Bake Oven Induced Variation of Surface Chemistry on Electrocoat Paint: Effect on Primer-Electrocoat Intercoat Adhesion

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The interplay of bake oven processing environment and surface/interfacial chemistry, and their effect on intercoat adhesion has been investigated for a model primer/electrocoat paint system. X-ray photoelectron spectroscopy (XPS) surface analysis established that a prominent ether component in the C 1s core level spectrum correlated with a polyether-based crater-control additive in the electrocoat that surface-segregates during cure. Laboratory-simulated bake oven experiments confirmed that better adhesion characteristics were realized by removal of this electrocoat overlayer through reaction with nitrogen oxides and high levels of moisture present in the cure environment of production direct-fired ovens. Details of the effect of bake oven atmosphere on cure chemistry for direct- versus indirect-fired ovens are presented.

INTRODUCTION

Commercial paint systems are complex assemblages comprising multiple layers of coatings. An essential requirement of such a paint system is that each layer performs its designated purpose, while at the same time remaining adhered to the adjacent paint layers. This latter requirement dictates that the paint system must be robust enough to contend with the range of coatings chemistries that may exist, as well as the range of processing conditions that would be necessary to apply and cure the coatings. Additives included in paint layers to improve properties, such as appearance and rheology, can often surface-segregate during cure and adversely affect adhesion. Surface modifications involving, for example, surface oxidation (e.g., UV, flame, or corona treatments) have been used to improve or insure a certain level of adhesion performance for some organic and inorganic substrates,[1-3] however, flame and corona treatments are not applicable to multi-layered paint systems.

In this study we report that the ambient atmosphere within the oven used to cure a coating can have a profound effect on the surface chemistry of the paint layer, with significant consequences on intercoat adhesion. It is demonstrated that an anti-cratering agent (ACA) in the electrocoat formulation migrates to the surface during the cure process to form an overlayer that causes loss of adhesion. This overlayer remains mostly intact when the electrocoat is cured using an indirect-fired oven, but diminishes upon cure in a direct-fired oven. This paper will thus focus on the synergy between bake oven cure chemistry and variations in material formulation chemistry, and their combined effect on paint intercoat adhesion. X-ray photoelectron spectroscopy (XPS) surface analysis techniques were employed to study these interactions.

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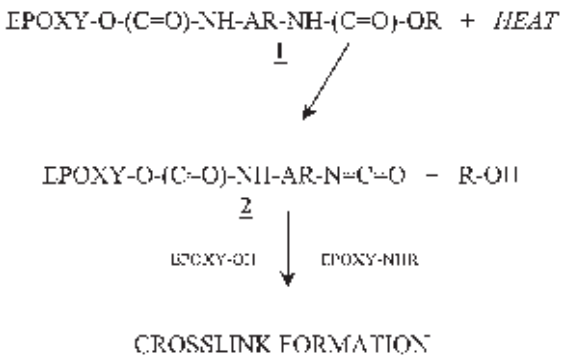
EXPERIMENTAL

Materials

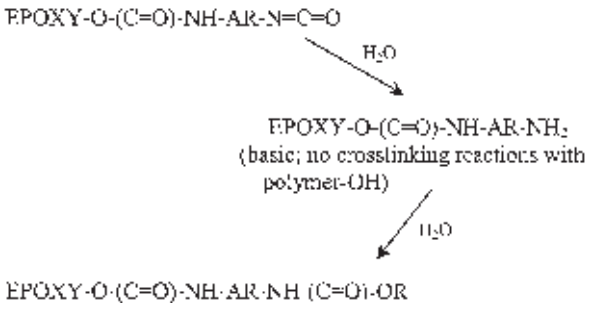
The electrocoat coatings used in this study are epoxy-based materials that are crosslinked primarily through urethane and/or urea linkages. The urethane and urea crosslinks are formed as a result of a reaction between a blocked isocyanate (an isocyanate functional group pre-

viously reversibly reacted with an alcohol or related material) and –OH and –NHR functional groups in the electrocoat formulation (equation (1)). The crosslinking reaction is temperature sensitive,



Equation 1

occurring efficiently in stable paint systems at temperatures typically above 150°C (300°F). The mechanism is generally thought to occur in the electrocoat coating through a nucleophilic addition of hydroxy or amine functionalized materials (epoxy) to either the blocked isocyanate, **1**, or the free isocyanate, **2**. Other low molecular weight, monofunctional nucleophilic materials containing an active, i.e., "acidic" hydrogen (e.g., H_2O), can interfere with this crosslink reaction and generate networks and coating surface chemistries much different than that which is desired (equation (2)).



Equation 2

In this study a model coating is formulated with an amine functional, polyether material, **3**, which as in commercial systems, is used as an ACA. The chemical

$$H_2N\text{-}(CH_2CH_2CH_2O)_x\text{-AR-}(OCH_2CH_2CH_2)_y\text{-}NH_2$$
3

nature and function of this additive dictates that it will be reactive with an isocyanate (through the amine functionality), prone to oxidation (through the ether linkages), and be surface active (where it controls crater formation).

Material Preparation

The model electrocoated coatings used to evaluate the variations in surface chemistry resulting from curing in direct-fired versus indirect-fired ovens were prepared under conditions simulating manufacturing conditions. Two types of ovens, typical of those used in OEM paint operations, were used to cure the coatings. One type, the direct-fired oven, is heated by the exhaust of natural gas combustion. The second type, the indirect-fired oven, uses air that passes through heat exchangers heated by natural gas combustion. After bake oven cure, the electrocoat panels from the indirect-fired oven remained gray in color, while those cured by the direct-fired oven turned slightly greenish.

"Acid-rinsed" electrocoat samples were prepared to determine if non-crosslinked amine functional materials were formed at the paint surface during the various cure processes examined. Materials of this type would be expected if cleavage reactions (e.g., hydrolysis) involving the urethane linkages occurred within the electrocoat or if amine functional material present in the electrocoat formulation bloomed to the surface during cure. The acid-rinsed samples were generated by first swabbing a 2×4 cm coupon of electrocoat on steel with 10% aqueous hydrochloric acid using a Q-tip, followed with a swabbing rinse with distilled water. Excess water beaded up and was removed by capillary action into a clean cotton cloth.

Fully painted systems were prepared by coating the model electrocoat with a melamine crosslinked polyester primer and a white acrylic urethane topcoat. Adhesion testing and subsequent interfacial surface analysis was conducted on these systems. The paint system employing an indirect-fired oven-cured electrocoat showed significant delamination. The paint system employing a direct-fired oven-cured electrocoat showed generally acceptable adhesion. With this latter system, interfacial analysis was conducted on small "corners" of paint delamination that were induced by cross-hatching and pulling with tape.

X-Ray Photoelectron Spectroscopy

XPS was used to identify differences in the surface chemistry of the electrocoats cured in the direct- and indirect-fired ovens, to determine the surface chemistry of the melamine crosslinked polyester spray primers, and to examine the interfacial surfaces that resulted from cross-hatch/tape generated adhesion loss. Further information regarding XPS and its applications towards the chemical characterization of surfaces can be found in references 4-6. XPS was performed using an SSX-101 spectrometer manufactured by Surface Science Instruments, Fisons Surface Science, Mountain View, CA. The probe depth for materials studied in this investigation was 2-3 nm. The excitation source utilized monochromatic Al K_α (1486.6 eV) radiation (100W) focused to a 600-µm diameter beam size. A low energy (1-3 eV) electron flood gun in combination with an Ni charge neutralization screen placed 1-2 mm above the sample were employed to minimize surface charging effects.[4] The base pressure of the spectrometer was 1×10^{-9} Torr. The analyzer was operated with a 150 eV pass energy for acquisition of survey spectra and a 50 eV pass energy for acquisition of core level spectra. Quantification of survey data was accomplished by means of routines based

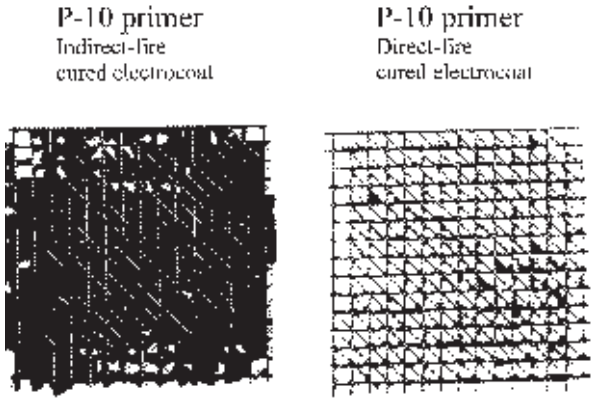


Figure 1—Photograph of scribe-tape adhesion test results of coating systems comprised of the model electrocoat, a melamine-crosslinked polyester primer (P-10), and a white acrylic urethane topcoat.

on Scofield photoionization cross-section values. The atomic compositions presented in the tables are calculated from an average of two separate analyses. A least-squares based fitting routine, supplied by the manufacturer, was used to fit the high resolution core level spectra. This routine was allowed to iterate freely on the peak positions, integrated peak areas, and peak widths (FWHM). An FWHM of approximately 1.3 eV was achieved for the components of the peak fits. Binding energies were referenced to the aliphatic C 1s line at 284.6 eV.

RESULTS AND DISCUSSION

Scribe and Cross-Hatch Adhesion Test Results

Figure 1 compares scribe-tape pull adhesion tests on coating systems comprised of the model electrocoat, a melamine-crosslinked polyester primer (P-10), and a white acrylic urethane topcoat. Results are shown for model electrocoats cured in both direct- and indirect-fired bake ovens. The photographs reveal that primer P-10 exhibited substantially better adhesion to the electrocoat cured using the direct-fired oven.

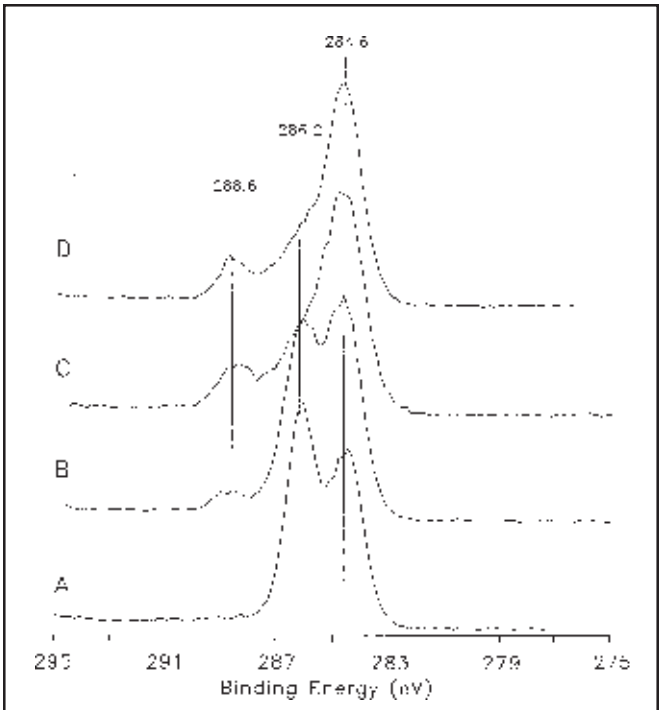


Figure 2—XPS C 1s core level spectra of (A) indirect-fire cured model epoxy, (B) interfacial substrate, (C) interfacial polyester surface, and (D) P-10 polyester coating control.

Analysis of Interfacial Surfaces Generated from Paint Adhesion Loss

INDIRECT-FIRED ELECTROCOAT CURE: Scribe/adhesion testing of the P-10 system incorporating an indirect-fired oven-cured electrocoat coating showed large areas of paint delamination on the test panels (*Figure* 1). The locus of failure visually appeared to occur at the electrocoat/primer interface since the interfacial substrate surface (electrocoat side) was gray like the electrocoat, while the interfacial paint surface (primer side) was white like the P-10 primer. *Table* 1 includes the XPS results from analysis of the interfacial surfaces. For the indirect-fired cure, the interfacial paint and substrate elemental compositions show important differences. The interfacial paint surface bears a resemblance to the P-10 control (bulk P-10 primer, generated by fracturing a "wafer" of the primer), with a slightly higher level of C,

Table 1—XPS-Measured Elemental Compositions of Interfacial Surfaces Generated from Primer/Electrocoat Adhesion Loss

	Elemental Composition—Atomic %							
Sample	C	O	N	Si	Al	Ti	Sn	Zn
PP-10 Control	67.1	23.5	5.2	1.7	2.3	0.2	—	—
Indirect-fired oven								
Interfacial paint	70.7	21.7	4.8	1.0	1.8	—	—	—
Interfacial substrate	75.7	20.6	3.6	—	—	—	—	—
Electrocoat surface	75.8	21.4	2.3	—	—	—	—	0.5
Direct-fired oven								
Interfacial paint	63.8	25.6	5.0	2.3	2.9	0.3	—	0.1
Interfacial substrate	68.8	22.9	5.6	1.3	1.4	—	—	—
Electrocoat surface	76.8	20.1	2.6	—	—	—	0.5	—

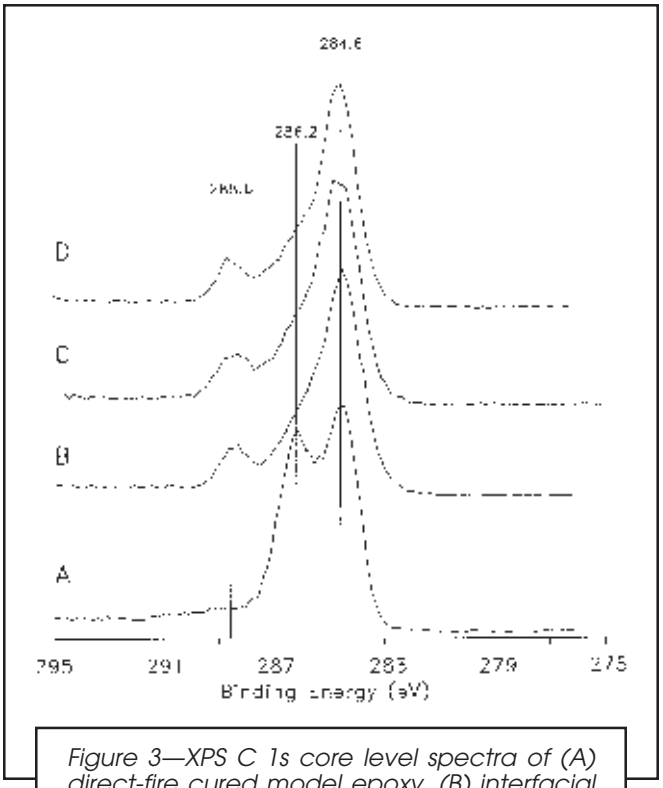


Figure 3—XPS C 1s core level spectra of (A) direct-fire cured model epoxy, (B) interfacial substrate, (C) interfacial polyester surface, and (D) P-10 polyester coating

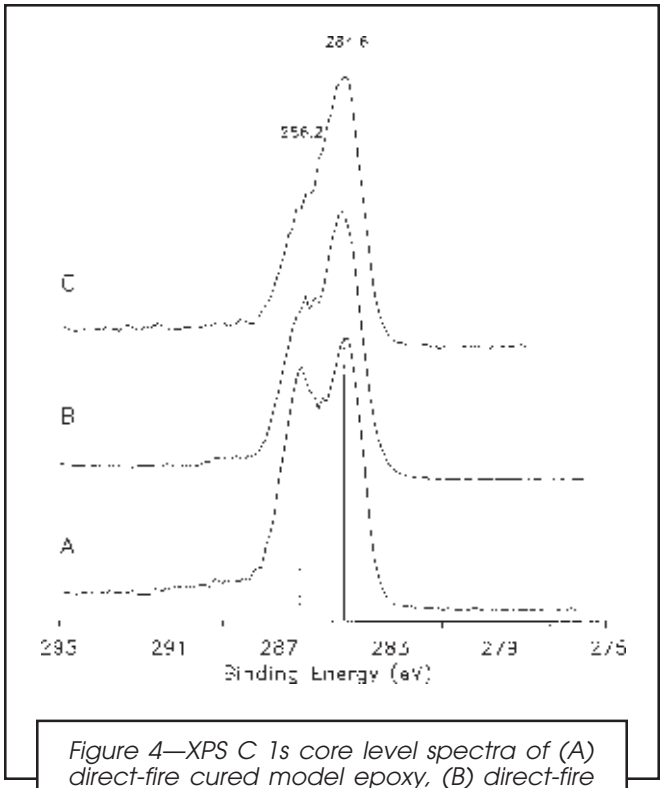


Figure 4—XPS C 1s core level spectra of (A) direct-fire cured model epoxy, (B) direct-fire cured model epoxy after acid rinsing, and (C) direct-fire cured model epoxy formulated without anti-cratering agent.

and lower levels of N, Si, and Al. The Si and Al are most likely components associated with pigments within the primer layer. In contrast, the interfacial substrate (electrocoat interface) was more similar in composition to the electrocoat surface. It contained a yet higher level of C, less O and N, and no detectable Si or Al.

The core level C 1s spectra acquired from the interfacial paint surfaces, along with the electrocoat top surface and primer control, are shown in *Figure* 2. The major components at 284.6, 286.2, and 288.6 eV binding energy correspond to carbon in the form of hydrocarbon (–C–R), ether (C–O–R), and ester (–CO_2R), respectively. The principal differences between the electrocoat standard and primer standard spectra are: (1) a lack of ester carbon (288.6 eV) and (2) a significantly enhanced ether carbon peak (286.2 eV) in the electrocoat. The spectra in *Figure* 2 show that progressively from A through D there is an increase in the ester peak, and a dramatic decrease in ether peak. The interfacial paint surface (*Figure* 2C) closely resembles the bulk primer control (*Figure* 2D). However, close observation of this spectrum (*Figure* 2C) reveals a slight increase in the ether component reminiscent of the electrocoat standard. The interfacial substrate surface appears to contain constituents of both the primer standard (ester moieties) and the electrocoat standard (ether moieties).

The elemental composition data and core level spectra both suggest that the locus of failure is not at a clean interface between the two paint layers but rather somewhere within an interphase layer that comprises constituents from both the P-10 primer and the model electrocoat material. The core level results suggest that this interphase is enriched in ether-containing material from the underlying electrocoat paint layer.

Direct-Fired Electrocoat Cure: Scribe/adhesion testing of paint systems that were prepared with an electrocoat coating cured in a direct-fired oven showed significantly better adhesion than that of the corresponding system involving the indirect-fired oven. The small amount of adhesion loss observed upon taping was spotty and more "random" in the loci of adhesion failure. Adhesion loss visually appeared to occur at both the electrocoat/steel interface as well as the electrocoat/primer interface that was observed for the previous system. *Table* 1 also includes the XPS-measured surface elemental compositions of interfacial surfaces generated as a result of adhesion testing of the paint system with the electrocoat baked in the direct-fired oven. The data represent analyses of a failure that appeared to be primarily associated with the electrocoat/primer interfaces rather than with the electrocoat/steel substrate interfaces. The interfacial surfaces generated in this system, unlike the interfacial surfaces associated with paint adhesion loss with the indirect-fired oven, were nearly identical in elemental composition to those of the cross-sectional surface of the P-10 control. Also, primer filler materials (Si and Al) were evidenced on both interfacial surfaces. These results suggest that adhesion failure appears to have occurred cohesively within the P-10 primer material itself.

The C 1s core level spectra of the interfacial substrate and paint surfaces from the direct-fired electrocoat system, *Figures* 3B and 3C respectively, were very similar and nearly identical to the C 1s core level spectrum of

the P-10 control (*Figure* 3D). No evidence for involvement of any other paint layer was observed.

The elemental composition and C 1s core level data both suggest that the adhesion loss is primarily associated with mechanical fracture cohesively within the bulk primer, not at the interface that is associated with primer/electrocoat adhesion. Based on these observations, it appears that there is a fundamental difference in the locus and mechanism of adhesion loss between the paint systems depending upon whether the electrocoat was cured in a direct- or indirect-fired oven. Therefore, additional efforts were undertaken to fully characterize the effects of direct- versus indirect-fired electrocoat bake ovens on electrocoat surface chemistry.

Table 2—XPS-Measured Surface Elemental Compositions of Electrocoat as a Function of Bake Oven Cure

	Elemental Composition—Atomic %				Atomic Ratios	
Sample	C	O	N	Sn	N/C	N/O
Direct-fired cure	76.8	20.1	2.6	0.5	0.034	0.129
Indirect-fired cure	75.8	21.4	2.3	0.5	0.030	0.107

Electrocoat Surface Chemistry as a Function of Direct- vs. Indirect-Fired Bake Oven

Surface Elemental Compositions: *Table* 2 compares the surface elemental compositions of the model electrocoat coating surfaces cured in indirect-fired and direct-fired ovens. These results show that the electrocoat material cured in a direct-fired oven is slightly enriched in N content relative to the material cured in an indirect-fired oven. This is shown by direct examination of the percent N composition as well as higher N/C and N/O ratios. Although these differences are small, repeat acquisitions at random spots yielded similar amounts of N-enrichment. Interestingly, high resolution N 1s core level spectra (not shown) of both indirect- and direct-fired electrocoat surfaces revealed a single peak at a binding energy consistent with the type of materials present in electrocoat polymers; i.e., urethanes, ureas, or substituted amines. No evidence of N moieties characteristic of nitro-, nitrate-, or other oxidized nitrogen species was detected.

High-Resolution C 1s Analysis: The C 1s core level spectra acquired from the indirect- and direct-fire baked electrocoats are shown in *Figures* 2A and 3A, respectively. It is readily apparent from a cursory examination of the spectra that the resulting electrocoat surfaces chemistry of the two oven process are not identical. Calculations indicated that, for both types of oven cure, the amount of ether-type carbon revealed in the C 1s spectra of the electrocoats was far greater than that expected for the bulk electrocoat paint itself. However, the differences appear to be present only in surface regions of the coatings since photoacoustic IR analysis (not reported here), which probes orders of magnitude deeper into the paint, shows little, if any, differences. The results reflect the surface segregation of an ether-rich material or the generation of ether-rich material during the cure of the electrocoat, independent of the type of oven. These possibilities can be verified by experiments involving rinsing the freshly baked electrocoat surface with dilute hydrochloric acid. This treatment will result in the formation of water compatible or soluble "salts" if basic moieties (e.g., amines) are present. Significant changes in the surface chemistry resulting from this treatment would then be strong evidence for the presence of these materials on the surface of the baked electrocoat.

Figures 4A-4C show the XPS C 1s core level spectra acquired from the direct-fired electrocoat, the direct-fired electrocoat after acid rinsing, and the direct-fired electrocoat formulated without an ACA, respectively. *Figures* 5A-5C give the same spectra for the electrocoat cured in an indirect-fired oven. All spectra show two main components: one at 284.6 eV, carbon as hydrocarbon (HC), and at 286.2 eV, carbon as ether (C–O). For the direct-fired case, acid rinsing resulted in a C 1s spectra (*Figure* 4B) quite similar to that acquired from the electrocoat formulated with no ACA (*Figure* 4C); i.e., a substantial reduction in the ether peak over the direct-fire cured surface (*Figure* 4A). The C 1s spectrum from the acid-rinsed indirect-fired electrocoat (*Figure* 5B) also showed a reduction in the ether peak over that for the indirect-fired only (*Figure* 5A), but the amount was still greater than for electrocoat cured without the ACA (*Figure* 5C).

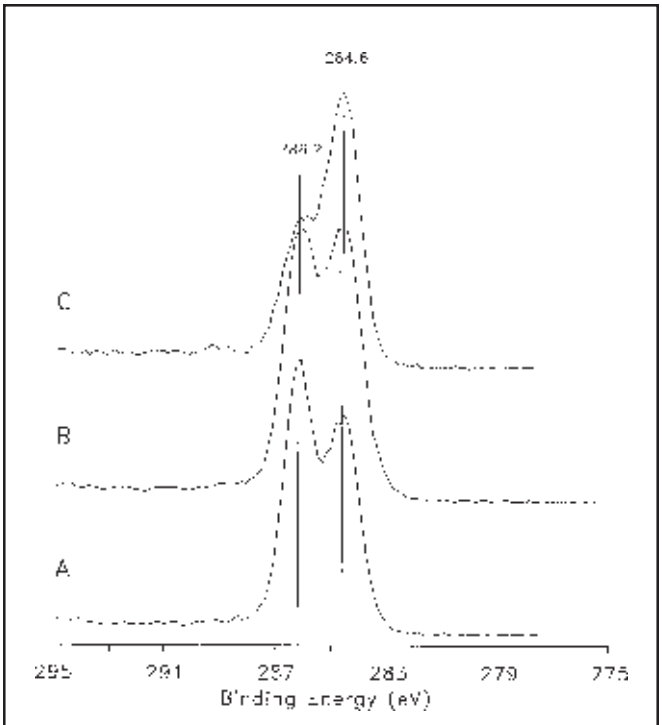


Figure 5—XPS C 1s core level spectra of (A) indirect-fire cured model epoxy, (B) indirect-fire cured model epoxy after acid rinsing, and (C) indirect-fire cured model epoxy formulated without anti-cratering agent.

Table 3—XPS C 1s Ether-to-HC Peak Ratios for Direct- and Indirect-Fire Cured Electrocoats after Acid-Rinse Treatments

	XPS C 1s Ether to HC Peak Ratio		
Sample	Initial	Acid Rinsed	No ACA
Direct-fired oven	0.83	0.61	0.43
Indirect-fired oven	1.21	0.94	0.48

The high-resolution XPS observations are more quantitatively described in *Table* 3, which shows ether-to-hydrocarbon ratios from the C 1s spectra given in *Figures* 4 and 5. The XPS data show that initially there is a 38% accentuation in the ether/HC ratio for coatings baked in indirect-fired electrocoat ovens relative to those baked in the direct-fired ovens. Acid rinsing lowered the direct-fire cured electrocoat ether/HC ratio by 32% (0.83 to 0.61), and the indirect-fire cured electrocoat ether/HC ratio by 24% (1.21 to 0.94). The electrocoats cured with no ACA exhibited much lower ether/HC ratios. With no ACA, the direct-fire cured electrocoat ether/HC ratio was slightly lower (by approximately 10%) than the indirect-fire cured.

These results suggest that regardless of bake oven scheme, the majority of the ether constituency observed on the electrocoat surfaces can be attributed to the ACA, **3**. The amine functionality appears still to be associated with the ACA, since it can be partially removed by acid rinsing. The portion of the ACA that is not removed by acid rinsing is most likely "solidly" crosslinked into the underlying electrocoat. However, the important difference noted is that the indirect-fired electrocoat surface contains substantially more ether-containing species before and after acid-rinsing than does the direct-fire cured electrocoat surface. This difference suggests that the environmental factors of bake oven cure can have a direct effect on the resulting electrocoat surface chemistry.

Direct-Fired vs. Indirect-Fired Ovens—Expected Differences in Oven Air Chemistry

The fact that differences in surface chemistry were observed, directly related to the type of cure oven utilized, requires comment with regard to oven air chemistry. Although no fundamental analysis of oven atmosphere chemistry was done in this study, a reasonable description of the differences in chemistry can be inferred from a general knowledge of indirect-fired and direct-fired ovens. In the discussion of the oven atmospheres that follows, the assumption is made that the air within each oven zone is minimally intermixed with other oven zones so that the moisture present in the uncured, just-deposited electrocoat film is minimally reflected in the oven atmosphere composition in latter zones; this assumption is made for discussion related to both types of ovens.

As the names imply, the air in an indirect-fired oven is heated through heat exchangers, which are themselves heated by burners fired by natural gas combustion. Therefore, no combustion of gases within the oven will be taking place. In contrast, the direct-fired oven atmosphere is heated directly by hot combustion gases that are generated as a result of burning natural gas. Based on this simple description of the two types of ovens, a fundamental difference in oven atmosphere would be expected to exist between the two types of ovens. The atmosphere within indirect-fired ovens would be largely that of the ambient air with appropriate adjustments in relative humidity related to the differences in temperature between outside and inside the oven. In contrast, the atmosphere within a direct-fired oven would be related to the combustion processes (of natural gas, i.e., CH_4) used within the oven system to heat the air:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + HEAT \quad (3)$$

$$N_2 + O_2 + HEAT \rightarrow \text{nitrogen oxides } (NO_X) \quad (4)$$

Assuming complete combustion in a direct-fired oven, the burning of natural gas would result in the formation of carbon dioxide and water, in addition to the heat that is actually used to heat the oven (equation (3)). Based on this reaction stoichiometry, the mole fraction of water formed would be 0.67; in reality the combustion process within the oven is conducted with air so the mole fraction of water in the oven would be about 0.13. The use of makeup air to control oven temperatures would reduce the water content to some extent so that this number represents an upper limit in water concentration. In practice, the direct-fired oven atmosphere is likely to be much more complex since some incomplete combustion will result in the formation of oxidized intermediates such as methanol, formaldehyde, and formic acid. The combustion process is further complicated in that it is conducted using air, which at the flame temperatures involved, would be expected to result in the formation of nitrogen oxides from the oxidation of ambient nitrogen (equation (4)). Nitrogen oxides (measured as NO_X) have been measured at levels of 5-10 ppm within direct-fired ovens.[8]

In short, the atmosphere within a direct-fired oven is likely to be more complex than that within an indirect-fired oven. The formation of combustion products like water and NO_X, which are potentially reactive materials toward polymeric systems used in paint materials, requires that one explore possible interactions between these combustion products (present in direct-fired ovens) and the polymer chemistry at coating surfaces that influence paint adhesion.

Laboratory Simulation: Effects of Direct-Fired Oven on the Surface Chemistry of Model Electrocoat Coating

The simulation of a direct-fired electrocoat oven requires that at least two factors be examined: the effects of nitrogen oxides (NO_X) and the effects of water, the principle reactive products of a natural gas combustion that is used to heat the air in the oven. Other combustion products, such as carbon dioxide and carbon monoxide, at this point have generally been assumed to play minimal roles in affecting the cure chemistry of electrocoat. Most reasonable reactions of carbon dioxide would involve the formation of carbonates and bicarbonates that would very likely be unstable at electrocoat bake-oven temperatures. These species, which were not detected,

would also be readily identifiable by XPS. Carbon monoxide, aside from its oxidation to carbon dioxide, would also be regarded as being generally minimally reactive. Other materials expected in the atmosphere of a direct-fired oven would be amines, solvents, and other organic materials from the electrocoat material itself. But these materials would be no different than what would also be present in an indirect-fired oven.

An experiment was conducted to determine how the surface chemistry of the model electrocoat might change as a function of NO_X exposure level during cure. In this experiment, nitrous oxide is introduced into an electric laboratory oven during paint cure. At these oven conditions the nitrous oxide then oxidizes to nitrogen dioxide to provide an "NO_X simulation" of a direct-fired oven. XPS was used to determine the surface chemistry differences induced from NO_X-containing "direct-fired" and NO_X-free indirect-fired (electric) oven environments. XPS high-resolution N 1s core level spectra acquired from the electrocoats cured in the "direct-fired" environment (data not shown) surprisingly did not show any detectable amounts of surface nitration. Although nitration of aromatics with NO_X is not an especially facile reaction, hydroxy functional groups of the type that are found on the backbone of the electrocoat epoxy polymer are easily oxidized to form nitrates and related functional groups (i.e., carbonyls, from decomposition of nitrates). The absence of higher binding energy nitrogen components in the XPS spectra, typical of NO_X oxidation of epoxy hydroxy groups, suggests that NO_X was in fact not in "contact" with the actual electrocoat polymer but rather some other overlayer. This suggestion is supported by examination of high resolution C 1s spectra (*Figure* 6) that show that the principle effects of NO_X on the electrocoat coating involve depletion of ether functionality. The C 1s results clearly show that minor amounts of NO_X (ca. 2 ppm) have a pronounced effect on the surface chemistry of the cured electrocoat coating. The XPS C 1s ether to HC peak ratios of the spectra in *Figure* 6 are given in *Table* 4.

The 2 ppm NO_X exposed sample, representing an industrial direct-fired oven (*Figure* 6B), had an ether to HC carbon ratio of 0.71 as compared to 1.29 for the 0 ppm NO_X control (*Figure* 6A), representing an industrial indirect-fired oven. These values parallel those obtained from the electrocoat surfaces prepared at an industrial facility in the direct- and indirect fired ovens, 0.83 and 1.21, respectively (*Table* 3). Interestingly, the laboratory simulation of the effects of NO_X on the surface chemistry of electrocoat also shows that higher levels of NO_X do not necessarily result in additional reductions in ether. In fact, the amount of ether is increased and levels out at an ether to HC ratio of 0.90, 0.90, and 0.81 for NO_X concentrations of 4, 10, and 25 ppm, respectively. This suggests that initial reaction of NO_X to remove the polyether surface components may be complicated by "other" chemical transformations, possibly oxidative transformations of the epoxy backbone of the electrocoat polymer that introduce carbon-oxygen bonds (ether).

Water, produced as a combustion product in the direct-fired electrocoat oven, can also have a significant effect on the surface chemistry of the electrocoat. Water at the 180°C bake temperature can hydrolyze urethane/urea linkages of the type that are present in the crosslinked electrocoat and the chemically bound polyether-based crater-control additive. Hydrolysis of both materials would result in the formation of amines (basic functionality), which if coming from the crater control additive, would be lower in molecular weight and more easily removed by acid rinsing, evaporation, or oxidation by NO_X. The reaction of water with the electrocoat polymer surface (assuming that the surface-active crater-control additive has been removed previously by some process) would generate non-volatile amines derived from the isocyanates used to prepare the base electrocoat polymer. If present on the surface after electrocoat bake, these basic moieties could interfere with the interfacial cure of certain, but not necessarily all, acid-catalyzed melamine-crosslinked primer coatings. Melamine crosslinked polyester coatings formulated with strong acid catalyzed, monomeric melamine systems would be expected to be most sensitive to this interfacial cure inhibition.

Table 4—XPS C 1s Ether-to-HC Ratios of Electrocoats Cured in an Electric Oven with NO_x Added

	ppm Added NO_x				
	0	2	4	10	25
Ether to HC ratio	1.29	0.71	0.90	0.90	0.81

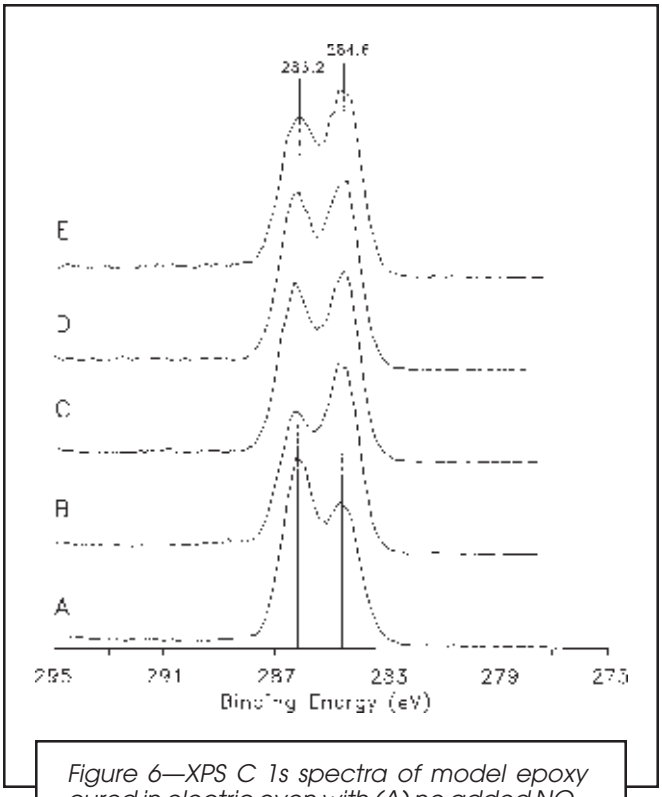
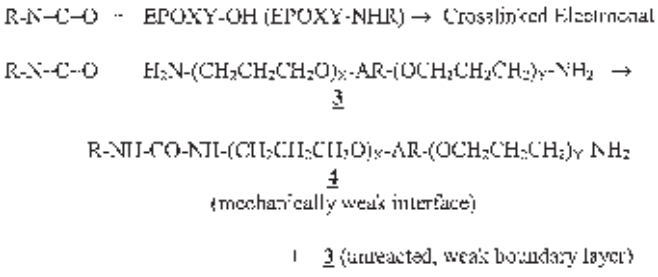


Figure 6—XPS C 1s spectra of model epoxy cured in electric oven with (A) no added NO_x, (B) 2 ppm NO_x added, (C) 4 ppm NO_x added, (D) 10 ppm NO_x added, and (E) 25 ppm NO_x added.

OVEN GASES, CURE, AND SURFACE CHEMISTRY

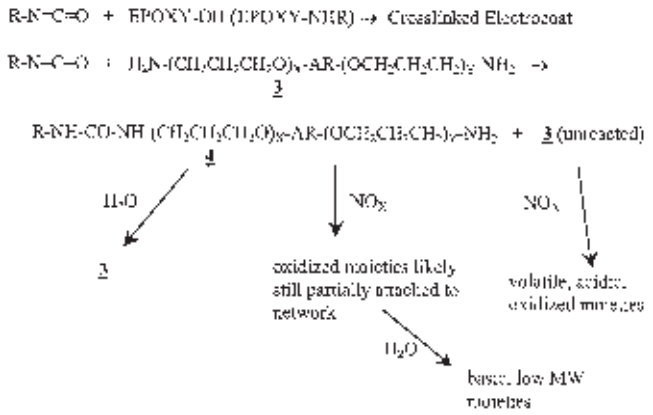
It is important to note that the action of oven atmosphere composition on the surface chemistry of coatings will be unique to the specific coating and processing conditions involved. This would make generalizations regarding in-service performance across coating systems risky, if not considered carefully. The atmospheric composition present within an indirect-fired oven is quite likely to have a minimal effect on the surface cure chemistry of the electrocoat (equation (5)). Electrocoat cure in an indirect-fired oven would proceed directly to the deblocking of the blocked



Equation 5

urethane electrocoat polymer to form free isocyanate functionality, which in the absence of any active hydrogen containing materials like the crater control additive, **3**, would proceed to afford the crosslinked electrocoat coating. The crater control effects of **3** require that it migrate and be present at the surface during cure. This requirement would result in the formation of a polyether functionalized urea material on the surface (**4**) that would likely have material properties that would afford a mechanically weak interface or, if present in an unreactive form, would afford a weak boundary layer. Both of these effects would impede the formation of a well-adhered coating system when a subsequent coating layer was applied. This is likely the scenario involved in the poor primer adhesion to indirect-fire cured electrocoats. Nevertheless, given acceptable adhesion performance, the absence of extraneous reactions occurring as a result of oven atmospheric conditions (involving, for example, reactive materials like NO_X and water) may make coating cure in the indirect-fired oven more robust for other paint systems.

In contrast, the surface chemistry that can occur in the direct-fired oven (equation (6)) is far more complex. The numerous reaction pathways potentially created by direct-fired oven cure make it more difficult for a surface to have predictable chemical properties. Also, compatible paint materials and systems developed employing direct-fired cure ovens may have been rendered more sensitive to process conditions for optimum performance. As a result, we would expect this process approach to be less robust than those involving indirect-fired ovens.



Equation 6

CONCLUSIONS

The interfacial chemistry of adhesion between melamine-crosslinked polyester coatings and epoxy coatings has been investigated using XPS techniques. This study has been conducted in light of process variations that can occur during both application and cure of these coating systems. For the epoxy coatings, XPS analysis has shown that the surface concentrations of a polyether-based crater-control additive will be less under cure in a direct-fired oven, and higher when the equivalent coating is cured in a indirect-fired oven. This difference in surface chemistry was attributed to the chemical actions of nitrogen oxides and water that are present in the cure environment of direct-fired ovens, which deplete the surface of the "adhesion w eakening" polyether-based additive. In contrast, the polyether additive remains on the surface of epoxy coatings baked with indirect-fired ovens, where cure takes place in a more inert environment.

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