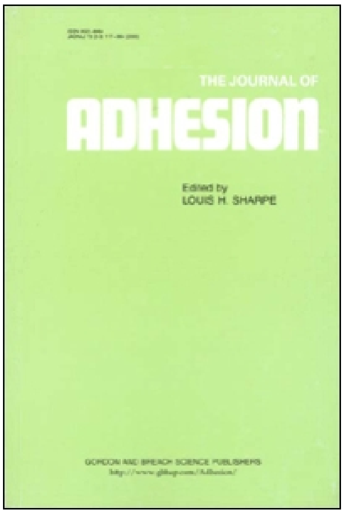

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Investigation of the "Surface" and "Interphase" Composition of Adhesion Promoter/Thermoplastic Olefin Systems: The Effect of Adhesion Promoter Bake Temperature

P. J. Schmitz[a]; J. W. Holubka[a]
[a] Ford Research Laboratory, Ford Motor Company, Dearborn, MI, USA

To cite this Article Schmitz, P. J. and Holubka, J. W.(1995) 'Investigation of the "Surface" and "Interphase" Composition of Adhesion Promoter/Thermoplastic Olefin Systems: The Effect of Adhesion Promoter Bake Temperature', The Journal of Adhesion, 48: 1, 137 — 148

To link to this Article: DOI: 10.1080/00218469508028159

URL: http://dx.doi.org/10.1080/00218469508028159

J. Adhesion, 1995, Vol. 48, pp. 137–148
Reprints available directly from the publisher
Photocopying permitted by license only

Investigation of the "Surface" and "Interphase" Composition of Adhesion Promoter/Thermoplastic Olefin Systems: The Effect of Adhesion Promoter Bake Temperature

P. J. SCHMITZ and J. W. HOLUBKA

Ford Motor Company, Ford Research Laboratory, Dearborn, MI 48121, USA

(Received April 8, 1994; in final form July 5, 1994)

The interfacial chemistry of model systems consisting of two adhesion promoting primers and a single Thermoplastic Olefin (TPO) substrate was examined. Two commercial adhesion promoter (AP) materials were applied to a commercially-available TPO material and either flash dried at room temperature or baked at 100°C. The surface composition of the AP films and TPO substrate, and the interfacial compositions of the AP/TPO systems were characterized using x-ray photoelectron spectroscopy (XPS). The AP films studied were based upon a chlorinated polyolefin (CPO). For one adhesion promoter film (AP-1), no chlorine was present at the surface suggesting a nonhomogeneous system. For the second adhesion promoter film (AP-2), the surface composition was about 15% CPO and 85% AP matrix. No changes in AP surface composition were evident for the different bake conditions for either AP. Interfacial compositions of the room temperature flashed materials were found to be very similar for both AP/TPO systems, with CPO being present for each and at similar concentrations. Interfacial compositions for the baked materials were also similar for the two systems, although the level of CPO at the interface increased for both the AP-1 and AP-2 relative to the unbaked materials. The relative increases observed were 46% and 41% for the AP-1 and AP-2 systems, respectively. The increase in the relative concentration of CPO at the interface with bake temperature suggests that there is a stronger interaction between the AP and TPO. The implication of these data is that a baked AP should result in a more robust paint system with respect to AP/TPO adhesion.

KEY WORDS thermoplastic polyolefin; TPO; chlorinated polyolefin; CPO; adhesion promoter; surface and interphase composition; effect of bake temperature; polymer-polymer adhesion.

INTRODUCTION

With the introduction of thermoplastics to the automotive industry, paint adhesion and long term durability, as with painted metal components, is a primary concern. Although plastic components have been in use for some time, fundamental interactions governing paint-plastic adhesion are still poorly understood. Due to the non-polar character of Thermoplastic Olefin (TPO) materials, and the absence of chemical functionalities that would promote adhesion, surface modification is required to provide suitable paint-adhering properties to this substrate.[1–3] A number of physical methods (*e.g.*, flame and plasma) are currently being explored as pre-treatments for TPO with varied success. Primer systems (*i.e.* chemical pretreatment) formulated with chlorinated polyolefins (CPO's) are commonly used as adhesion promoters (AP) for TPO systems. The mechanism for the interaction of the AP films with TPO that is critical for adhesion has not been clearly defined. However, it is generally believed that the CPO is the principal constituent of the AP that binds the AP film to the TPO through some interdiffusion and/or reaction phenomenon. In our testing of painted TPO systems we have found that changing a process variable, such as increasing the paint bake temperature, can improve adhesion performance. In an effort to learn more about the mechanisms governing adhesion in TPO systems, and the effect of paint bake temperature, we were motivated to study AP/TPO systems and their "surface" and "interphase" compositions. The objective was to ascertain the effect of bake temperature on the CPO concentration at the surface of the AP film, as well as at the AP/TPO interface. This study sets the initial ground work for painted TPO by improving our understanding of AP/TPO systems through the identification of component interactions resulting from process related issues, such as bake temperature.

In the work presented here, X-ray photoelectron spectroscopy (XPS) has been utilized to characterize the surfaces of two AP films and a single TPO substrate, as well as the interfacial surfaces of these AP/TPO systems for different AP bake temperatures. These results are our first attempt at understanding the interactions and adhesive properties of AP/TPO systems and the role of the AP bake.

EXPERIMENTAL

Materials

The TPO plaques and adhesion promoter materials that were used in this study were obtained from commercial sources. The TPO used was composed of polypropylene, and other olefin materials, and an ethylene-propylene rubber phase, approximately 30% rubber by weight. The specific formulations of the adhesion promoters utilized in this study are proprietary. However, the AP primers can be described generically as composed of a polyester/acrylic polymer matrix combined with an Eastman Kodak CPO material referred to as CP343-1.

AP films were applied to the TPO plaques with film builds on the order of 0.2 mils (0.005 mm). Following application of the AP, the plaques were either flash dried at room temperature or baked at 100°C for 30 minutes. Interfacial TPO surfaces were generated by solvent stripping of the AP film using spectroscopic grade xylene. Plaques were rinsed with xylene until the AP film was removed and the TPO surface was visible. After baking at 100°C, the AP films were more resistant to solvent attack and, therefore, gentle rubbing with a cotton swab was required to remove them.

The Eastman Kodak CPO material, CP343-1, is a component of both AP systems. Therefore, a thin film of this material was cast on a silicon wafer and used as a reference for the XPS measurement of the AP's CPO composition.

All materials were analyzed "as received" or "as prepared" unless otherwise stated. TPO samples referred to as "bulk" were generated by slicing through the plaque with a clean razor to expose bulk material.

X-ray Photoelectron Spectroscopy

XPS analyses were performed using an SSX-101 spectrometer manufactured by Fisons Surface Science, Mountain View, CA, USA. All spectra were acquired using monochromatic Al-K_α radiation (1486.6 eV) focussed to a 600 μm spot and operated at 100 W. Charging effects were minimized by the use of a low energy (1–3 eV) flood gun in conjunction with a Ni charge-neutralization screen. Core level binding energies were referenced relative to the aliphatic carbon line at 284.6 eV. All data reduction routines utilized were supplied by the instrument manufacturer.

RESULTS AND DISCUSSION

TPO and CPO standards

Results from XPS analyses of uncoated TPO plaques are shown in Table I. The surface of an unwashed TPO plaque was observed to contain C, O, Si, and Na. The Si and Na are most likely adventitious contamination or residues remaining from the molding operation. Power washing, using an acid-based wash system, resulted in the removal of the Si and Na contaminants, as well as the majority of the surface oxygen. After the power wash, carbon was observed to dominate the surface (98.6%), consistent with the olefinic components of TPO. However, a small amount of oxygen (*ca.* 1.4%) was observed to remain on the surface. Similar results were observed for the XPS "bulk" composition of the TPO plaque, Table I. The exact

TABLE I
XPS Quantitative Results for Reference TPO and CPO Materials

	Elemental Composition, Atomic %				
Reference Materials	C	O	Cl	Si	Na
Unwashed TPO Plaque:					
Area #1	91.0	6.9	—	1.4	0.8
Area #2	91.5	6.8	—	1.2	0.5
Power Washed TPO Plaque:					
Area #1	98.7	1.3	—	—	—
Area #2	98.6	1.4	—	—	—
Bulk TPO:					
Area #1	98.4	1.6	—	—	—
Area #2	98.0	2.0	—	—	—
Eastman CP343-1:					
Area #1	90.1	1.0	8.4	—	—
Area #2	89.7	1.0	9.4	—	—

nature of the oxygen observed has not been determined. The low levels detected could be accounted for by adventitious contamination.

XPS results for the Eastman CP343-1 material are also shown in Table I. As expected, the material is comprised primarily of carbon and chlorine with a small oxygen contribution from a maleate functionality that is part of the CPO backbone. From the quantitative data, the percentage of chlorinated, maleanated, and unfunctionalized propylene units can be estimated. The XPS results are consistent with the following polypropylene fragment distribution: 66% unfunctionalized, 33% chlorinated, and 1% maleanated. This composition, based on the XPS survey results, would correspond to a CPO with 24 wt% chlorine, consistent with the 20 wt.% reported by the manufacturer.[4]

AP/TPO Surface Composition

XPS results from the surfaces of the AP films on TPO, flash dried and baked at 100°C, are summarized in Table II. For the AP-1 material, only C and O were detected at the surfaces of these films. The absence of chlorine at the surface is surprising and suggests that AP-1 may not form a homogeneous film. These AP's are composed of a base resin (*e.g.*, polyester/acrylic polymers) combined with a CPO component. Therefore, the oxygen observed at the surface of the film is mainly associated with the AP base resin. Comparing the unbaked and baked AP surfaces, very little change in the surface composition was observed other than a very slight increase in oxygen concentration as evidenced by the small increase in the O/C atomic ratio. The increase in oxygen could result from a slight oxidation of the film surface or from some adventitious contamination from the bake ovens.

For AP-2, carbon, oxygen, and chlorine are all observed at the AP surface as is evident from the data in Table II. The presence of the chlorine indicates the presence of CPO at the immediate surface of the AP. Using the experimentally-derived

TABLE II
XPS Quantitative Results for AP Surfaces: Flash Dried *vs.* Baking at 100°C

	Elemental Composition, Atomic %				Atomic Ratios	
AP/TPO Systems	C	O	Cl	Si	O/C	Cl/C
AP-1: Flashed at R.T.						
Area # 1	95.8	4.2	—	—	0.044	—
Area # 2	95.9	4.1	—	—	0.043	—
AP-1: Baked at 100°C						
Area # 1	95.4	4.6	—	—	0.048	—
Area # 2	94.7	5.3	—	—	0.056	—
AP-2: Flashed at R.T.						
Area # 1	87.6	11.0	1.4	—	0.13	0.016
Area # 2	86.9	11.8	1.3	—	0.14	0.015
AP-2: Baked at 100°C						
Area # 1	90.9	7.7	0.6	0.8	0.085	0.0069
Area # 2	91.2	7.8	0.5	0.6	0.086	0.0055

composition of the CPO reference material, Table I, the surface of the AP-2 is estimated to be 15% CPO and 85% AP matrix. When the AP is baked at 100°C rather than flash dried, a small amount of silicon is observed at the surface of the baked AP. The source of this material is not known but likely is either a surface active component of the AP material or an adventitious contaminant from the bake oven. The presence of the silicon contamination makes it difficult to assess any subtle changes in surface composition derived from the bake treatment, although it is clear that significant thermally-induced changes are not observed. It can be said with certainty, however, that CPO is present at the immediate surface for the AP-2 material, where none was observed for AP-1. The significance of the difference in the surface concentration of the CPO for the two materials is unknown. Since XPS measures only the average composition over first 50 Å of material, the degree of inhomogeneity of AP-1 may be very small.

AP/TPO Interfacial Composition

To measure the interfacial CPO concentration at the AP/TPO interphase, the AP films were stripped by rinsing with xylene. The assumption is made that if some of the CPO has become either mechanically or chemically bound to the TPO it will remain on the TPO surface following the solvent rinse. Therefore, any differences in the degree of interaction of the CPO and TPO for the two AP systems, and changes in interactions with bake temperature, should be measurable by looking at the relative CPO concentration remaining following solvent rinsing. The elemental composition of the TPO surface following the solvent rinse was measured using XPS. The results are summarized in Table III. As is evident from these data, carbon, oxygen, and chlorine are all observed at the rinsed surface for the AP-1 and AP-2 materials and for both the unbaked and baked systems. The relative chlorine and oxygen concentrations, for both the AP-1 and AP-2 materials, are higher for the

TABLE III
XPS Quantitative Results for AP/TPO Interfaces: Flash Dried *vs.* Baking at 100°C

AP/TPO Systems Xylene Rinsed	Elemental Composition, Atomic %				Atomic Ratios	
	C	O	Cl	Si	O/C	Cl/C
AP-1: Flashed at R.T.						
Area #1	95.5	2.1	2.4	—	0.022	0.025
Area #2	95.8	1.9	2.3	—	0.020	0.024
AP-1: Baked at 100°C						
Area #1	91.8	3.9	4.3	—	0.042	0.046
Area #2	91.0	4.2	4.7	—	0.046	0.052
AP-2: Flashed at R.T.						
Area #1	93.8	3.7	2.5	—	0.039	0.027
Area #2	93.7	3.7	2.6	—	0.039	0.028
AP-2: Baked at 100°C						
Area #1	91.4	5.1	3.5	—	0.056	0.038
Area #2	91.0	5.1	3.9	—	0.056	0.043

baked systems as evidenced by the higher Cl/C and O/C atomic ratios listed in Table III. These data suggest that baking of the AP has, in some way, increased the interaction of the CPO and TPO substrate thus making it more resilient to solvation and subsequent removal by the xylene. However, from just the elemental composition little can be said about the differences, if any, in the residual CPO concentrations for the two AP systems.

The elemental composition data reveal that there has been an increase in the residual CPO and/or AP matrix remaining after the xylene rinse for the baked *vs.* unbaked system. However, it is of interest to know not only the elemental composition of the residual interphase but the relative concentration of the CPO, AP matrix and TPO present, to evaluate which paint system allows for the greatest degree of interaction between the CPO and TPO under identical process conditions. The concentration of each component at the surface can be estimated using the elemental compositions of the pure components present (CPO, AP matrix, and TPO) and the experimentally-observed compositions following solvent rinse. The experimentally-observed compositions should be representative of some linear combination of the pure materials barring any gross segregation phenomenon. The elemental compositions of the CPO and TPO were measured and reported in Table I. The elemental composition of the AP-1 matrix is assumed to be equivalent to that measured for the AP surface composition (Table II) due to the lack of any contribution from the CPO at the surface. The elemental composition of the AP-2 is approximated by subtracting out the CPO contribution measured at the surface of the flash-dried film. This results in an elemental composition of 86.7% C and 13.3% O for the AP-2 matrix. Since there are three components of the AP/TPO system (CPO, AP matrix, and TPO) and there are only three elements to be considered, simultaneous equations can be solved to determine the relative percentage of each component at the solvent-rinsed surface. Results from this type of an analysis are reported in Table IV.

To verify that the compositions listed in Table IV are reasonable, we have used the XPS core level spectra obtained from each of the reference components (the CPO, TPO, and AP matrix) and from the solvent-rinsed surfaces. If the elemental composition at the surface can be represented by some combination of the reference materials then the core-level spectra from the surface should also be represented by the same proportional combination of the reference core-level spectra. That is, synthetic core-level spectra can be generated by the addition of the reference core-level spectra, in the same percentages given in Table IV, and compared with the

TABLE IV
Relative CPO, AP Matrix, and TPO concentrations based on XPS elemental compositions

AP/TPO Systems	% CPO	% AP Matrix	% TPO
AP-1: Flashed at R.T.	26%	25%	49%
AP-2: Flashed at R.T.	29%	20%	51%
AP-1: Baked at 100°C	38%	62%	0%
AP-2: Baked at 100°C	41%	32%	27%

core-level spectra measured for the given solvent-rinsed surface. If the calculated compositions are reasonable then there should be a good correlation between the experimental and synthetic spectra. Shown in Figures 1 and 2 are the C(1s) synthetic spectra superimposed on the experimental spectra for the AP-1 and AP-2 systems, respectively. As is evident, there is a good correlation between the experimental and synthetic spectra. For the correlation between the experimental and synthetic spectra to be meaningful there must be a measurable difference in the reference spectra and the interfacial spectra, otherwise any random combination of the reference spectra will result in a good fit. Shown in Figures 3 and 4 are the C(1s)

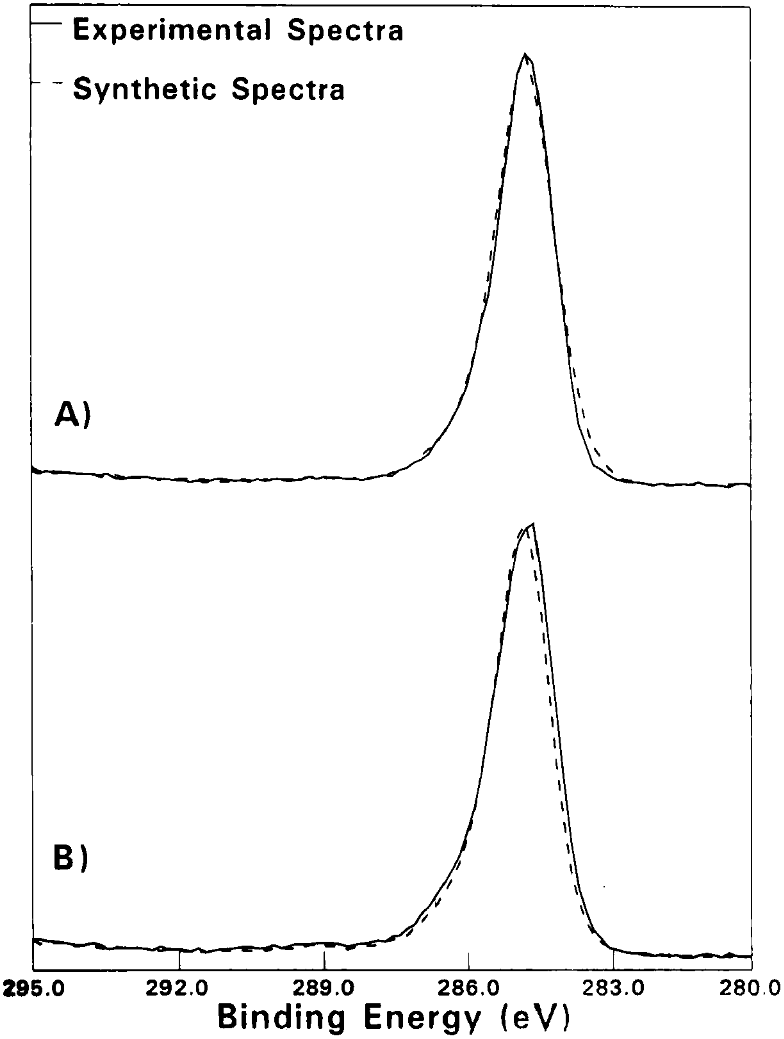

FIGURE 1 XPS C(1s) experimental and synthetic spectra of AP-1 on a commercial TPO material, xylene rinsed: A) R.T. Flashed; B) 100°C Bake.

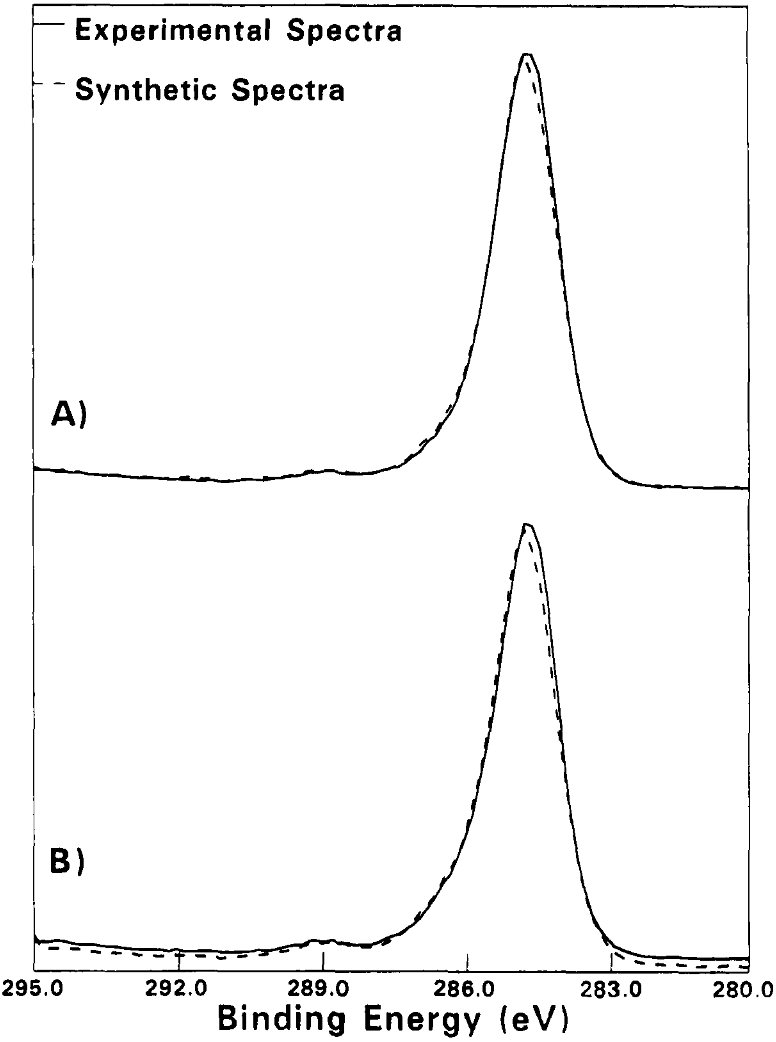

FIGURE 2 XPS C(1s) experimental and synthetic spectra of AP-2 on a commercial TPO material, xylene rinsed: A) R.T. Flashed; B) 100°C Bake.

experimental spectra from the AP-1 and AP-2 that were obtained from the 100°C-baked and solvent-rinsed surfaces, superimposed upon the reference spectra. These results, especially those of the AP-2 materials in Figure 4, illustrate that the reference C(1s) spectra are significantly different from the spectra obtained from the solvent-rinsed surfaces and that the good fit between the experimental and synthetic spectra are not coincidental. Similar results are observed for the oxygen core-level spectra, although due to the lower signal-to-noise the correlation is somewhat harder to assess. The results from the oxygen core-levels, therefore, have been omitted here for brevity. Overall, these results show that the composition for the solvent-rinsed

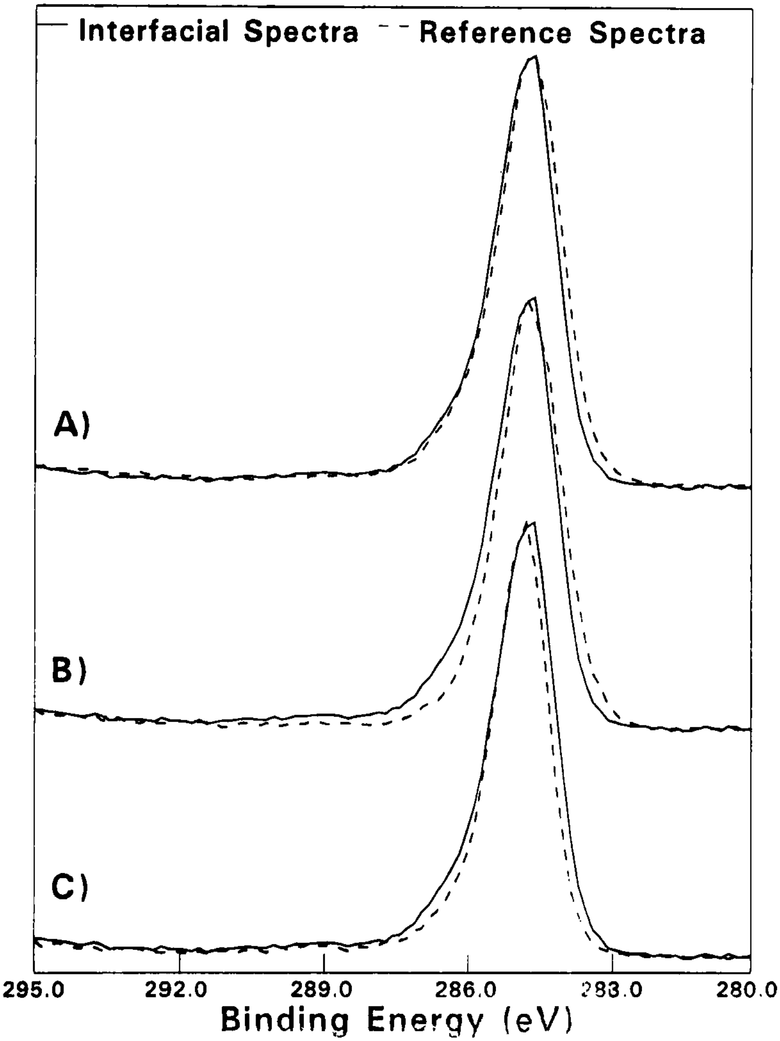

FIGURE 3 XPS interfacial C(1s) spectra of AP-1 on commercial TPO, baked at 100°C, superimposed on the systems' reference spectra: A) CPO reference spectra; B) TPO reference spectra; C) AP matrix reference spectra.

surfaces can be approximated using a linear combination of the reference materials, and that the compositions determined are consistent with the core-level spectra observed.

Comparing the compositions of the AP-1 and AP-2 materials for the R.T.-flashed systems, Table IV, the results are very similar. As is evident, there is a contribution from the TPO indicating that the surface is not completely covered by the residual components of the AP. The relative percentages of TPO, CPO, and AP matrix are almost identical, suggesting little difference in the degree of interaction between the

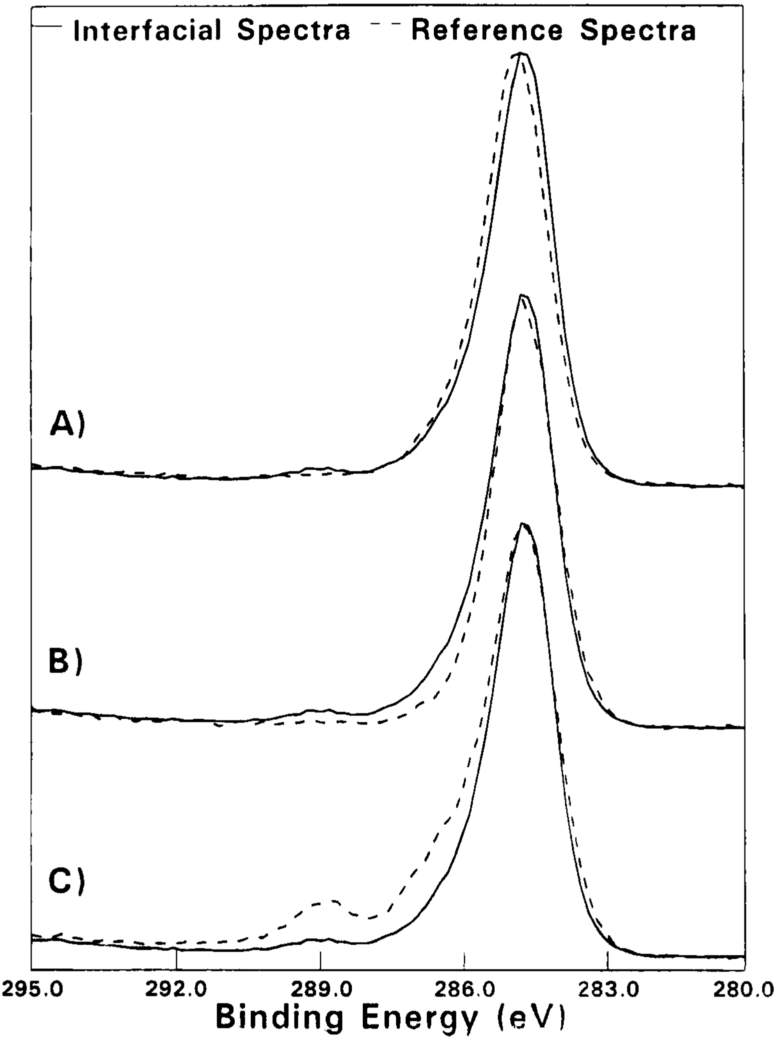

FIGURE 4 XPS interfacial C(1s) spectra of AP-2 on commercial TPO, baked at 100°C, superimposed on the systems' reference spectra: A) CPO reference spectra; B) TPO reference spectra; C) AP matrix reference spectra.

AP-1 and AP-2 materials and the TPO following the R.T. flash. Results from the systems baked at 100°C show an increase in the relative percentage of CPO and AP matix remaining at the surface for both the AP-1 and AP-2 materials following the solvent rinse. The changes observed represent an increase in the CPO concentration over the R.T.-flashed systems of 46% and 41% for the AP-1 and AP-2 materials, respectively. Again, the relative concentrations of the CPO are about the same for the two systems, suggesting that the degree of interaction of the AP's with the TPO are very similar.

Proposed Mechanism of Adhesion

Although the data presented clearly show that there is an interaction between the CPO and TPO, and that the degree of interaction increases for the baked system, the true mechanism of adhesion can not be ascertained from these measurements. No change in the high resolution core-level spectra was observed, suggesting that a chemical reaction between the CPO and TPO has not occurred. If a reaction has not occurred, then interdiffusion or mechanical adhesion of the two systems is likely the predominant mechanism. Due to the lack of physical evidence, one can only speculate as to the details leading to the mechanical interlocking of the AP primer and the TPO. A scenario consistent with our observations can be described as follows. One could envision that during the application of the AP primer, solvent swelling of the TPO rubber phase will occur allowing for the diffusion of the primer components, namely the CPO, into the rubber phase. As the solvent evaporates and the rubber phase contracts, fragments of the CPO from the AP will be mechanically trapped and act to anchor the primer to the TPO substrate. The observation of an enhanced interaction of the CPO and TPO with higher bake temperature can then be rationalized by an enhanced diffusion of the CPO into the rubber phase at the higher temperatures. Together with this scenario of higher diffusion, it is also possible that at the higher bake temperatures there is a compositional rearrangement in the TPO surface which increases the rubber concentration and, thus, enhances the probability of primer/CPO entanglement. Our observations are consistent with either of the mechanisms described above or a combination of the two.

CONCLUSIONS

We have completed a study of the surface composition of a commercially-available TPO material and two adhesion promoter films. We have also examined interfacial surfaces of the AP-1/TPO and AP-2/TPO systems for the unbaked and baked processing conditions.

The chlorinated polyolefin of AP-1 does not appear to be homogeneously distributed throughout the AP film. No chlorine was observed at the surface of the AP films; higher levels of chlorine were observed at the AP/TPO interface. The AP-2 surface was composed of about 15% CPO and 85% matrix. Like the AP-1, higher levels of CPO were observed at the AP/TPO interface for the AP-2/TPO system. The significance of the difference in the distribution of the CPO in the film for the two materials is unknown. Since XPS measures only the average composition over the first 50 Å of material the degree of inhomogeneity of AP-1 may be very small. Using the relative concentration of CPO observed at the solvent-rinsed interfaces, a comparison can be made for the relative degree of interaction of the CPO and TPO for the two paint systems. As was evident from the data, there appeared to be equivalent concentrations of CPO residing at the interface. These results suggest that the two AP systems are very similar with regards to the degree of interdiffusion and/or reaction with the TPO.

The effect of AP bake temperature on the interaction of the CPO with the TPO was also evaluated in this study. Results showed that baking the AP at 100°C *vs.* a

R.T.-flash resulted in a 46% and 41% increase in the relative CPO concentration at the solvent-rinsed surface for the AP-1 and AP-2 systems, respectively. The increase in the relative concentration of CPO with bake temperature suggests that there is a stronger bond created between the AP and TPO at the higher bake temperature. These observations are consistent with an enhanced diffusion of the CPO into the TPO at the higher bake temperatures or possibly a compositional rearrangement in the substrate surface at the higher temperatures which enhances the degree of interaction. Regardless of the exact details of the adhesion mechanism the implication of these data is that a baked AP will result in a more robust paint system with respect to the AP/TPO adhesion.

This work demonstrates the usefulness of XPS for investigating the interfacial compositions of the AP/TPO systems. Through the use of standard materials of the system components, interfacial/interphase compositions can be measured and followed as function of process conditions. This method works well for these AP/TPO systems due to the limited number of components and their relatively simple structures.

References

1. J. J. Cocco, *SAE International Congress and Exposition*, Detroit, MI, paper # 890519, 1989.
2. R. Ryntz, *SAE International Congress and Exposition*, Detroit, MI, USA, paper # 900524, 1990.
3. K. Krueger Davis and P. D. Clark, *SAE International Congress and Exposition*, Detroit, MI, USA, paper # 910092, 1991.
4. S. B. Fry, P. J. Greene, D. W. Magouyrk, K. Middleton, E. J. Sacksteder, *Polym. Paint Colour J.* **180**, 732 (1990).