



Studies on the Adhesion of Radiation Cured Coatings to Metal Substrates

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Synopsis

Coil coating is a high-speed process for applying paints to flat metal sheet, and as such should be the perfect partner for radiation curing systems. So far it has not been possible to achieve the necessary level of performance. One of the prime requisites for most Coil Coating products is durability, from a coating that is applied and cured on flat metal and then shaped and fabricated into complex assemblies. This places great demands on the flexibility and adhesion of the system. In conventional coatings the adhesion is helped by the solvents which aid surface wetting, and the high temperature cure relieves stresses within the coating. Both of these are absent from radiation curing formulations.

This paper compares the behaviour of conventional and radiation cured coatings, and seeks to explain some of the critical differences, using both conventional test methods and some more sophisticated analytical techniques.

Introduction – The Whys and Wherefores

“Coil Coating Finishes First” – this is not a partisan statement of the likely winners in the race for environmental coatings development, but the fundamental principle of coil coating. Paint application and cure is carried out on flat metal, which must then be recoiled for storage and shipment. When it reaches the customer it is de-coiled, cut to size, punched, drilled, bent, drawn, folded, clinched, and fastened in a multitude of ways which it must withstand without any deterioration of the coating, either functional or cosmetic. Whether the ultimate end use is a filing cabinet, a microwave oven or the cladding of a new corporate headquarters, the demand is for lasting good looks and protection. In the case of external building products, which account for more than half the coil market, this can involve life expectancies in excess of 20 years even in harsh environments. Adhesion is a most critical property, not just in the “as produced” condition, but also after all the stresses of fabrication and service – Mechanical (bending), Physical (Water and UV exposure) and Chemical (Water, Atmospheric Pollutants, and Acid Rain)

A Ray of Sunshine

Coil coatings are almost universally solvent based. A wide range of coating chemistries is employed in commercial quantities including epoxy, acrylic, polyurethane, fluorocarbon, plastisol and polyester. Each has a characteristic property profile to justify its market position, what they have in common is the ability to be applied and “cured” at high speed. All current coil coating lines employ high temperature ovens to achieve the required cure speed.

However, over the last ten years there has been a great deal of speculation concerning the potential for radiation curing in the coil coating industry.

The demands of the process and the characteristics of the chemistry are so closely matched: -

- ❖ The application and curing of the coating at high speed to a flat substrate with minimal environmental impact while maximising energy efficiency and control.

- ❖ Other industrial sectors have made much faster progress, perhaps we can learn something from them: -
- ❖ UV curing has been successfully applied to the printing of paper and plastic film – so it must be flexible;
- ❖ It is widely used on optical fibres –flexible, hard *and* sticks to glass – a difficult substrate;
- ❖ Large volumes of radiation cured coatings are used on wood and board products – so it can not be too expensive.

Our own studies of radiation cured products for coil coating have concentrated on UV- curing formulations for thin clear lacquers and lightly pigmented primers (through-cure requires penetration of the light right down to the substrate), whereas for highly pigmented and thick films electron beam (EB) curing is necessary. This study will be confined to UV cured primers and their behaviour in comparison to conventional thermally cured systems in use today.

As has already been stated adhesion and flexibility are very difficult to separate, and previous studies ⁽¹⁺²⁾ have focused on the use of thermo-mechanical analysis to define optimal values for the modulus, glass transition temperature (T_g) and cross-link density in coil coatings. Applying these findings to UV cured formulations is not without problems as they generally dictate a higher molecular weight, lower functionality system, with a low monomer content. This is difficult to achieve without the use of solvents.

The current study is further restricted by the experience with acid functional adhesion promoters in systems based on the free radical curing of acrylate functional resins and diluents. Despite a dramatic improvement in dry adhesion, their acidic nature has been shown to result in an increased water sensitivity and consequent failures in wet testing and weathering ⁽³⁾.

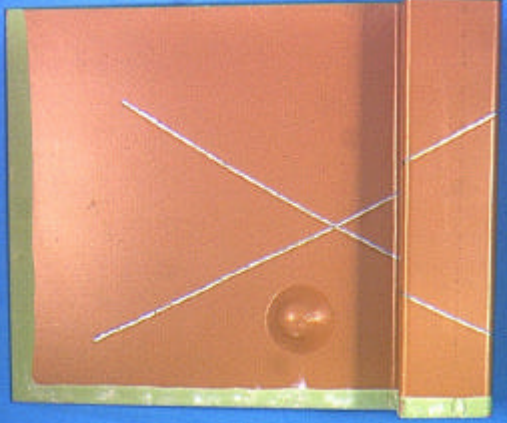
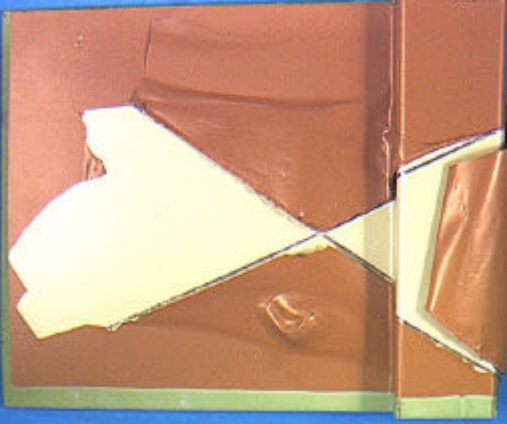

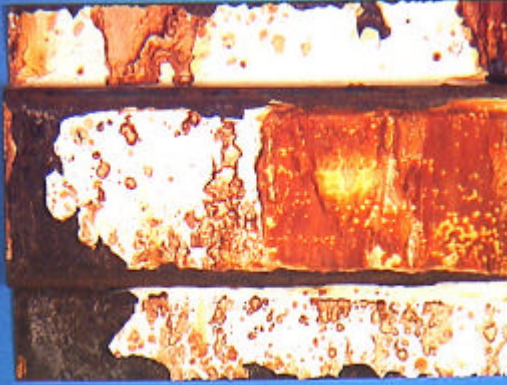
Most recently our attention has been directed towards the cationic UV cure of cycloaliphatic epoxide based primers in a coil coating system.

Adhesion

One of the classic weathering tests for our industry is the ASTM B117 salt spray, generally performed, for coil coating systems, on panels incorporating a cross scribe, a right angle bend, and a reverse impact. There is considerable debate as to the absolute relevance of this test to natural weathering, as there is concerning the relative performance under differing natural climatic conditions. However it is used here (Figures 1-4) to illustrate the critical importance of adhesion and interfacial interactions to the lifetime of coated metals.

In the un-weathered state all of these samples appeared to have excellent adhesion, but the traditional test techniques were not capable of predicting the salt spray failures.

New techniques are needed for probing the interface and achieving a better understanding of the scientific processes involved.

<p>Figure 1. The salt spray result we all hope for, indicating a functioning coating system, with good adhesion and compatibility at all interfaces.</p>	
<p>Figure 2. A good result for the primer, and for the topcoat, but they obviously don't like each other!</p>	
<p>Figure 3. No obvious signs of paint damage, but it is no longer adhering to the substrate.</p>	
<p>Figure 4. A "Bad" result but not a bad product. The coating is a polyvinylidene difluoride (PVdF), capable of 25-30 years weathering. The problem is the complete lack of adhesion to, and interaction with, the substrate.</p>	

Traditional Adhesion Testing

Sticky Dollies ...

The most direct technique for measuring adhesion is the “Pull-Off” test⁽⁴⁾ wherein a “dolly” is glued on to the surface of the coating under test and a device is then attached which generates a direct pulling force. The load at which the coating becomes detached is a direct measure of adhesion. BUT ... It cannot measure adhesion values exceeding the bond strength of the dolly adhesive (usually a 2-K epoxy) – AND it is generally not applicable to thin flexible substrates due to the mechanical configuration.

Coil coatings are always applied on thin flexible substrates, they have excellent adhesion to the substrate and many are unreceptive to conventional adhesive bonding. All you can measure with this technique is the strength of the epoxy – topcoat bond, or the buckling load for the substrate.

Scratches and scrapes...

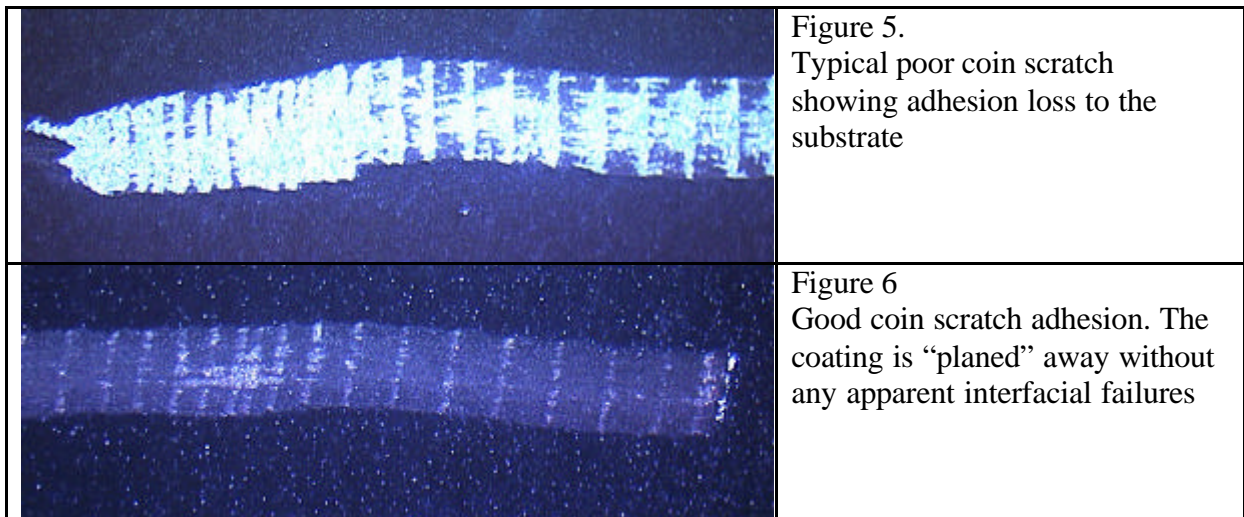
Other traditional techniques for assessing adhesion are simple and straightforward with little need for sophisticated equipment - the Thumbnail, Coin scratch,⁽⁵⁾ and crosshatch tests.

When you start to look a in little more detail, more questions arise: -

Whose thumb nail? How much pressure?

What size coin? From which country? And what denomination (what metal)? How new is the coin (sharp edges or worn)? How much pressure?

How do you interpret the results? A ranking order is the most that is readily achieved and even this may vary between operators.

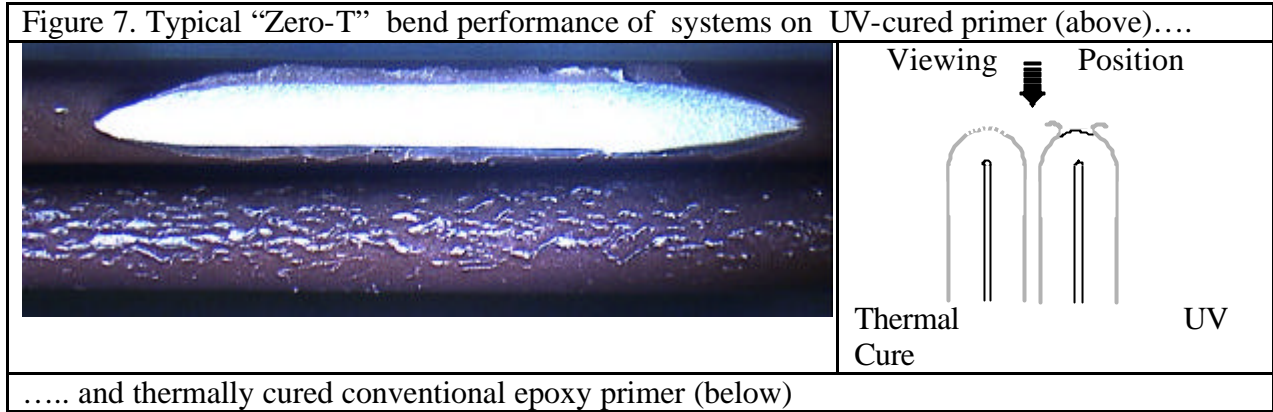


It's a Rip-Off –

After performing the conventional crosshatch test it is normal to apply “Scotch Tape” (a very specific traceable “standard-sticky” grade) which is then peeled off rapidly to lift off any loosely adhering particles. Even then there remains the question of what you should use to make the scribes in the crosshatch (a scalpel, a penknife, or a tungsten carbide scribe)? How much pressure? What spacing should there be between the scribes?

..... And bumps and bends

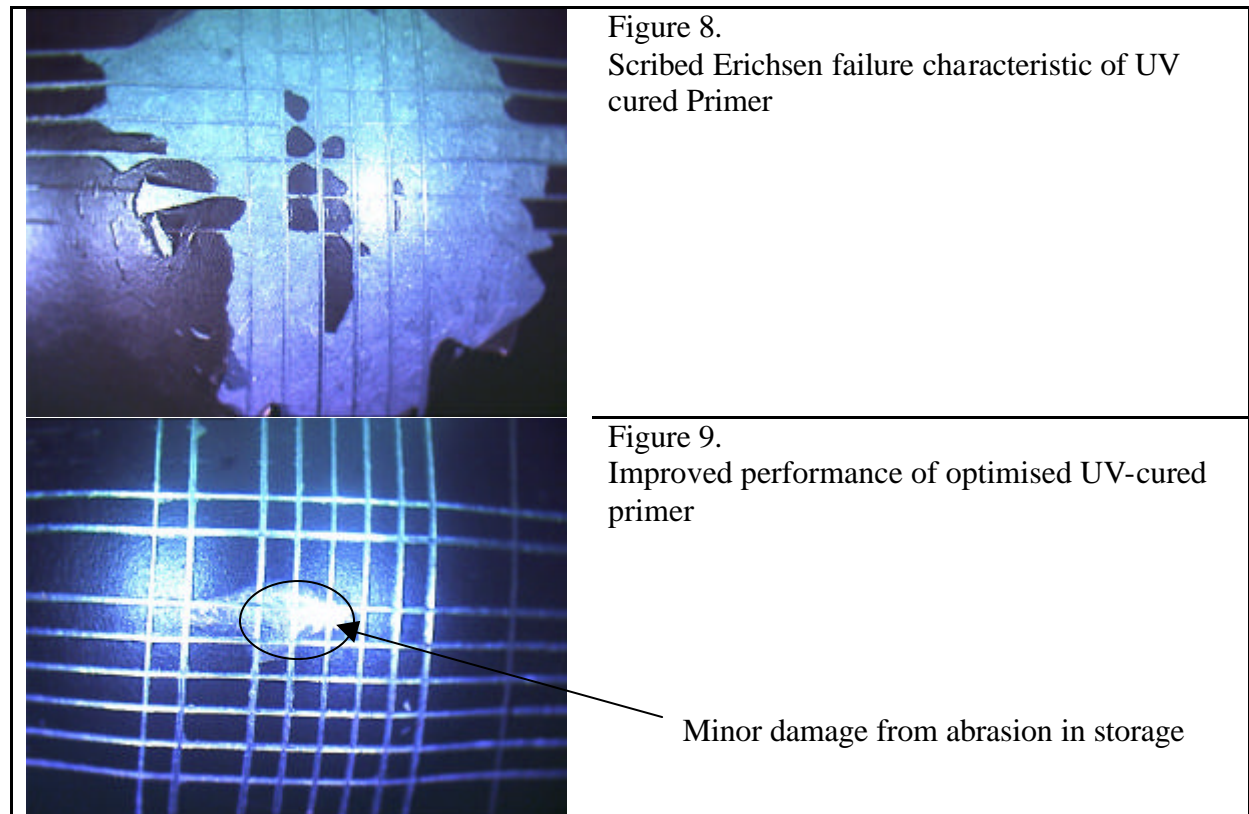
Traditional tests designed to measure the *flexibility* of a coating also have a major contribution to make to the evaluation of adhesion. The T-Bend test⁽⁶⁾, though designed to measure extreme flexibility, generates severe tensile stresses within the coating. Strain mis-matches between coating and substrate can lead to serious adhesion defects. It is not unexpected for systems to show cracks on the tightest 0-T bends, all but the most flexible thermal systems do, but it is important that they maintain adhesion.



Impact⁽⁷⁾ and Erichsen⁽⁸⁾ tests may also give simultaneous and sometimes confused data on flexibility and adhesion.

In order to improve the discrimination of the impact and Erichsen tests they may be combined with the crosshatch, so that the deformation actually occurs through the scribed area.

Different sections of the deformation area will experience different degrees of strain, thus when the Scotch Tape is applied and removed the paint detachment pattern gives some semi-quantitative information on adhesion, and its relationship with flexibility.



A Long Hot Soak

Another test often used in the coil-coating field is a boiling water soak. This certainly exposes some weaknesses in intercoat interactions, particularly in the case of PVC plastisol, and polymer film laminates. It is not a test generally recommended for assessing adhesion because the test may actually cause the failure rather than measuring it. Prolonged exposure to boiling water is likely to lead to a number of modes of failure, including: -

- ❖ Penetration from cut edges along the interfaces.
- ❖ Diffusion through the body of the paint film, attacking the interfaces.
- ❖ Exposure at temperatures well above the glass transition point T_g of the polymer, dramatically increases the susceptibility to water transmission.
- ❖ Accelerated diffusion through the body of the paint film dissolving pigments and fillers leading to osmotic blistering.
- ❖ High temperatures equally may have a strong accelerating effect on the hydrolytic degradation of the base polymer and cross-links.
- ❖ Minor components of the paint film (e.g. catalyst residues) in combination with water ingress at high temperatures may destroy interfacial interactions.

Whatever Next

A better technique is needed for analysing the actual process of adhesion at the interface. Some indicative results may be possible using the EDAX function of electron microscopy, but in order to achieve the best resolution of interfacial chemistry more sensitive instruments are needed. We have been collaborating with Professor John Watts of the University of Surrey in the use of highly sophisticated spectroscopic analysis to characterise surfaces before coating, and on both interfacial surfaces after generating an adhesive failure.

When its good its very very good

But we have a classic “Catch 22” situation, it is easy to characterise bad adhesion, and it is easy to prepare samples from failed specimens to examine the surface characteristics. The difficulties start when you try to do the same thing to study a “good” sample. We need to understand just what it is that promotes good adhesion, the substrate surface and pretreatment, the chemistry of the coating, the cure conditions, etc., etc. When the adhesion is good, how do you generate a failed interface -- when it won't!

Figure 10.

THREE POINT BENDING - SAMPLE PREPARATION

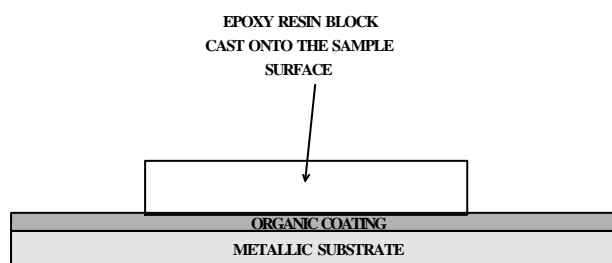
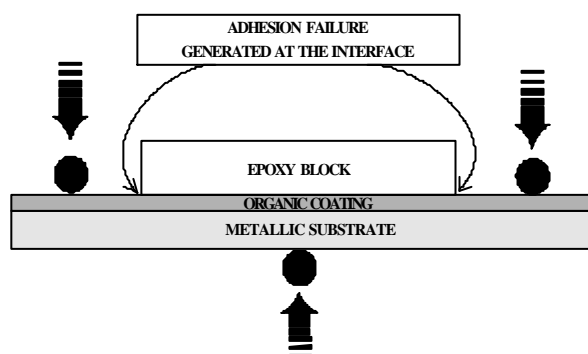


Figure 11.

THREE POINT BENDING - SCHEMATIC



One suggested technique which we have evaluated is the “3-point bend” (Fig 10,11)⁽⁹⁾ in which an epoxy resin block is cast onto a coated sample. When fully cured the assembly is

subjected to “3-point bending” in an Instron tensile test machine. The stresses are concentrated at the interface and the adhesive strength can be measured quantitatively (provided that failure occurs at the desired interface, and that the result is not affected by exposure to the epoxy).

In our experience this test has not been particularly effective in quantifying adhesion, but has sometimes facilitated the exposure of interfaces for further analysis.

An alternative method for exposing interfaces is based upon immersion in hot N-methyl pyrrolidone (NMP) a technique which has been suggested by Van Ooij⁽¹⁰⁾ for quantification of adhesion. As for the 3-point bending test, we have not found this to give useful quantitative results for these systems⁽¹¹⁾ but it can be very useful in exposing interfaces.

Materials

Thermally cured coatings

In this study, the thermally cured primer used was based on a “7-type” epoxy resin derived from epichlorohydrin and bisphenol A. This process results in the formation of secondary hydroxyl groups, which can participate in the cross-linking (curing) reactions.

Epoxy resins generally have a relatively low molecular weight and are somewhat inflexible materials, but they do confer excellent adhesion and chemical resistance in the films into which they are incorporated. Due to their solid nature organic solvents are required as carriers in order to cast thin uniform films. In the coil coating process it is normal for the solvents evaporated off during the heating process to be incinerated both for environmental reasons and to provide heat for the ovens. In order to form films that provide greater corrosion resistance the epoxy resin is thermally crosslinked by an amino based resin. This involves a trans-etherification reaction between the alkoxy groups on the urea-based resin and the hydroxyl groups in the epoxy resin.

The different components used in the formulation are given in Table 1.

Table 1 - Formulation of the thermally cured primer.

Component	Function
Epoxy Polymer	Primary Resin
Aromatic / Ester Blend	Solvent
Urea Formaldehyde Resin	Crosslinking Agent
Inorganic Pigments	Anticorrosive Pigment
Acrylic Resin	Flow Agent
<i>Formulations were produced with and without the flow aid</i>	

Radiation cured coatings

The UV coating under investigation was a cationic UV-cured system. It consisted of the components listed in Table 2. The cationic photoinitiator ($\text{Ar}_3\text{S}^+\text{PF}_6^-$) is a complex salt with large light sensitive organic cations and weak inorganic anions. When it is irradiated with UV light of the appropriate wavelength, a Brönsted acid is formed according to the scheme in Appendix II^[12]. After decomposition of only a small amount of the photoinitiator, polymerisation is very rapid and films may be substantially cured in less than a second.

Table 2 - Formulation of the UV cured coating.

Component	Function
Diluent	reactive diluent
Inorganic Pigments	anti-corrosive pigments
Cycloaliphatic Di-epoxy Resin	reactive resin
Co-resin	adhesion promoter
Triaryl sulphonium salt of phosphorus hexafluoride	cationic photoinitiator
Acrylic Resin	flow agent
Polyol	chain transfer agent
Amine functional Additive	dispersing aid

EXPERIMENTAL

The coatings were applied to panels of zinc galvanised steel which had undergone a commercial chromate based pretreatment.

Sample Preparation

The thermally cured coating was applied on the substrate using a wire wound bar, (ASTM D4147-93), heated in a high velocity recirculated air oven and quenched in cold water to simulate a coil coating line. The dry film thickness of the layer was 7-8 μm . As far as the cure of these systems is concerned, the two major parameters are the oven dwell time and the peak metal temperature (PMT) reached by the metal before it is removed from the oven. A PMT of 224°C was achieved in 30 seconds with an oven air temperature of 280°C.

The UV coating was applied on the substrate in the same way as for the thermally cured system. It was then cured under a medium pressure mercury vapour lamp at a power of 150 W cm^{-1} (lamp power per unit length) using a conveyor speed of 15 m min^{-1} .

Topcoat

The topcoat used in this study was a thermally cured polyester-melamine. It was applied in the same way as the primers but at a greater dry film thickness (20-25 μm). It too was thermally cured for 30 s to 224°C PMT.

The degree of “cure” was assessed on the “just primed” and “primed and topcoated” systems. The technique used was the “MEK Rub Test”⁽¹³⁾ wherein a cloth soaked in propan-2-one is wrapped around a finger and rubbed back and forth on the panel. The number of “double rubs” (DR-MEK) to achieve penetration to the substrate is recorded.

It is not considered to be necessary, or even always desirable, for a primer alone to have a high cross link density, so long as the overall system exceeds the 100 DR.

Table 3 – “Cure” by MEK resistance

“Cure” DR-MEK Thermally Cured Primer				“Cure” DR-MEK UV cured primer		
oven dwell time (s)	Primer Alone	Topcoated	conveyor speed (m/min)	cure time (s)	Primer Alone	Topcoated
30	4	>100	15	1.2	15	>100

Both systems achieve the necessary level of “cure” but it is noticeable that the un-topcoated UV-cured primer has a significantly higher level of cross-linking than the thermal

Table 4 - Results of the Erichsen Test (7mm. Indentation)

Percentage adhesion after mechanical deformation						
Thermally Cured Primer				UV Cured Primer		
oven dwell time (s)	Primer Alone	Topcoated	conveyor speed (m/min)	cure time (s)	Primer Alone	Topcoated
30	63	100	15	1.2	93.3	95.3

In this case the radiation-cured primer seems to behave better - until it is topcoated

Table 5 – T-Bend Testing

(Two figures are quoted – “No Cracks” implies that there is absolutely no visible damage to the coating; “Adhesion” allows cracking so long as there is no loss on Sellotaping the bend.

“T-Bend” Flexibility / Adhesion					
Thermally Cured Primer			UV Cured Primer		
Cure time (30s)	Primer Alone	Topcoated	Conveyor Speed (15m/min) Cure time (1.2s)	Primer Alone	Topcoated
T-Bend Adhesion	0-½	0-½		2+	2+
T-Bend “No Cracks”	½-1	½-1		1-1½	1-1½

The thermal system is consistently best, most critically in the “Adhesion” category

Despite our best efforts in formulation, there is definitely something different in the fundamental adhesive behaviour of these two primer systems. The conventional arguments for reduced performance from the UV cured system - viscosity, wetting characteristics and lack of a heat treatment, which may promote stress relaxation, are not valid in this case. The two systems were similar in viscosity and wetting behaviour, and both were topcoated with a

thermally cured polyester, allowing cure completion and stress relaxation. There are obvious differences in cure in respect of gel or set-up time, and in the effects of the migration and evaporation of the carrier solvent, but none of the conventional testing gives any indications of what the effects are or how to proceed.

Techniques are needed to characterise the chemical nature of the interfaces, to identify the species responsible for good / bad adhesion, and thus to suggest strategies for improvement.

Stay right there!

There is a suggestion that some formulation components seem to migrate preferentially to the interfaces... for this to be relevant in the present study they must move very fast!

The UV primer takes only a second to cure, and even the conventional thermal primer needs only 30 seconds. It would be reasonable to expect that there would be minimal segregation of formulation components in such a short time.

However this is not the case, and significant segregation has been detected in both systems of this study by the use of XPS and ToF-SIMS analysis.

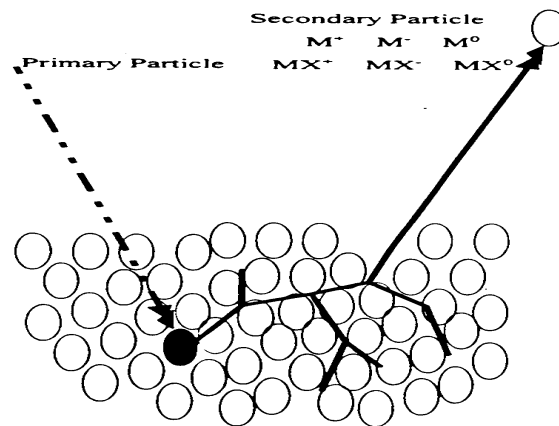
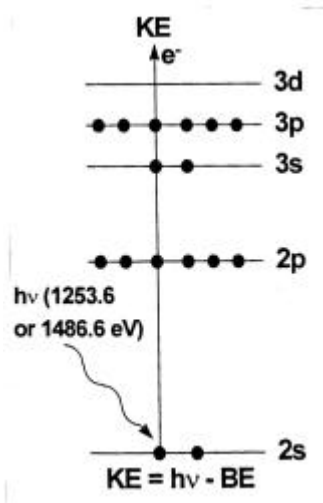


Figure 12
X-Ray Photoelectron Spectroscopy (XPS) examines the characteristic emission spectra of the surface elements upon bombardment with (typically Aluminium $K\alpha$) x-rays. The oxidation state and the environment of the individual atoms can be identified from the spectrum.

Figure 13
Time of Flight Secondary Ion Mass spectrometry (ToF-SIMS) is a similar principle but using a heavy ion bombardment (Ga^+) which can displace atoms, molecules or fragments of molecules from the surface. This pattern can yield a very precise knowledge of the surface chemistry.

ToF-SIMS has demonstrated beyond doubt that the cationic photoinitiator in the radcure primer migrates to the metal interface⁽¹⁴⁾ where it can produce a weak boundary layer, limiting the adhesion potential of this system.

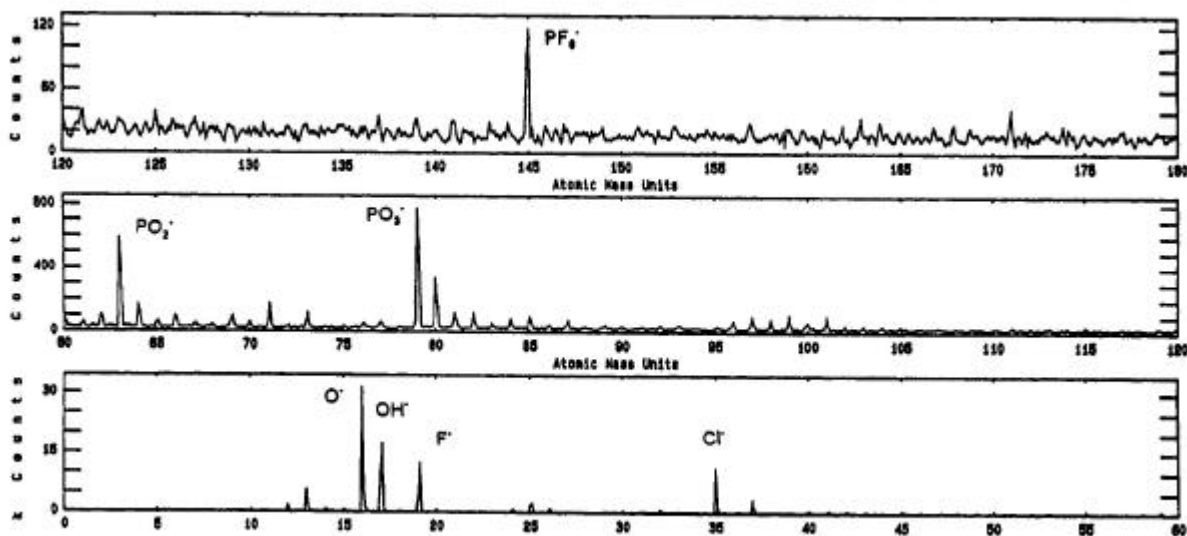


Figure 14 – Negative ion ToF-SIMS spectrum of the metal side of the interface beneath a cationic UV cured primer indicating the surface concentration of Triaryl sulphonium salt of phosphorus hexafluoride, the photoinitiator⁽¹⁴⁾

A similar effect is seen with the thermal primer using XPS, (Table 6) where nitrogen levels suggest that the amino resin exists at the interface at a much higher concentration than the “bulk theoretical”. The atomic ratio suggests that the extreme interface is almost pure crosslinker. This may be exaggerated as the adhesion failure was generated by soaking in hot N-methyl pyrrolidone NMP which itself contains ~14% N and arguably may have left residual contamination, but this was not seen when the metal itself was similarly treated.

Surface segregation, in this case, results in enhancement of adhesion properties.

Table 6. Quantitative Surface Analyses by XPS of Thermally Cured Primer Samples

Sample	Interfacial Surface	Atomic %							C/O ratio
		C	O	N	Al	Zn	Si	P	
Unpainted Galvanised Steel (HDG)	metal	39.7	46.2		10.4	3.6			0.86
NMP-soaked HDG	metal	40.9	49.3		6.9	2.9			0.83
Thermally Cured Primer	metal	65.5	21.5	12.1		0.2		0.7	3.04

Calculated Nitrogen in thermally cured system ~ 3%

Nitrogen in urea formaldehyde crosslinker ~12%

The thermal system also shows a strong segregation if the acrylic flow agent is incorporated⁽¹⁵⁾. In this case it migrates to the air interface where its effects upon surface tension obviously justify its use. However there may be circumstances where this too can form a weak boundary layer and may interfere with e.g. adhesive bonding. When coated with the polyester topcoat this is not a problem as the flow aid is compatible with, and soluble in the over-layer in which it is also a formulation component.

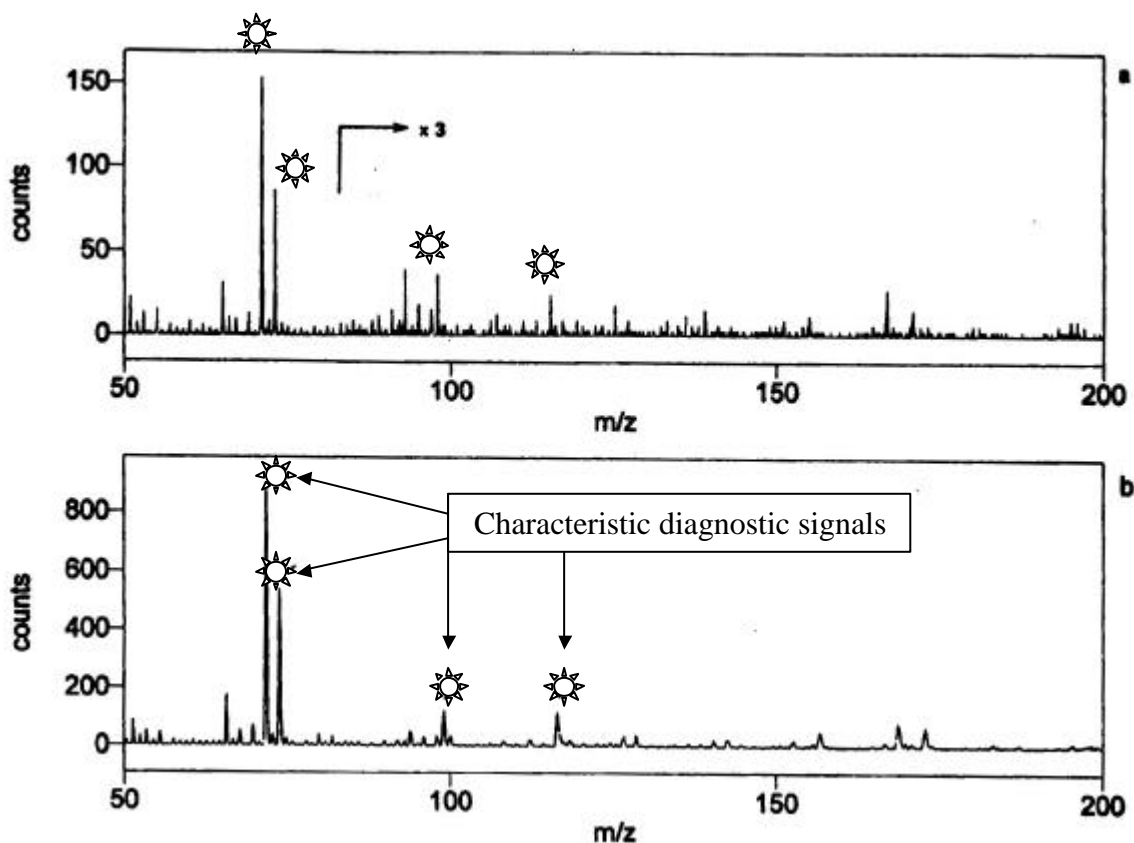


Figure 15 - Negative ion ToF-SIMS spectra of a) the upper surface of the thermally cured epoxy primer containing flow agent, and b) the pure polyacrylate flow agent⁽¹⁵⁾

Summary

The intention of this paper was to demonstrate some of the differences between conventional and radiation curing systems in a coil coating application and to show how they can be evaluated using conventional “paint tests” and surface analytical techniques.

The traditional test methods describe effects but offer little information concerning the causes or potential remedies. XPS and ToF-SIMS are shown as powerful tools to identify the chemical species involved in adhesion, pointing the way to a better understanding and formulation development.

Instruments like these can never be seen as routine tests, they are simply too sophisticated, too demanding and too expensive, but as research tools for resolving specific problems they provide a very valuable addition to the paint chemist’s tool-box.

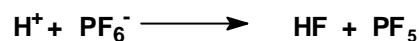
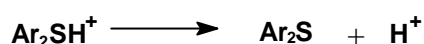
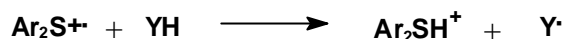
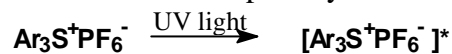
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Appendix II

The Chemistry of cationic radiation curing

1. Chemical Reactions involved in the photolysis of the initiator

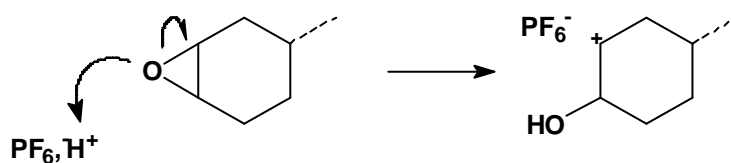


N.B. YH, which supplies the protons, can be a molecule of the resin, a polyol or residual water.

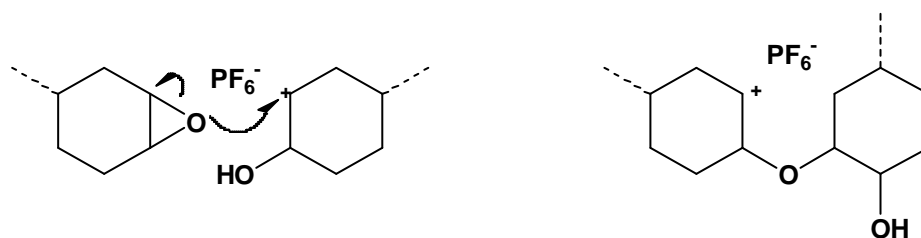
2. Cross-linking – Cationic Polymerisation Reactions

The cure of the coating involves the proton of the Brønsted acid generated during the photolysis of the photoinitiator. This proton attacks the epoxy groups of the di-epoxy cycloaliphatic resin and a carbonium ion is formed; a) below. The carbonium ion reacts with more epoxide, and hence polymerisation occurs; b) below. The propagation step is in competition with a secondary ring opening reaction with the diluent

Reaction with the polyol gives rise to a chain transfer process, as the proton is very mobile.



(a)



(b)