6.7	29.7
Corona 30	33.0	6.7	26.3
Corona 50	49.9	20.3	29.6
Corona 70	49.3	16.4	32.9

The initial treatment has almost no effect on surface free energy whilst a significant increase in the polar energy component was noted with treatments 50 and 70, suggesting increased presence of oxygen or nitrogen bearing molecules

XPS Compositional Data

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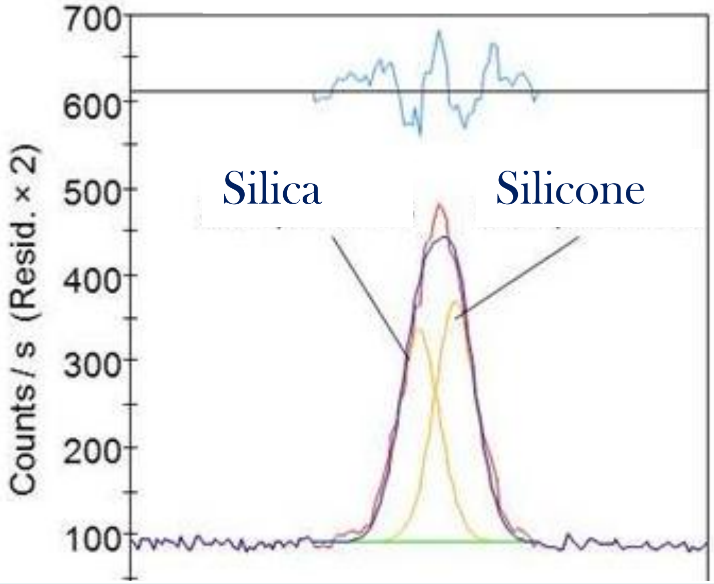
Further understanding of the changes in surface chemistry were gained by evaluating compositional information by XPS (at%)

	Carbon	Oxygen	Nitrogen	Silicon	Sodium	Zinc	O/C ratio
Control	71.0	24.2	2.4	2.1	0.0	0.2	0.34
Corona 30	70.8	23.1	2.0	3.3	0.5	0.3	0.33
Corona 50	69.1	26.8	2.4	1.6	0.0	0.0	0.39
Corona 70	64.2	29.5	1.8	3.9	0.4	0.2	0.46

Silicon is a familiar contaminant on polymers surface and may be a result of the presence of PDMS or similar, for this reason the Si2p chemistry was investigated further

Silicon Chemistry by XPS

Treatment level 70



- The chemistry of the silicon was investigated initially by peak fitting high resolution Si2p spectra.
- Two components were revealed, one attributed organic and one inorganic.
- Increase in the organic silicone on the corona 30 setting and increases in the inorganic silica on the 50 and 70 treatment levels

Silicon contribution				
	Binding Energy (eV)		Proportion Si Type (%)	
	Silicone	Silica	Silicone	Silica
Control	102.0	103.2	55.7	44.3
30	101.9	103.1	58.8	41.2
50	102.3	103.4	52.3	47.7
70	102.5	103.5	53.1	46.9

ToF-SIMS Assignment

Nominal Mass	Assignment	Attributed Compound
23	Na^{+}	Non binder component
28	Si^{+}	Organic and inorganic silicon
29	$C_2H_5^{+}$	Saturated hydrocarbon
31	CH_3O^{-}	Acrylic
39	K^{+}	Non binder component
43	$SiCH_3^{+}$	PDMS
43	$C_3H_7^{+}$	Saturated hydrocarbon
45	$SiOH^{+}$	Inorganic silicon
55	$C_3H_3O^{-}$	Acrylic
57	$C_3H_5O^{+}$	Uncrosslinked DGEBA
57	$C_4H_9^{+}$	Saturated hydrocarbon
64	Zn^{+}	Non binder component
69	$C_4H_5O^{+}$	Acrylic ★
71	$C_5H_{11}^{+}$	Saturated hydrocarbon
85	$C_4H_5O_2^{-}$	Acrylic
105	$C_7H_5O^{+}$	Polyester
109	$C_6H_5O_2^{-}$	Acrylic
109	$C_7H_9O^{+}$	Acrylic ★
135	$C_9H_{11}O^{+}$	DGEBA
147	$Si_2C_5H_{15}O^{+}$	PDMS
149	$C_8H_5O_3^{+}$	Polyester
163	$C_6N_6H_7^{+}$	Melamine
165	$C_{13}H_9^{+}$	DGEBA
177	$C_7N_6H_7^{+}$	Melamine
207	$Si_3C_5H_{15}O_3^{+}$	PDMS
221	$Si_3C_7H_{21}O_2^{+}$	PDMS
281	$Si_4C_7H_{21}O_4^{+}$	PDMS

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Untreated coating

known

silicone identified by XPS

unexpected

★ Example of peak assignment

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High Resolution ToF-SIMS

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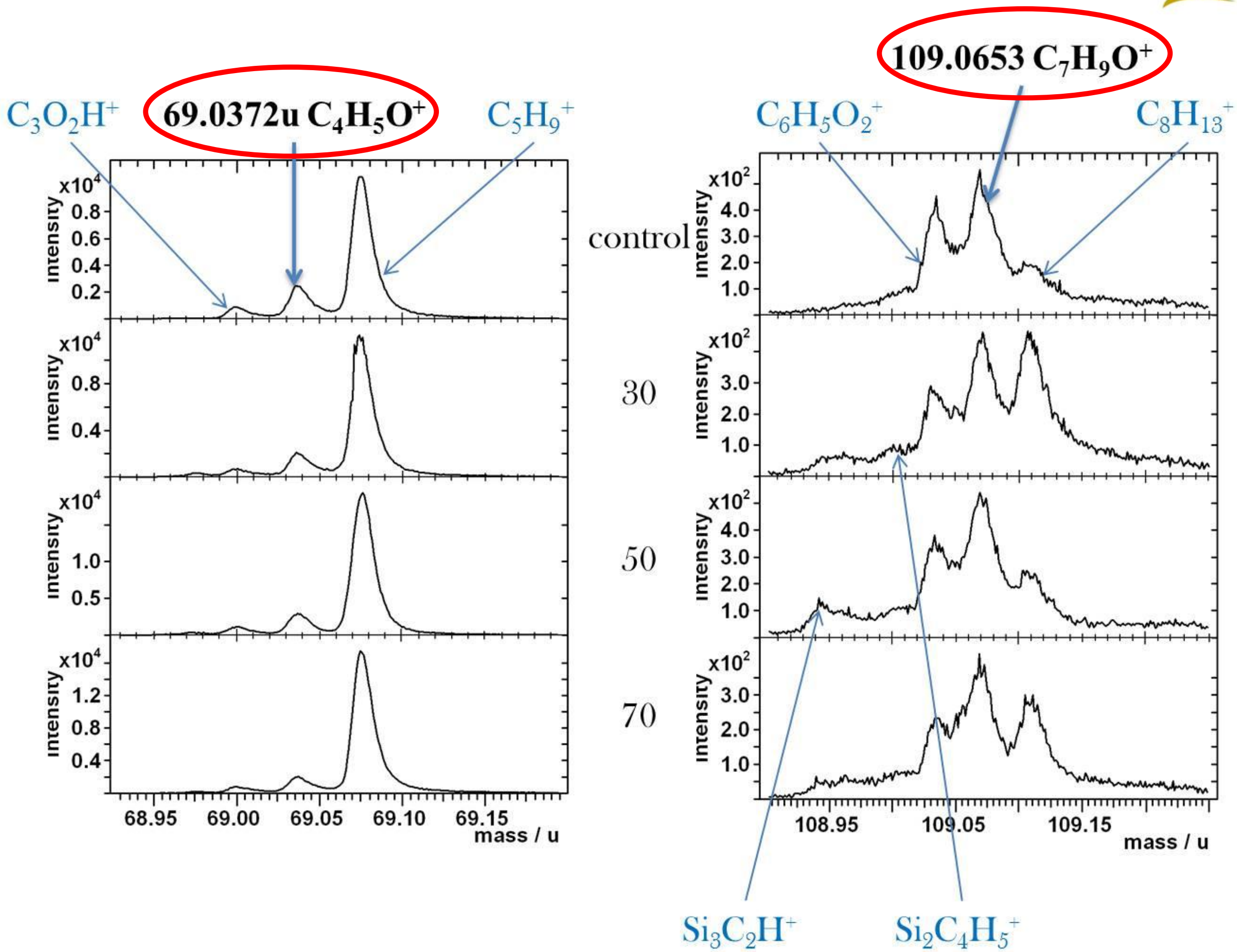
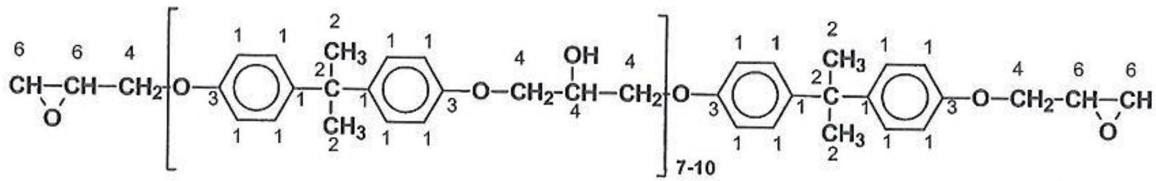


Acrylics

all confidences within 100ppm

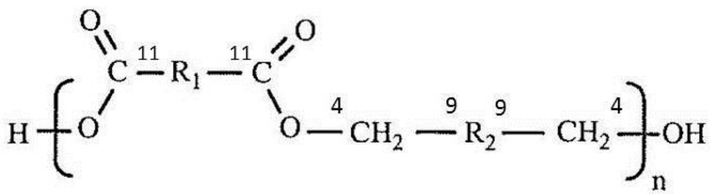
Molecular Composition

Commercial coil coating employed, exact formulation not known but based on this laboratory's extensive work on coil coatings, typical components will be:

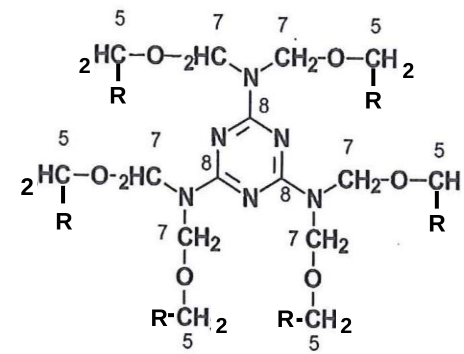


Typical DGEBA epoxy resin

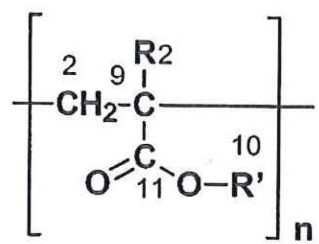
Typical polyester resin



Where R1 can be an aromatic or alkyl chain and R2 can be a linear or branched aliphatic chain



Melamine formaldehyde resin



Typical Acrylic

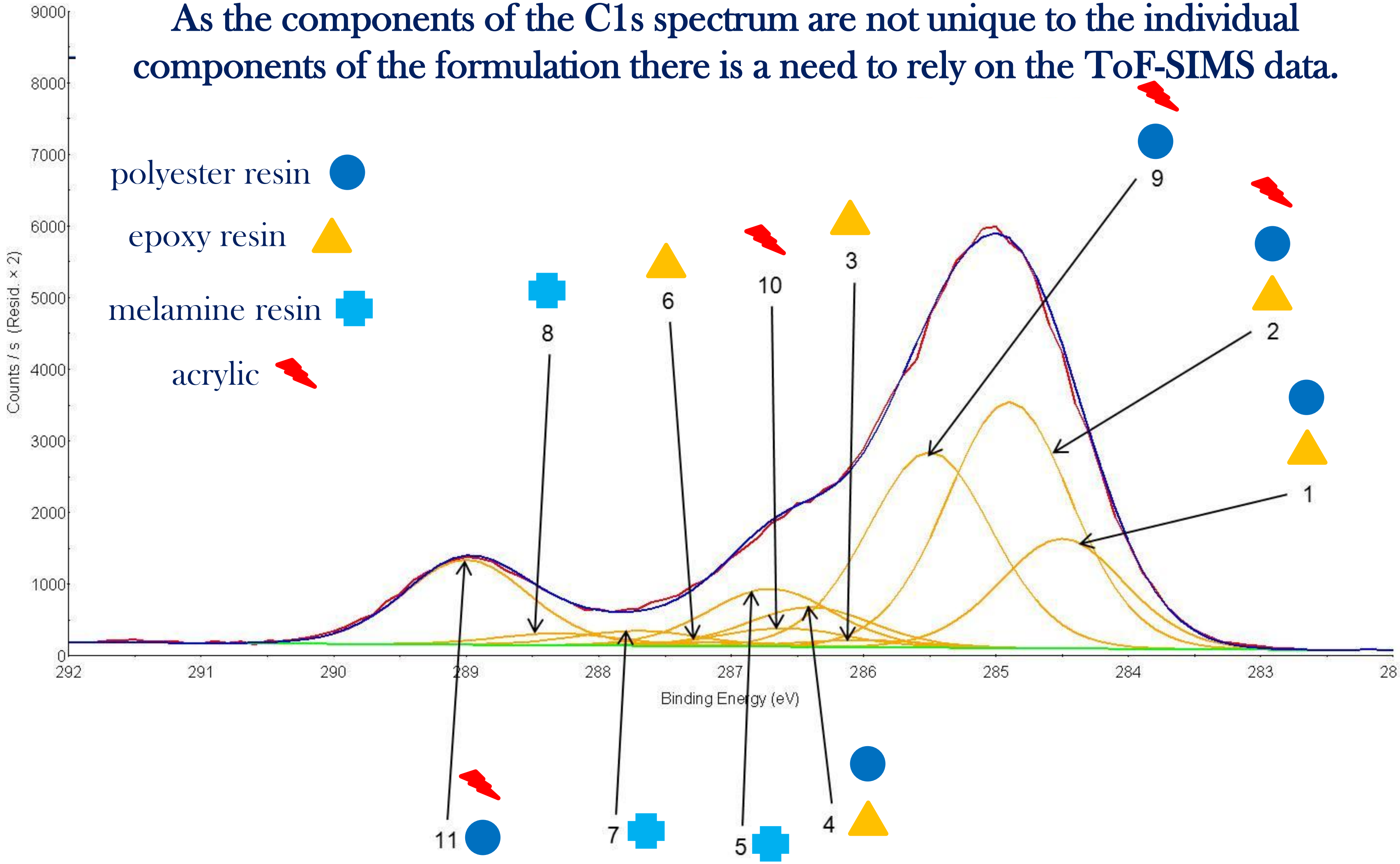
Figs. from Leadley et al. (1998)

Coil Coating C1s Spectra

After Leadley, S.R. et al. (1998) Perruchot, C, et al (2002)

Untreated surface

As the components of the C1s spectrum are not unique to the individual components of the formulation there is a need to rely on the ToF-SIMS data.



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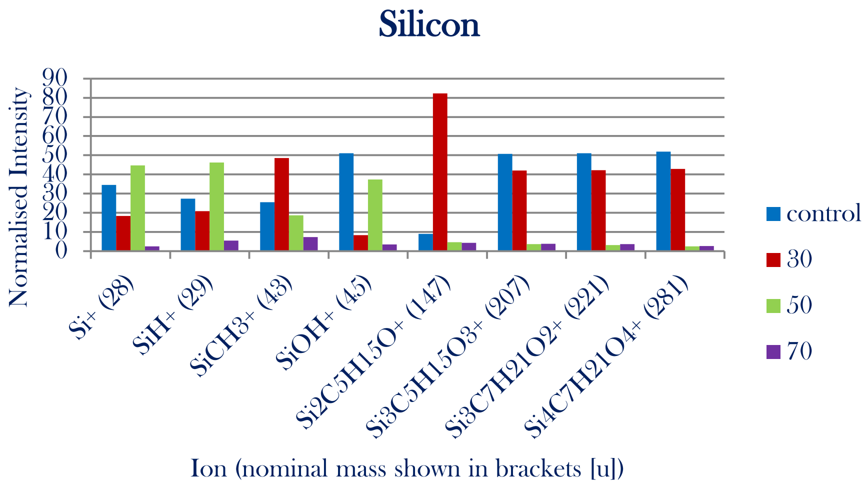
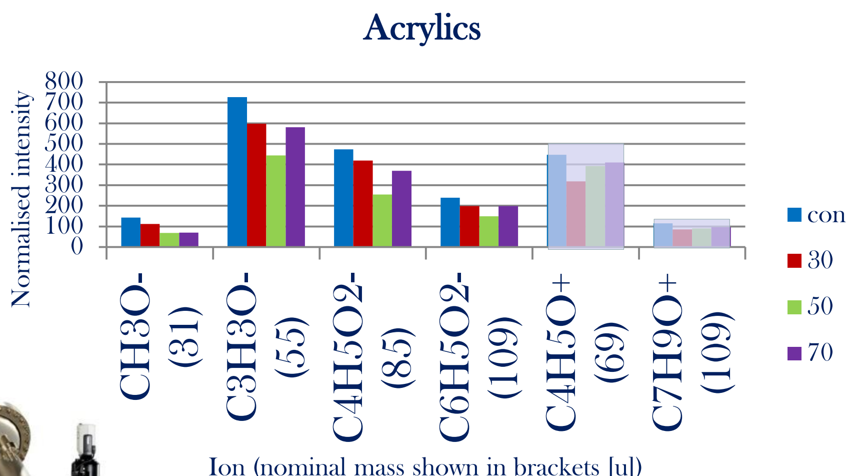
ToF-SIMS Intensity Data

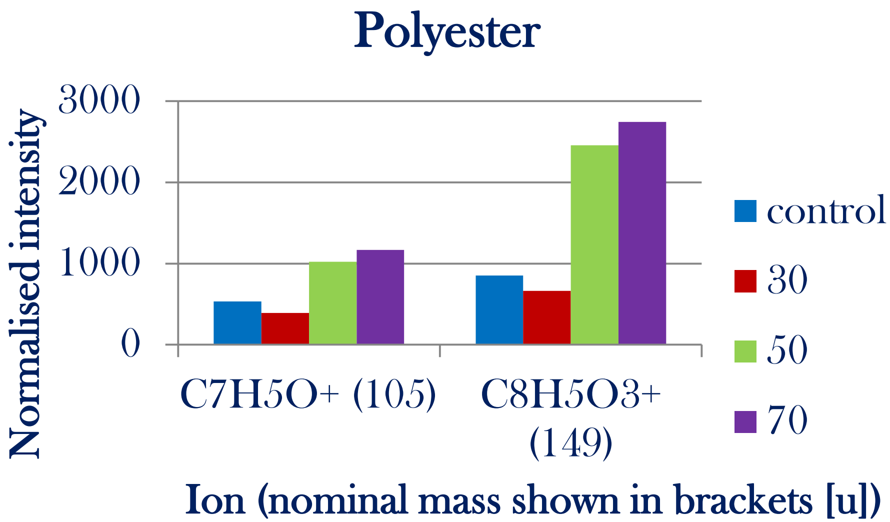


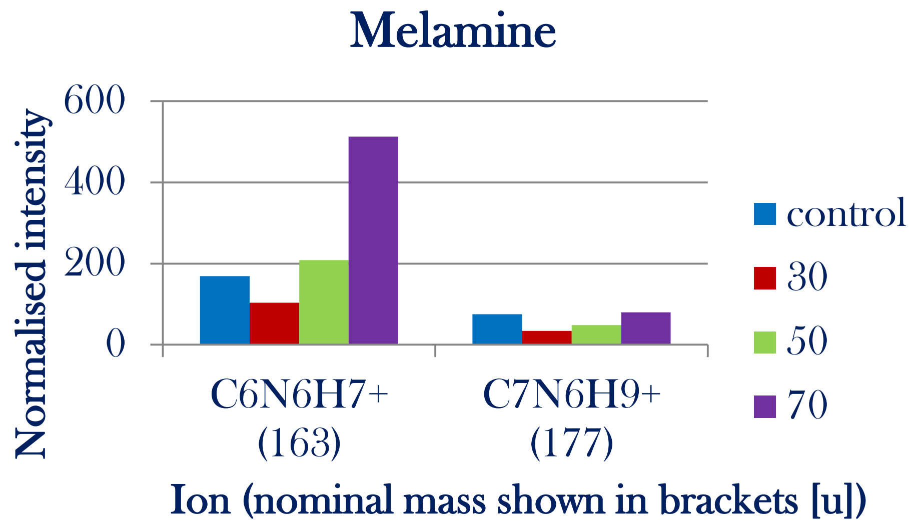


- CDT shows acrylic type components reduced in intensity with concomitant increase in other components
  - The larger PDMS chains degrade leaving lower molecular weight species
  - On higher treatment power this is shown with all characteristic ions to almost completely be removed.
  - In the 50 corona treatment power there is a corresponding increase in inorganic silicon bearing ions of low molecular weight, such as SiOH and SiO_2 suggesting that chain scission is occurring and either the PDMS is converted to silica, more filler is being revealed or a combination of these two effect (consistent with surface energy results)

A trend can be seen in the negative acrylic ions (highlighted) where the relative concentration decreases with increasing treatment power

ToF-SIMS Binder Data





The removal of the PDMS and other segregants reveals the molecules and functionalities attributable to the binder components

Conclusions

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- Full production formulations contain many components not usually encountered in model samples
- Binder characterised by polyester, melamine, epoxy and (unexpected) acrylic functionalities
- Minor components have been shown to segregate to the surface (silicone and acrylics)
- On CDT a surface typical of the binder is exposed and may be further oxygenated
- CDT increases the surface free energy of the material

Acknowledgements

Huntsman PU
Dr Chris Phanopoulos
Dr Servaas Holvoet

ArcelorMittal
Dr Perrine Calvez
Dr Jan Wielant

Questions?