Exudation Processes in Hydrogenated Bisphenol-A-Based Epoxy Coatings: Spectroscopic Study

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SYNOPSIS

Surfaces of hydrogenated bisphenol-A (DGEHBPA)-based epoxy resins cross-linked with polyamide based on dimer fatty acid and triethylenetetramine coatings were studied using ATR FTIR spectroscopy. These studies illustrate that for nonpigmented coatings the surface species resulting from the coatings' exposure to ambient conditions generate noncross-linked epoxies, whereas for pigmented coatings, polyamide is the primary surface component. The presence of these species is attributed to the adsorption on pigment particles and small, yet significant amounts in nonstoichiometry changes introduced into the system during formulation. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Although the processes leading to exudation of small molecules in polymer matrices have been recently addressed for latex films[1-4] and melamine/polyester coatings,[5] only limited studies on the surface exudation in epoxy coatings have been reported. For example, Foister[6] considered the dynamic surface property changes due to amine migration during cross-linking of the bisphenol-A based epoxy/primary amine system. These studies indicated that the primary amine cross-linking agents can act as surfactants that decrease surface tension during the initial stages of curing. The surface activity of the amine is reduced, however, when cross-linking reactions go to competition.

Based on these few isolated examples and the cross-link density considerations,[7] migration of small molecules will be affected by the cross-link density changes as well as by other factors, for example, internal stresses in a polymer and its surface tension. Furthermore, if a polymer network is not completely cross-linked, it is likely that uncross-linked molecules may migrate and, under suitable thermodynamic conditions, diffusion or exudation out of the film may occur. Although this process can be inhibited by the presence of rigid nonpermeable aggregates in a form of crystalline or semicrystalline

segments[8] or inorganic particles such as pigments, it is usually unavoidable when the polymer network degrades. As a matter of fact, degradation studies[9] of polyurethane topcoats over epoxy/polyamide primers, in which dynamic mechanical analysis (DMA) and photoacoustic (PA) FTIR were utilized, indicated that the inorganic pigment phase enhances rigidity of the cross-linked network, but decreases cross-linking density. The latter was attributed to the presence of pigment particles that may inhibit cross-linking reactions. The mobility is therefore further expected to change with network degradation.

Because of the presence of the light-absorbing aromatic groups, conventional bisphenol-A-based epoxy coatings have poor gloss retention when exposed to ultraviolet (UV) radiation. Such systems can be composed of a diglycidolether hydrogenated bisphenol-A (DGEHBPA)-based epoxy resin and cross-linked with a polyamide based on dimer fatty acid and triethylenetetramine. The structures of these components are shown below:
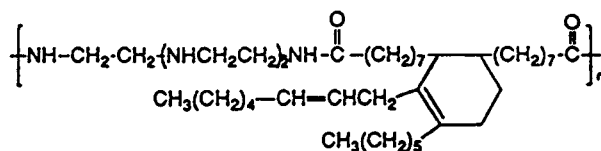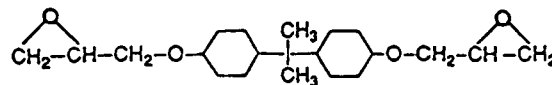
When such systems are cross-linked, UV stability is improved by the replacement of the UV-sensitive aromatic structures with more stable cyclohexane groups. Less rigid cyclohexane makes these epoxy-based resins good candidates for the low-viscosity applications in high-solids coatings.[10] This inherent advantage, however, may be overwhelmed by the accumulation of oily substances on the surface upon exposure to sunlight.[11] Although one would hypothesize that such unpredictable behavior could result either from degradation or exudation of the uncross-linked sole fraction of the network or both, this study will examine the molecular level processes responsible for this behavior. Furthermore, an ultimate goal is to establish how pigmentation and stoichiometric imbalance may affect mobility and exudation processes.

EXPERIMENTAL

Coatings Preparation

A typical formulation of the coating is given in Table I. All components of the pigmented base were placed in an aluminum beaker and ground in a high-speed grinder. The polyamide resin was dissolved in n-butanol and the solution was added to the mixture of pigmented base, which was continuously ground until all components were uniformly dispersed. Such prepared fluid was allowed to settle for 2 h before it was cast on an aluminum and/or polyester transparency substrate. The coatings were baked at 60°C for 2 h and 100°C for 1 h. The formulation as well as the preparation procedures of nonpigmented coatings were the same. In this case, no pigment was added, eliminating the use of a high-speed grinder. Coated panels were exposed to an ordinary indoor fluorescent light (Sylvania, 34W, F40 CW/SS, GTE) and were analyzed at various exposure times.

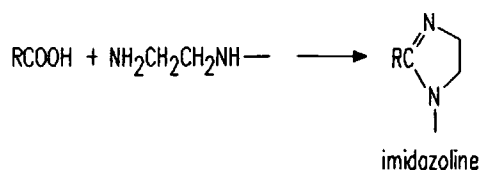**Table I   Formulation of Pigmented Epoxy/Polyamide Coating**

Component	w/w (%)	v/v (%)
Epoxy resin (Shell)	23.4	26.7
Rutile TiO$_2$ (DuPont, R-960)	33.5	10.4
Bentone 27	0.50	0.35
Methanol (Baker)	0.30	0.47
Nuosperse 657 (Tenneco)	0.10	0.12
Beetle 216-8 (Cyanamid)	0.50	0.62
Curing agent base		
Polyamide (Pacific Anchor)	10.5	13.5
n-Butanol (Mallinckrodt)	31.1	47.8

Spectroscopic Measurements

ATR FTIR spectra were recorded on a Digilab FTS-20 Fourier transform infrared spectrometer with a resolution of 4 cm^{-1} and the mirror velocity at 0.3 cm/s. An ATR attachment with varying angle of incidence from 30° to 60° and equipped with a KRS-5 crystal was used. To achieve a better signal-to-noise ratio, each ATR FTIR spectrum represents 400 co-added scans. All spectra were ratioed against the KRS-5 crystal. For semiquantitative assessments, the spectra were normalized to the band resulting from the polymer backbone vibrations that does not change intensity. The instrument was purged with purified air (Balston). Transmission FTIR spectra were recorded on a Mattson Cygnus-25 single-beam spectrometer with a resolution of 4 cm^{-1}. The spectrometer mirror velocity was at 0.316 cm/s, and the instrument was also purged with purified air (Balston).

RESULTS AND DISCUSSION

As the first step in such an analysis, it is necessary to establish the origin of the infrared bands for unreacted components of the epoxy network. Figure 1, traces A and B, show transmission FTIR spectra of pure epoxy resin and polyamide cross-linker. Their band assignments are based on the literature[12-14] and are summarized in Tables II and III, respectively. Although the majority of the bands listed in Tables II and III are attributed to the —CH$_2$— normal vibrations, we will focus only on those bands that are due to the functional groups of the cross-linker and the epoxy resin. In the spectrum of pure polyamide (Fig. 1, trace B), the 1663 cm^{-1} band is attributed to amide I of the secondary amide groups, whereas the 1612 cm^{-1} band is assigned to a combination of the tertiary amide and imidazoline normal vibrations. Since the polyamide was prepared in the condensation reaction of the dimer fatty acid and triethylenetetramine (TETA), both secondary and tertiary amides can be formed along with the formation of imidazoline shown below[15]:

$$\text{RCOOH} + \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}— \longrightarrow \text{RC} \underset{\underset{|}{\text{N}}}{\overset{\text{N}}{\diagdown}}$$

imidazoline

giving the band at 1612 cm^{-1} due to the N—C=N vibration.

Table II Tentative Infrared Band Assignments for DGEHBPA Polymer

Wavenumber (cm^{-1})	Band Assignment
3493	OH stretching
3053	CH stretch in oxirane group
2938	ν_{as} of CH_2 and CH_3
2962	ν_s of CH_2 and CH_3
1465	δ_{as} of CH_3 and δ of CH_2
1449	δ of CH_2 in cyclohexane
1386, 1369	CH_3 bending in $-C(CH_3)_2$
1310	CH_2 nonplanar wagger
1254, 910, 847	Vibrations of oxirane group
1159	ν_{C-O} in CH_2-O-
1099	ν_{C-O} in ether of cyclohexane
974	Cyclohexane ring vibration
910	Symmetric $C-O-C$ stretching
760	CH_2 wagger in cyclohexane
702	CH_2 wagger

Such species, however, have an inherent affinity to form hydrogen bonding with the neighboring species. If this is the case, the 1612 and 1663 cm^{-1} bands will be sensitive to the temperature changes. To confirm the above assignments, transmission FTIR spectra of polyamide were recorded at various temperatures were recorded. As illustrated in Figure 2, the temperature increase causes the 1663 cm^{-1} band to shift to a higher frequency, whereas the 1612 cm^{-1} band remains unchanged. These results indicate that the secondary amide groups can form hydrogen bonding that dissociates at elevated temperatures,[16] causing the shift to higher frequency. On the other hand, the 1612 cm^{-1} band due to tertiary amide and/ or imidazoline does not change since hydrogen bonding in such structures is unlikely to occur. The complementary changes in the $N-H$ stretching region resulting from heating are illustrated in Figure 3. The band at 3278 cm^{-1} shifts to high frequency due to a dissociation of the hydrogen-bonded $N-H$ groups.[17]

The spectral changes resulting from the temperature changes of the polyamide are also reflected in the 1420–550 cm^{-1} region and are shown in Figure 4. The band at 1307 cm^{-1} due to the $C-N$ stretching modes of cis-secondary amide groups as well as the bands at 823 and 775 cm^{-1} due to $N-H$ wagging modes of the cis-secondary amide groups become weaker upon heating. Such spectral changes are attributed to the conformational transformations of the secondary amide groups from the cis to more thermally stable trans conformation.

Having identified the relevant spectral features

of pure components, let us establish how pigmentation and cross-linking may affect the bands of reactive groups. ATR FTIR spectra of both pigmented and nonpigmented epoxy coatings are illustrated in Figure 5, traces A and B, respectively. For comparison, the spectra of pure components are also included (traces C and D). The apparent changes resulting from cross-linking can be found in the 1610–1660 cm^{-1} region. The band due to the secondary amide groups at 1666 cm^{-1} is not present and the 1612 cm^{-1} band due to the tertiary and imidazoline groups shifts to 1605 cm^{-1}. At the same time, the intensity of the 1556 cm^{-1} band is greatly reduced, and a shoulder at 1640 cm^{-1} is detected. Furthermore, a comparison between pure epoxy resin and the reacted species spectra indicates that the band at 3053 cm^{-1} attributed to the $C-H$ stretching bands in the epoxy ring disappears, and the bands at 1254, 910, and 847 cm^{-1} decrease significantly. These spectral changes are attributed to the cross-linking reactions, during which amine and secondary amide groups react with epoxy rings. A shoulder at 1640 cm^{-1} in the cross-linked system spectra (Fig. 5, traces A and B) is most likely due to secondary amide groups. It becomes weaker because secondary amide groups may also participate in the ring-opening reactions. The amide I band shifts from 1666 to 1640 cm^{-1} because of the stronger molecular interactions, most likely in a form of the hydrogen bonding between the secondary amide groups in a solid

Table III Tentative Infrared Bands Assignments for Polyamide

| Wavenumber (cm^{-1})	Band Assignment
3287	ν_s NH
2926	ν_{as} CH_2
2855	ν_s CH_2
1663	Amide I band of secondary amide
1612	Amide I band of tertiary amide and $N-C=N$ of stretching of imidazoline
1558	Amide II band ($N-H$ bending and $C-N$ stretching)
1458, 1366	CH_2, CH_3 bending
1258	Amide III band ($C-N$ stretching and $N-H$ bending)
1182, 1138	$C-N$ bending
1011	Cyclohexene ring
948	δ_{CH} in $CH=CH$ of aliphatic chain
916	δ_{CH} in $CH=CH$ of cyclohexane
723	CH_2 wagger in $(CH_2)_n$ $n \geq 4$
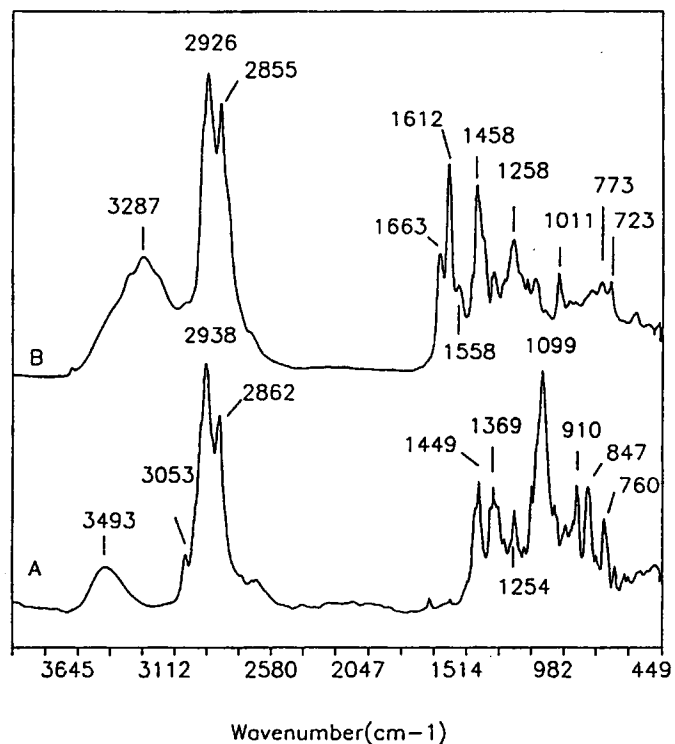
Figure 1   Transmission FTIR spectra of unreacted components: (A) epoxy; (b) polyamide.
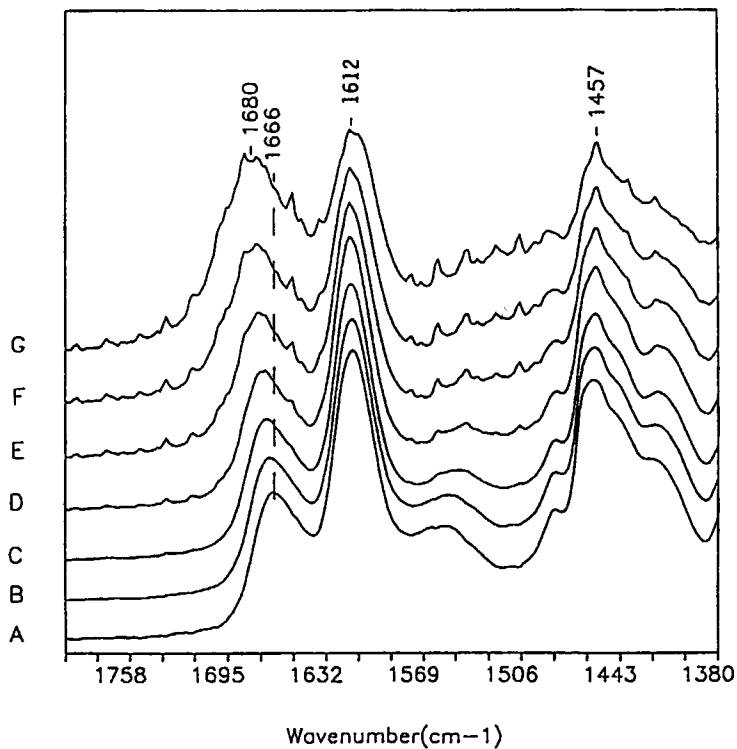

Figure 2   Transmission FTIR spectral changes in the 1800–1380 cm^{-1} region of polyamide upon heating: (A) 25°C; (B) 50°C; (C) 75°C; (D) 100°C; (E) 125°C; (F) 140°C; (G) 150°C.
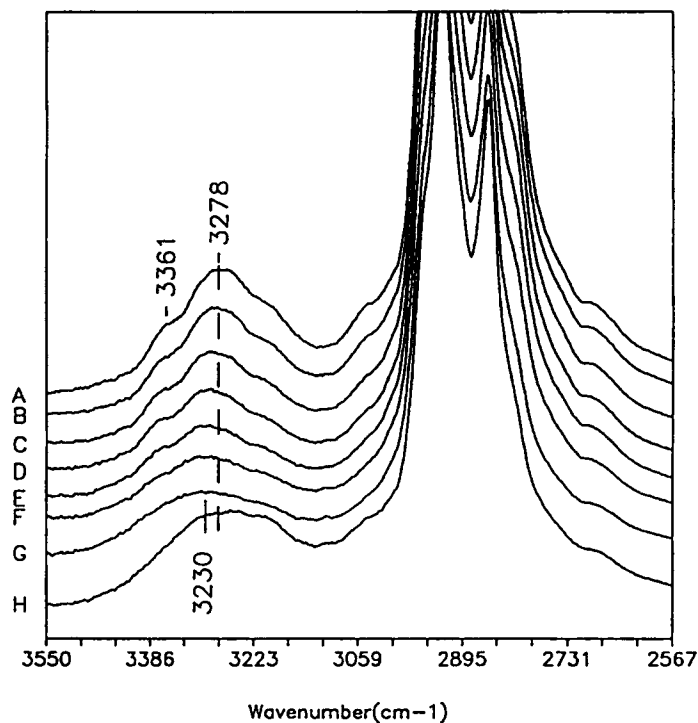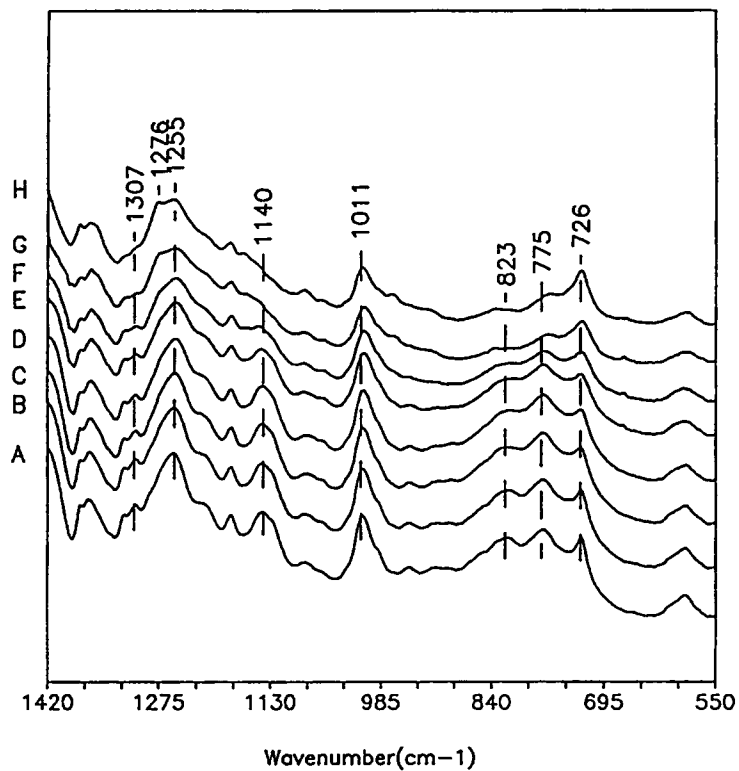
Figure 3 Transmission FTIR spectral changes in the 3350–2567 cm^{-1} region of polyamide upon heating: (A) 25°C; (B) 50°C; (C) 75°C; (D) 100°C; (E) 125°C; (F) 140°C; (G) 150°C; (H) cooled to 50°C.

Figure 4 Transmission FTIR spectral changes in the 1420–550 cm^{-1} region of polyamide upon heating: (A) 25°C; (B) 50°C; (C) 75°C; (D) 100°C; (E) 125°C; (F) 140°C; (G) 150°C; (H) cooled to 50°C.
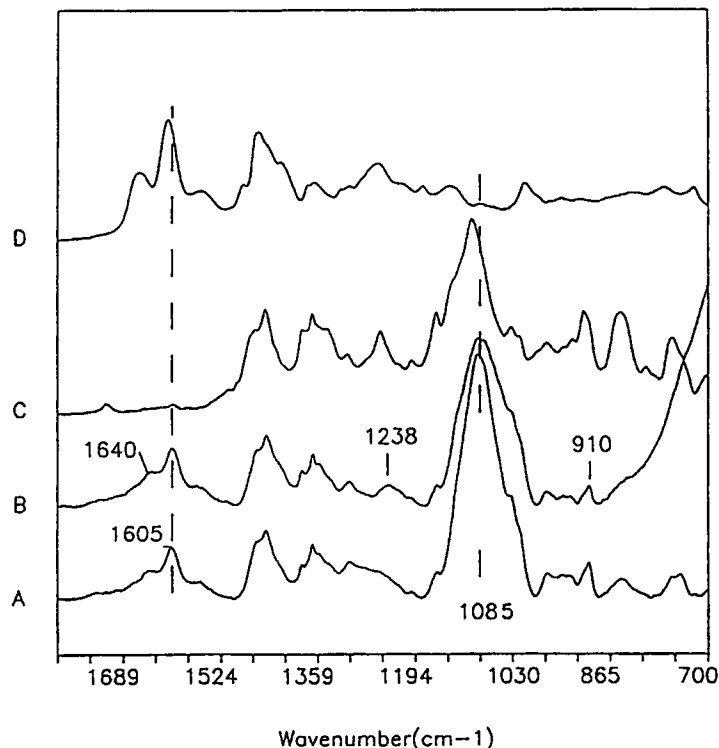
Figure 5 FTIR spectra of epoxy coatings: (A) ATR spectra of nonpigmented coatings; (B) ATR spectrum of pigmented coatings; (C) transmission spectrum of unreacted epoxy component; (D) transmission spectrum of unreacted polyamide.

state. Although the band at 1254 cm^{-1} is present in both epoxy and polyamide spectra, it is not detected in the spectra of coatings because most of the oxirane groups and secondary amide groups are used up during the cross-linking process.

Finally, to establish the temperature effect on the cross-linked network, Figure 6 illustrates FTIR transmission spectra of epoxy coatings recorded at various temperatures. Because the N—H bonds participate in the cross-linking reactions, and more OH groups are formed, the 3600–3100 cm^{-1} region is dominated by the OH stretching vibrations. As the temperature increases, the amount of free OH groups represented by the band at 3570 cm^{-1} increases. This is attributed to dissociation of the hydrogen-bonded OH groups at higher temperature, as demonstrated by the shift of the 3397 cm^{-1} band to 3423 cm^{-1}.

As indicated earlier, pigmentation may influence mobility of nonreacted species in a polymer network. For that reason, surface changes in pigmented and nonpigmented coatings were monitored by ATR FTIR as a function of the exposure time to ambient conditions. The spectra were recorded before and after the coatings were rubbed to remove possible

substances generated during exposure. The bands at 1605 and 1085 cm^{-1} will be used to evaluate the chemical changes in polyamide and epoxy components, respectively. ATR FTIR spectra of nonpigmented coatings, before and after rubbing, are presented in Figure 7. For the coatings exposed for 3.5 months (traces A), the band at 1085 cm^{-1} resulting from the epoxy component decreases after rubbing. This observation indicates that easily removable surface epoxy-containing species are present on the surface. Upon extended exposure times, the intensities of this band diminish continuously upon rubbing (traces B) until no detectable changes are observed (traces C). These results suggest that at the early stages of exposure there are unreacted, removable epoxy components on the surface. Upon further exposure, these species further react with the residual reactive functional groups of polyamide to form a cross-linked network and, therefore, cannot be removed upon extended exposures. This assessment is supported by the spectral changes observed for the 846 and 900 cm^{-1} bands characteristic of the epoxy rings. As illustrated in Figure 8, these bands become weaker after extended exposure times, indicating that, indeed, there are unreacted epoxy
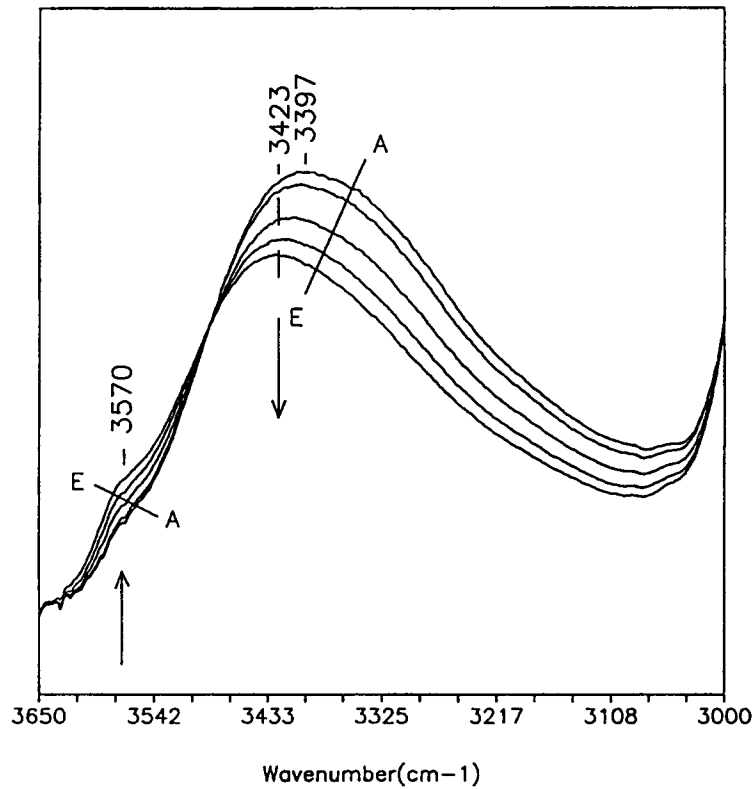
Figure 6 Transmission FTIR spectral changes in the 3650–3000 cm^{-1} region of epoxy coatings upon heating: (A) 25°C; (B) 50°C; (C) 75°C; (D) 100°C; (E) 125°C.
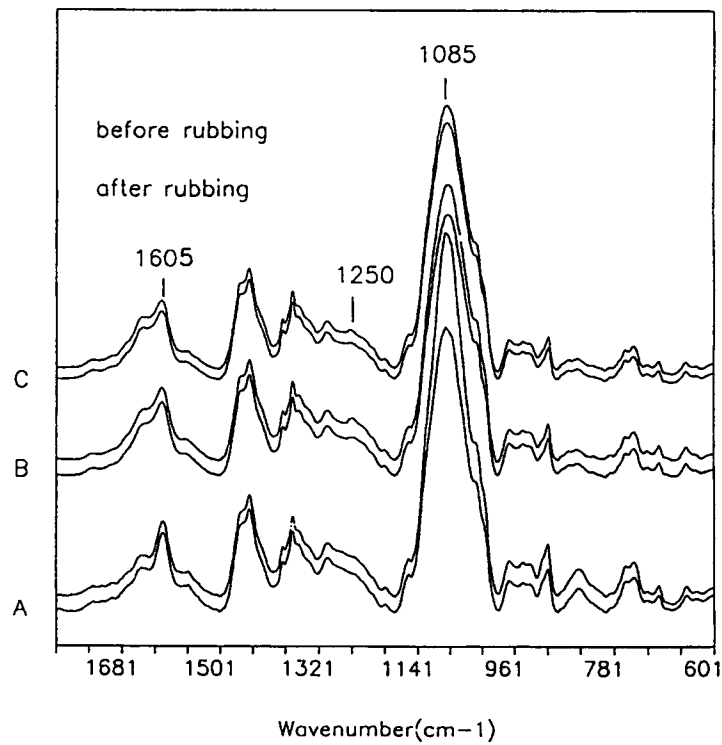

Figure 7 ATR FTIR spectral changes of nonpigmented epoxy coatings before and after surface rubbing with different exposure times: (A) 3.5 months; (B) 10 months; (C) 14.5 months. In each pair of spectra, the upper trace represents the spectrum before rubbing, and the lower trace, after rubbing.
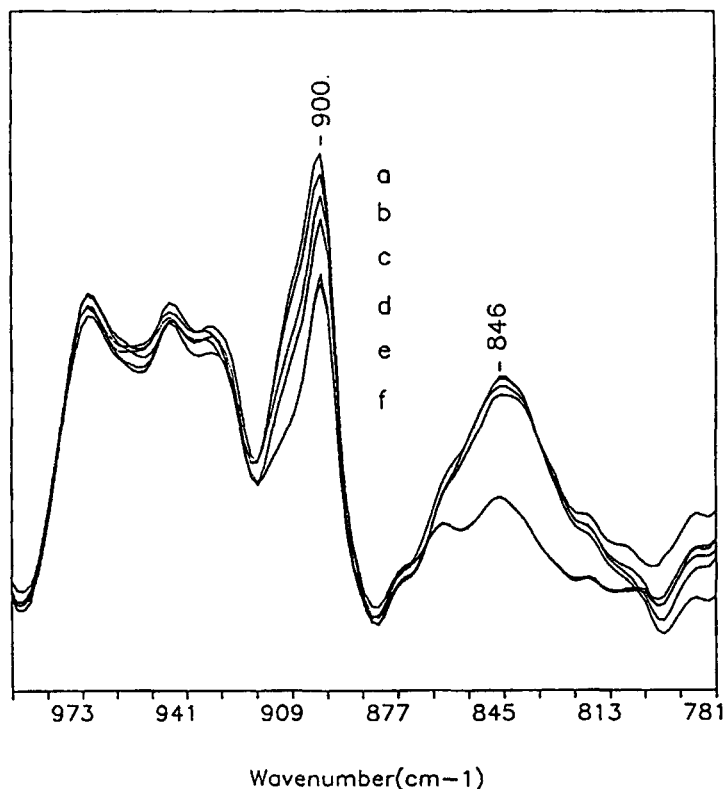
Figure 8   ATR FTIR spectral changes of nonpigmented epoxy coatings in the 1000–800 cm⁻¹ region with different exposure times: (a) before and (b) after surface rubbing, 3.5 months; (c) before and (d) after surface rubbing, 3 months later after (a) and (b); (e) before and (f) after surface rubbing, 7 months later after (c) and (d).

components on the surface that undergo the epoxy ring-opening reactions leading to cross-linked networks. The spectra illustrated in Figure 9 also indicate the band centered at 1605 cm⁻¹ due to the N—H bending normal vibrations of polyamide groups that increase in intensity, indicating that the amount of polyamide component on the coating surface increases upon exposure. The above results also indicate that even for the nonpigmented coatings cross-linking of the epoxy and polyamide is not complete and the not completely reacted epoxy component continues to cross-link, approaching completion upon further exposure. At the same time, uncross-linked polyamide, although in very small amounts, tends to migrate to the surface.

The analysis of parallel experiments conducted on pigmented coatings shows that the presence of inorganic pigment leads to the substantially different behavior. As demonstrated in a series of the spectra of the fingerprint region shown in Figure 10, there are no detectable spectroscopic surface changes before and after rubbing. In contrast to the nonpigmented coatings, these data indicate that no re-

movable molecular components are found on the coatings' surface. However, when such pigmented coatings are exposed to artificial sunlight, the spectral changes illustrated in Figure 11 are detected. An increase of the polyamide band at 1605 cm⁻¹ upon exposure is observed, which is accompanied by an increase of the 1461 cm⁻¹ band attributed to the CH_2 bending mode in polyamide. Furthermore, an increase of the bands due to secondary amide groups at 1670 and 1641 cm⁻¹ is detected. These observations indicate an excess of polyamide near the surface, but after 14 months of exposure (trace C, Fig. 11), a broad band centered at 1734 cm⁻¹ dominates this spectral region. This observation suggests that at longer exposure times a slow oxidative degradation on the coatings' surface occurs.[18,19]

In an effort to further enhance chemical information about the structures that develop upon exposure, Figure 12(a) illustrates the difference spectrum (B − A) obtained by a subtraction of the nonpigmented coating 3.5 months exposure spectrum (A) from that of the coating exposed for 14.5 months
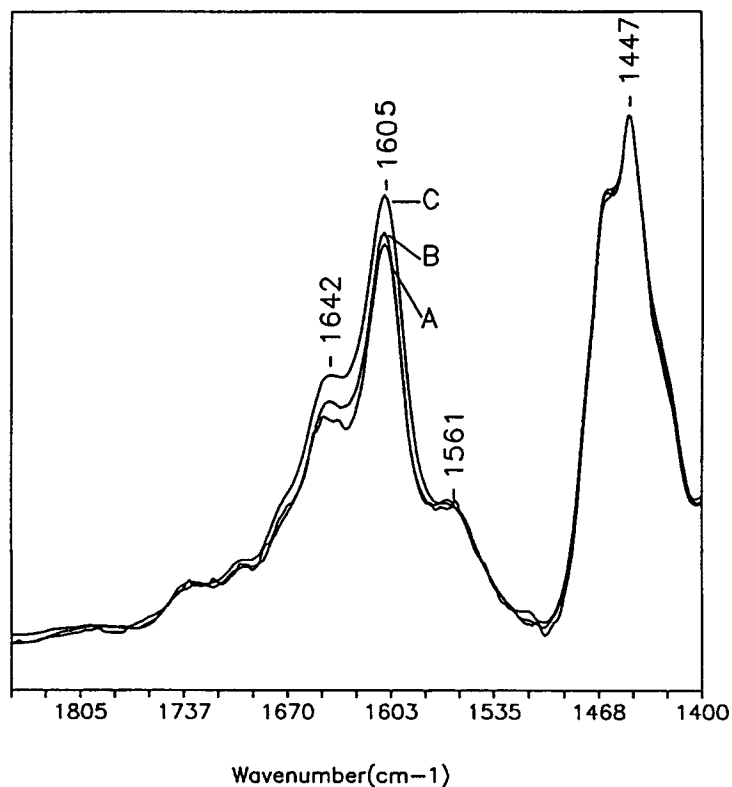
Figure 9 ATR FTIR spectral changes in the 1850–1400 cm^{-1} region of nonpigmented epoxy coatings with different exposure times: (A) 3.5 months; (B) 6.5 months; (C) 14 months.
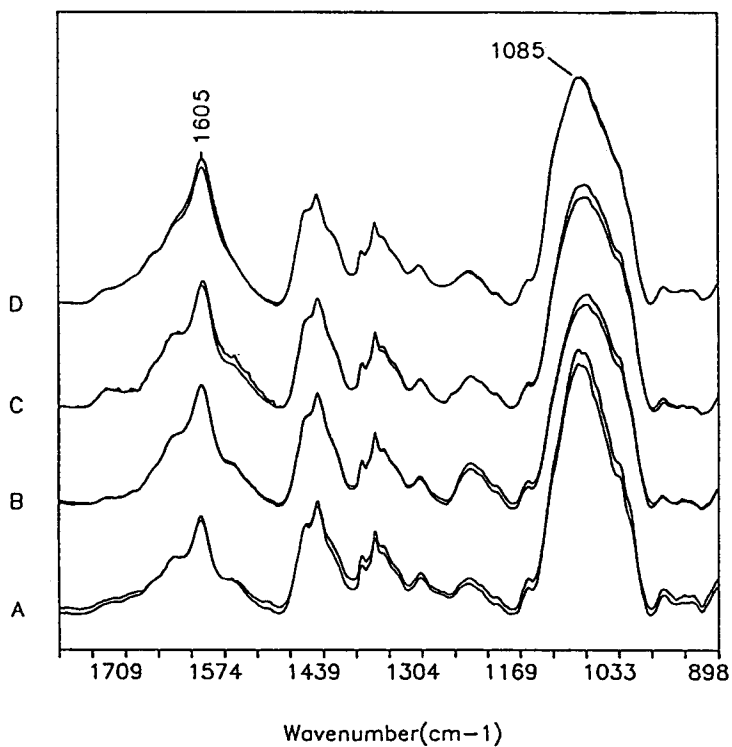

Figure 10 ATR FTIR spectral changes of pigmented epoxy coatings before and after surface rubbing with different exposure times: (A) 6.5 months; (B) 10 months; (C) 14 months; (D) 14 months, being rubbed trice during exposure. In each pair of spectra, the upper trace represents the spectrum before rubbing, and the lower trace, after rubbing.
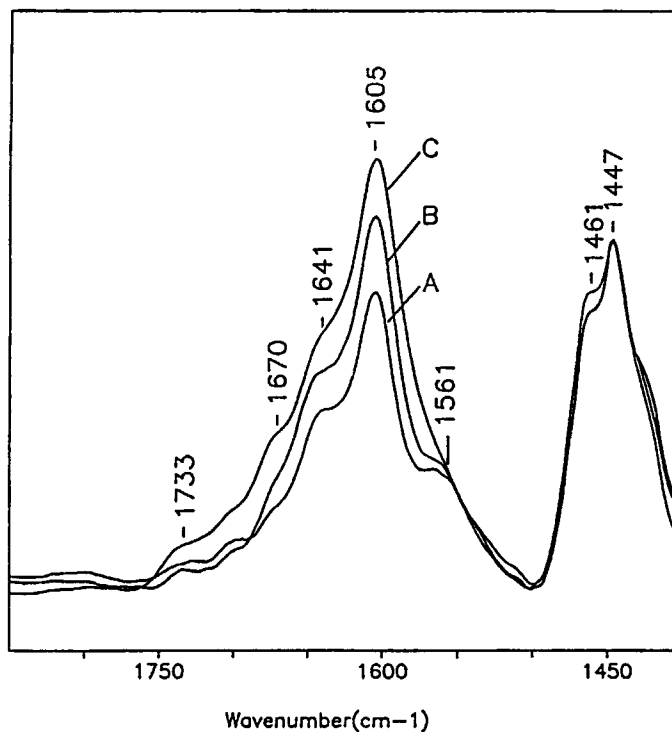
Figure 11   ATR FTIR spectral changes in the 1850–1400 cm^{-1} region of pigmented epoxy coatings with different exposure times: (A) 6.5 months; (B) 10 months; (C) 14 months.

(B). An increase of polyamide and a significant decrease of epoxy groups are demonstrated by a positive band at 1630 cm^{-1} and a negative band at 1085 cm^{-1} of the difference spectrum (trace C), respectively. Similarly, the difference spectrum of pigmented epoxy coatings before and after 7 months of exposure is shown in Figure 12(b). A comparison of the difference spectra shown in Figure 12(a) and (b) indicates that for pigmented coatings the polyamide content increases on the surface and the extent of the epoxy content decrease is smaller, indicating that polyamide has an enhanced tendency to migrate to the surface, but this tendency is greater in the pigmented coatings.

With these experimental data in mind, it is appropriate to address the question as to why the tendency of polyamide migration to the surface differs between the pigmented and nonpigmented coatings. Considering the components and their compositions, the only difference between the two systems is the presence of TiO$_2$ pigment. Therefore, it is reasonable to attribute different exudation behavior to the influence of inorganic pigment. However, before we further analyze the consequences of pigmentation on the behavior of the epoxy/polyamide system, let us realize that there is a significant number of OH groups attached to the surface of pigment parti-

cles.[20,21] They originate from the TiO$_2$ pretreatment using more photolytically stable SiO$_2$ and alumina-containing hydroxyl groups. Thus, in pigmented coatings, there is a greater chemical affinity for hydrogen-bonding interactions between the surface OH groups, epoxy backbone, N—H, and carbonyl groups on polyamide. As a result, adsorption of macromolecular binders on the pigment particles may cause the binder functional groups to attach to the surface of pigment particles; therefore, part of such species are not available for cross-linking. Hence, incomplete cross-linking occurs, causing a sole, uncross-linked fraction of the system to migrate to the surface in order to compensate for an excess of the surface energy.

Another question that should be addressed is why polyamide, not epoxy, shows a greater tendency for migration to the surface in both pigmented and nonpigmented coatings. Although to provide quantitative assessments to this question more data are required, qualitatively, such behavior may be related to the surface energy differences between polyamide and epoxy resins. Since polyamide exhibits lower surface tension ($\sim$ 35 dyn/cm) than that of its epoxy counterpart ($\sim$ 50 dyn/cm),[22] it may have a greater driving force for preferential migration to the surface to compensate for this energy excess.
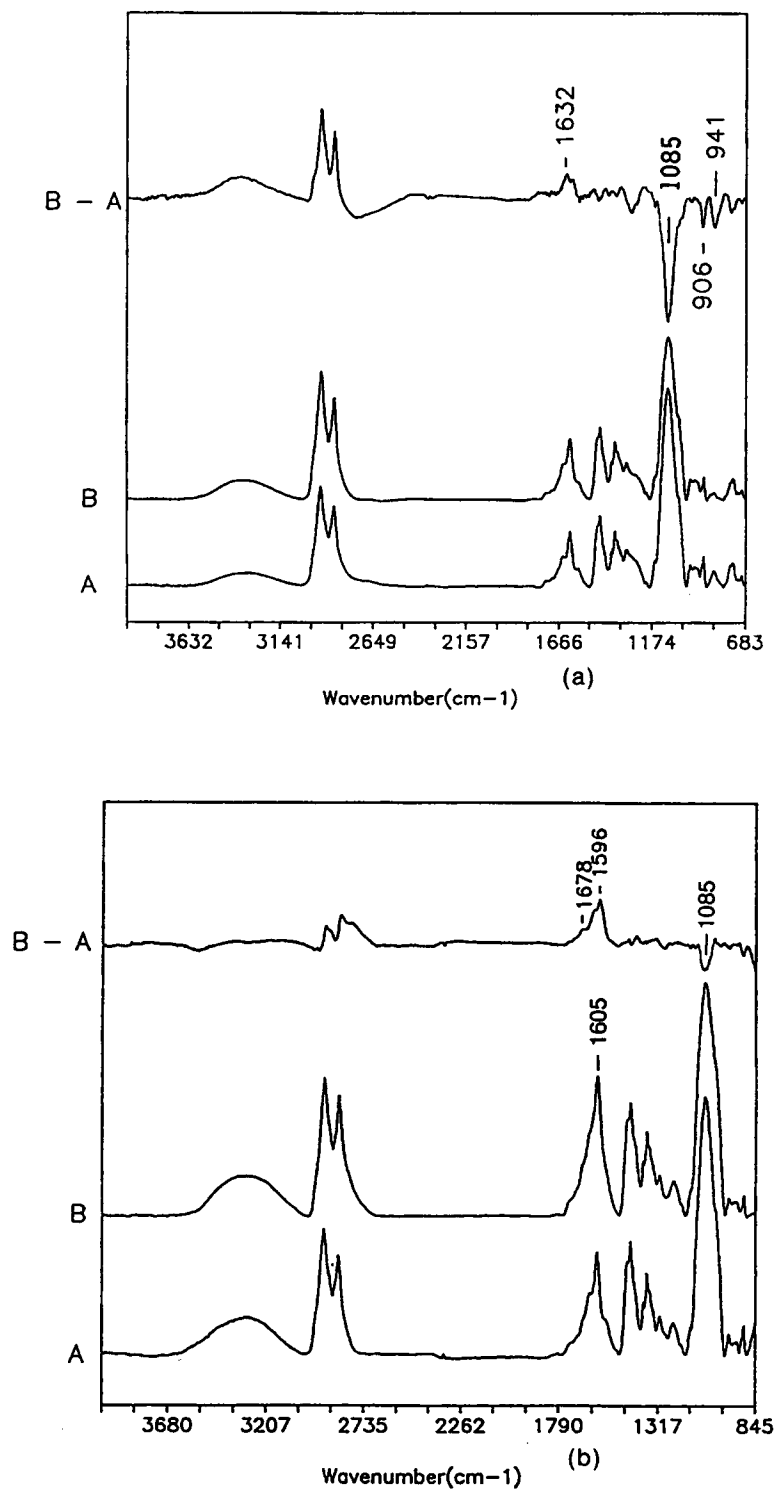
Figure 12 (a) ATR FTIR spectral changes of nonpigmented epoxy coatings upon exposure: (A) 3.5 months; (B) 14.5 months; (C) difference spectrum of (A) from (B). (b) ATR FTIR spectral changes of pigmented epoxy coatings upon exposure: (A) before and (B) after 7 months; (C) difference spectrum of (A) from (B).

Further analysis will focus on the distribution of both polymers across the film and the differences between the film–substrate (F–S) and film–air (F–A) interfaces. For that reason, the coatings were initially deposited on aluminum foil. The coatings were exposed for 20 months to ambient conditions and analyzed spectroscopically. Both F–A and F–S interfaces were analyzed using ATR FTIR, and the resulting spectra of nonpigmented and pigmented coatings are shown in Figures 13 and 14, respectively. A comparison of the F–A and F–S spectra for both coatings indicates that the changes in pigmented and nonpigmented coatings are similar. However, there is a significant difference between the F–A and F–S interfaces for each coating. It appears that more polyamide is present on the F–A, as demonstrated by the stronger bands in the 1700–1500 cm^{-1} region. This observation supports the hypothesis that polyamide prefers to migrate to the surface (F–A). The band at 1605 cm^{-1} due the N — H bending modes in amide groups of the F–A spectrum shifts to 1625 cm^{-1} for the F–S interface, indicating that there are also chemical differences between the two interfaces.

To identify the origin of the 1605 cm^{-1} to 1625 cm^{-1} shift, the F–A interface of a nonpigmented coating was exposed to D$_2$O, followed by washing it

with NaOH. Such a sequence of treatments provides the use of the aqueous phase without affecting the 1600 cm^{-1} region where the OH bending mode of H$_2$O would occur. The resulting ATR FTIR spectra are shown in Figure 15 and indicate that, after washing, the band at 1605 cm^{-1} shifts to 1625 cm^{-1}, exactly the same wavenumber as that obtained from the F–A and F–S interfaces. Since the spectral changes upon NaOH treatment are attributed to the hydrolysis reaction of the imidazoline group,[12] it is believed that the similar hydrolysis reaction occurs at the F–S interface during exposure. It should be remembered that Al$_2$O$_3$ is present on the surface of aluminum and Al$_2$O$_3 \cdot$ H$_2$O can be formed. This species is known as a basic catalyst for the hydrolysis of imidazoline. This hydrolysis reaction is shown below:

$$RC \overset{N}{\underset{N}{\big|}} \quad \xrightarrow{\text{alkali, H2O}} \quad RC \overset{O}{\overset{\|}{}} - NHCH_2CH_2NH -$$
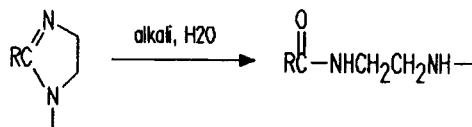
The analysis of Figure 15 also indicates that there are no intensity changes of the bands at 1625 and 1605 cm^{-1}. This indicates that the extinction coefficient is approximately the same for the two bands, excluding the possibility that the intensity differ-
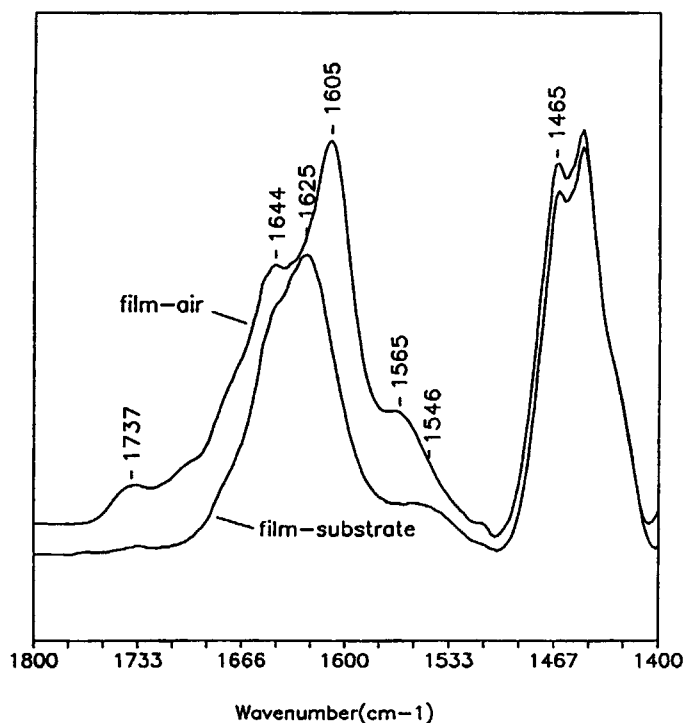

Figure 13 ATR FTIR spectra of F–A and F–S interfaces of nonpigmented coatings; exposure time: 20 months.
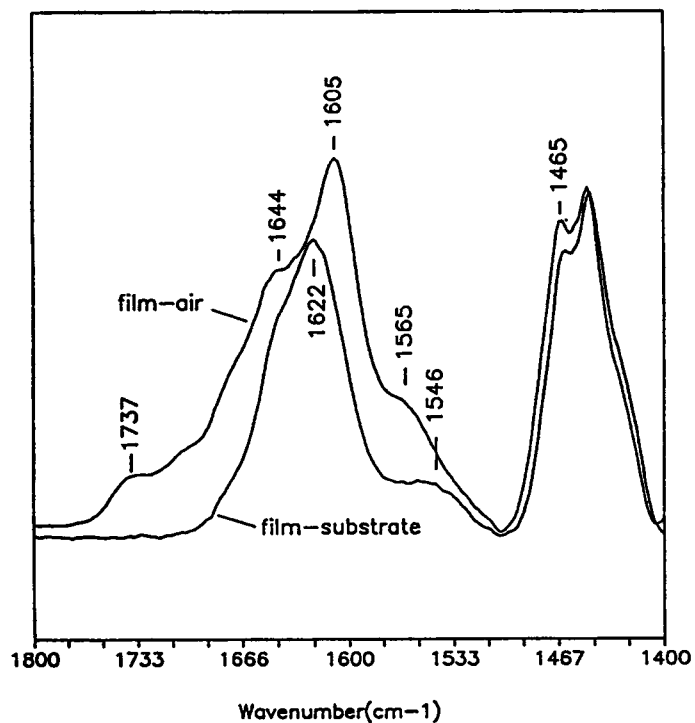
Figure 14   ATR FTIR spectra of F–A and F–S interfaces of pigmented coatings; exposure time: 20 months.
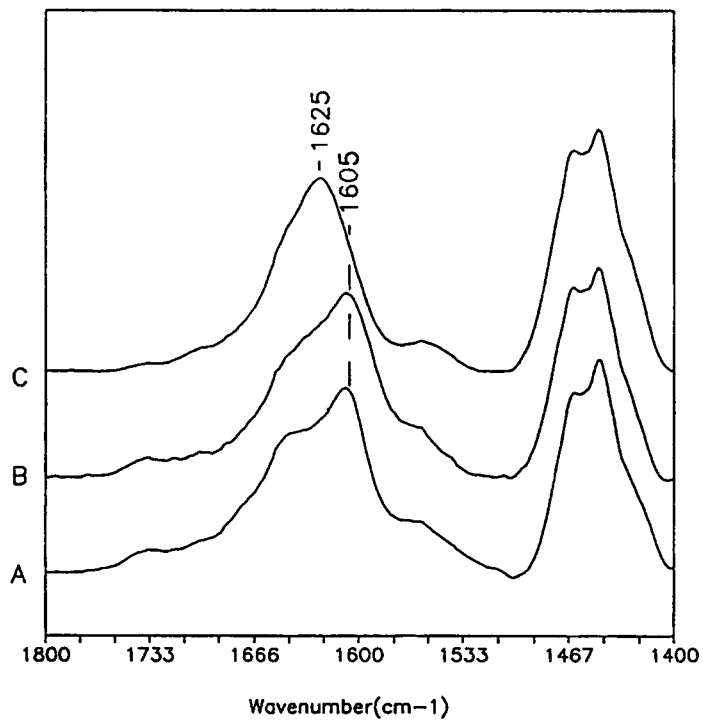

Figure 15   ATR FTIR spectra of nonpigmented epoxy coatings: (A) before and (B) after treatment with D_2O, then (C) treated with NaOH.

ences in the 1630–1600 cm^{-1} region between the F–A and F–S interface spectra are due to the differences of the absorption coefficient.

One of the attractive features of ATR FTIR spectroscopy is the capability of surface depth profiling. By changing an angle of incidence in an ATR cell, infrared spectra at surface depths can be recorded.[23-26] The depth of penetration is defined as a distance from the sample surface at which the amplitude of the evanescent wave decays to $1/e$ of its initial intensity,[26] and by changing the angle of incidence, the penetration depth can also be changed. Figure 16 shows the spectra of both pigmented and nonpigmented coatings recorded at different incidence angles. In the case of nonpigmented coatings, there is no detectable difference in the polyamide band intensity at 1605 cm^{-1} (trace B). For pigmented coatings, however, the 1605 cm^{-1} band becomes stronger as the angle of incidence increases (trace A), indicating that there is a greater concentration of the polyamide molecules on the F–A interface. These assessments are consistent with the previously discussed spectral changes resulting from the exposure experiments. In pigmented coatings, polyamide surface content increases upon exposure (Fig. 11), whereas for nonpigmented coatings, ac-

cumulation of polyamide on the surface is much slower (Fig. 9); therefore, the concentration gradient is not observable.

CONCLUSIONS

For nonpigmented coatings, there are removable, unreacted epoxy components on the surface that appear at the early stage of exposure. Upon extended exposures, however, they form cross-linked networks and become nonremovable. The increase of polyamide components on the surface is very slow, and there is no observable gradient of components through the coatings. For pigmented coatings, there are no removable components at the surface (F–A) and the polyamide content increases at the surface at longer exposure times. The concentration of polyamide on the surface is greater than that in the bulk. For both pigmented and nonpigmented coatings, a higher concentration of polyamide at the F–A interface is observed because polyamide molecules tend to migrate to the F–A interface. A slow oxidative degradation that occurs on the F–A surface occurs during the exposure at ambient conditions.
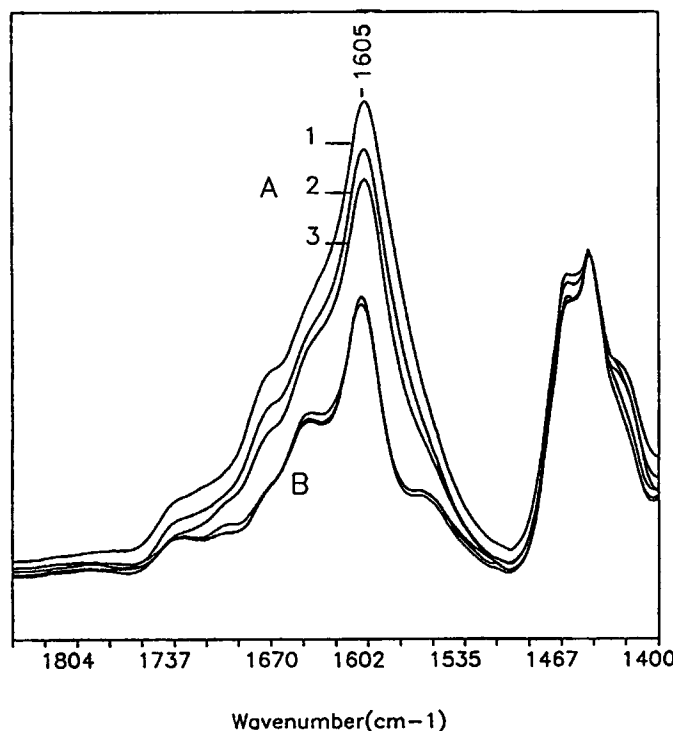

Figure 16 ATR FTIR spectra in the 1850–1400 cm^{-1} region of epoxy coatings as a function of depth penetration: (A) pigmented coating; (B) nonpigmented coating. (1) 60°, (2) 55°, (3) 45° of incidence angle. Both samples were exposed for 14 months.

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