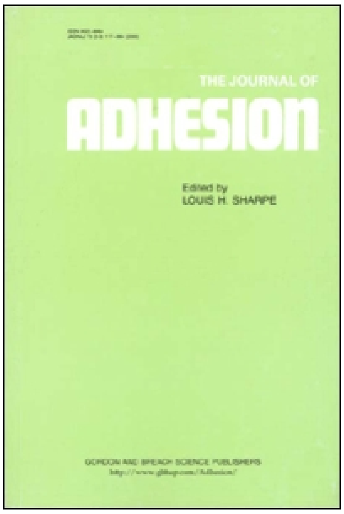

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Reflection Absorption Infrared Studies of the Surface Diffused Residues on a Humidity/Temperature Aged Urethane PSA

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Reflection absorption infrared spectroscopy (RAIR) has been used to study the bulk-to-surface diffused residue that occurs when a polyurethane adhesive containing a polypropylene glycol-tolylene diisocyanate (TDI) elastomer and terpene phenolic resin is given prolonged exposure to heat and humidity. By transferring the tacky residues to a RAIR sample mirror blank and utilizing *in-situ* vacuum thermal desorption techniques, the components of the residue were separated and their unique IR spectra obtained. In this way the residue was found to consist solely of non-TDI reacted polypropylene oxide and both alcohol soluble and insoluble resin fractions. The ratio of polyol to resin in the surface diffused residue is 0.67:1 compared to 1.75:1 in the original adhesive. Missing absorption bands at 1390 and 1265 cm^{-1}, a new band at 1110 and increased intensity in the 1735 carbonyl and 1225 cm^{-1} bands imply definite chemical differences between the alcohol soluble resin fraction in the surface residue and the bulk material. Specifically, separation of the gem-dimethyl groups and formation of an ester are implied. The alcohol insoluble resin fraction in the residue appears to have a lower molecular weight distribution than the starting material.

I. INTRODUCTION

The formation of urethane pressure sensitive adhesives (PSA) can be accomplished by the *in-situ* polymerization of polyether polyols with polyisocyanates in the presence of certain tackifying resins.[1–4] Two general requirements for these resins is that they be compatible with the cured elastomer and have low reactivity toward polyols and isocyanates. One such class of resins is the terpene phenolics, although members of this class having relatively high phenolic character (OH number $> \sim 100$) tend to be slightly too reactive toward isocyanates.

Accordingly, terpene phenolic resins of decreasing hydroxyl numbers were studied. It was found that when the hydroxyl number was lower than about 35, deleterious effects were observed after aging the resulting adhesives at elevated temperatures and humidity. The aging of these adhesives resulted in the bulk-to-surface diffusion of a residue that could be transferred to a test surface.

It was of interest to us to study the nature of this residue through the use of a technique known as Reflection Absorption Infrared (RAIR) Spectroscopy.[5-12] In this application the surface residue was studied indirectly by transferring it to an aluminium mirror, thus enabling the small amount of surface material involved to be separated from the underlying bulk. Also, the ability to heat the samples *in-situ*, in the RAIR vacuum chamber, was indispensable for separation of the residue components by thermal desorption.

II. EXPERIMENTAL

A. RAIR equipment

Figure 1 shows a schematic of the RAIR apparatus. In all the experiments described here the sample chamber and monochromator chamber were operated together and pumped with a 4″ diffusion pump to below 5×10^{-7} Torr. Further details of the spectrometer's vacuum adaptation will be discussed elsewhere.

The samples consisted of 3 cm × 10 cm × 3 mm sputter-aluminized glass slides coated with the organic film under study. The RAIR spectrometer, a modified Perkin Elmer 283B, is operated in vacuum in a single beam mode so single beam spectra are also obtained from blank aluminized mirrors. This reference spectrum is then digitally subtracted from the single beam sample spectra to produce the resultant sample spectra shown in Figures 2–8. The digital subtraction capability was also critical in differentiating the spectra of the residue components.

As mentioned in the introduction, the *in-situ* heating capability was an important aspect of this study. The sample heater is an integral part of the RAIR apparatus and need not be described here. Suffice

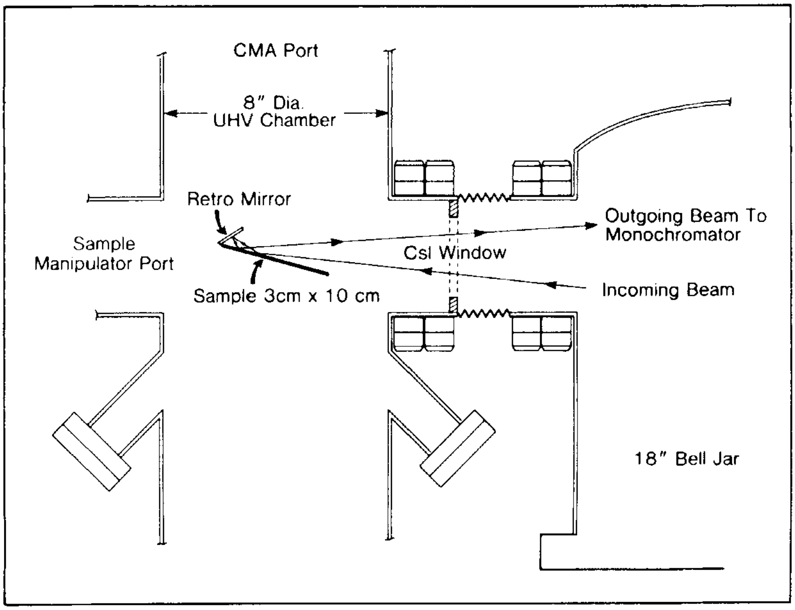

FIGURE 1 Schematic of the RAIR apparatus.

it to say the sample glass blank was heated by thermal conduction from intimate contact with a substrate heater of the same size and shape as the glass blank itself. The temperature was measured with a Chromel-Alumel thermocouple junction, made from 8 mm diameter wires, held in contact by its own spring tension against the organic film side of the sample blanks. Typically, the average rate of heating in vacuum was approximately 6C/min. over the range of 20C to 90C.

B. Adhesive preparation

Adhesives were prepared by first dissolving the tackifying resin in polyoxypropylene polyols, then mixing this solution with a low molecular weight prepolymer of tolylene diisocyanate and polyoxypropylene diol. The entire mass was coated on a polyester film at a thickness of 0.05 mm to effect a cured adhesive under the influence of heat and catalyst. In forming the adhesive, 100 parts of elastomer were combined with 50 parts of resin. Post curing was allowed to occur at ambient conditions for at least one week before subjecting the adhesive films to humidity aging at 32C, 90% RH for 90 hours. The samples were then allowed to equilibrate for four hours under ambient conditions.

The tackifying resin was fractionated in the following manner. Resin (550g), isopropanol (1219g) and ethanol (281g) were heated to reflux. After the resin had dissolved the solution was allowed to cool to room temperature. The insoluble precipitate fraction was separated from the supernatant liquid which in turn was evaporated to yield what is termed the alcohol soluble fraction. These two fractions, after being thoroughly dried, had distinct physical properties and were extremely helpful in the analysis of the residue.

Table I gives the molecular weights, by number and weight, their ratio P (polydispersity), the hydroxyl number and the solubility index for the resin and its fractions. The molecular weight data were obtained by gel premeation chromatography using refractive index detector and a polystyrene standard. Solubility index is defined as the maximum percentage of ethanol in a blend of MEK and ethanol which dissolved the resin at 25C.

TABLE I
Physical properties of the starting PSA tackifying resin and the alcohol soluble and insoluble fractions. See text for definition of column headings

	Solubility index	OH#	Mn	Mw	P
Starting resin	40	27	860	1076	1.25
Alcohol soluble fraction	48	33	768	955	1.24
Alcohol insoluble fraction	36	23	957	1199	1.25

C. Sample descriptions

Table II describes the various types of samples prepared. In all cases the substrates were air oxidized aluminum, sputter deposited on glass slides. Such an uncoated substrate served as a reference blank as well. There are two basic kinds of samples described here. The primary type was formed by contact transferring the bulk-to-surface diffused residue from the PSA to the reflective mirror substrate. The second type was formed by coating from solution onto the aluminium substrates using a wire wound bar. The latter type served to provide IR reference spectra. As will be seen, these spectra were instrumental in identifying

TABLE II
Description of the types of samples prepared for RAIR analysis. In each case the substrate is sputter deposited aluminum on glass

Sample	Type	Preparation
A	PSA surface residue	Transferred from polyester film handspread exposed to 90% RH, 32C for 90 hours
B	PSA surface residue	Transferred from polyester film handspread exposed to lab ambient for 90 hours
C	Alcohol soluble resin fraction	Coated with #8 Meyer bar from 1% solution in MEK
D	Alcohol insoluble resin fraction	Coated with #8 Meyer bar from 1% solution in MEK
E	Polypropylene oxide, (non-TDI reacted) Mol. Wt. ~6000	Coated with #8 Meyer bar from 2% solution in n-heptane

the spectra of the residue components when the latter were separated by the *in-situ* vacuum thermal desorption.

For the first type, hand spreads of the full PSA were made on polyester film. After the subsequent aging, the adhesive handspreads were applied to the aluminized mirror blank, pressure rolled by hand, and then peeled off. The residue left on the mirror, if any, was then the sample studied.

III. RESULTS AND DISCUSSIONS

A. PSA surface residue composition—absence of carbamate linkages

The primary goal is to discover what has apparently diffused to the surface of the catalyzed, humidity/temperature aged adhesive. As described previously, this has been done by contact transferring the surface residue to a RAIR sample mirror.

Figures 2(a) and (b) show clearly the effect of the 90% RH/32C environment compared to the laboratory ambient when aging the polyester film handspreads for 90 hours. The laboratory ambient aged sample apparently has little or no bulk to surface diffusion occurring.

To identify what the out-diffused residue in the heat/humidity aged case of Figure 2(b) is we must determine the organic constituents responsible for that spectrum. Comparing 2(b) and 2(c) it is clear that the residue material is not some lightly different form of the complete

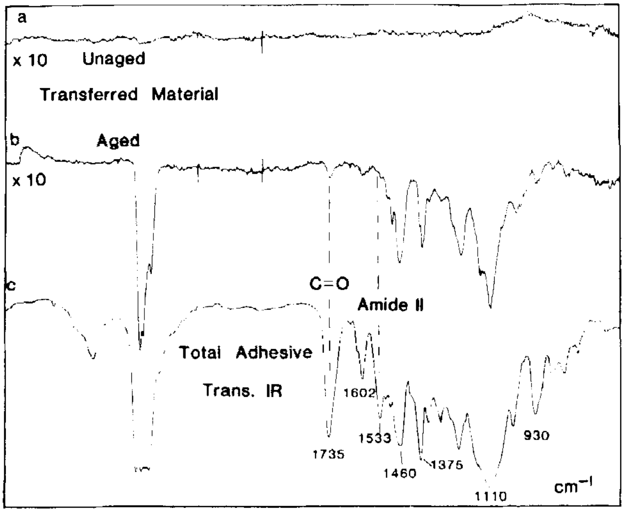

FIGURE 2 a), b) RAIR spectra from the PSA surface diffused material that transferred to the aluminum sample blank, c) Transmission IR spectrum from a bulk sample of the total adhesive material.

adhesive. Figure 2(c) is a bulk transmission IR reference spectrum of the total adhesive. In particular we note the complete absence of any hydroxyl or amide II bands at 3320 and 1530 cm^{-1} respectively, a strong reduction in the 2880 cm^{-1} band (attributable to the symmetric C-H stretch of the CH_3 groups) and highly attenuated carbonyl and aromatic bands at 1735 and 1602 cm^{-1} respectively.[13] This is sufficient evidence to conclude that there is no tolylene diissocyanate (TDI) derived components in the out-diffused residue, *i.e.* it contains no TDI reacted elastomer. However, we can verify this beyond any doubt by considering next the reference spectra from the major ingredients of the adhesive system.

Figure 3 compares the RAIR spectra from the plain, non-TDI reacted polypropylene oxide (polyol) and the alcohol and insoluble resin fractions. In these cases thin films of these materials were cast from solutions onto the RAIR mirror blanks as described in Table II. In particular we note that none of the three spectra contain any aromatic band at 1600 cm^{-1}. Only the resin fractions would be expected to show such a band and this occurs as a very small band at 1620 cm^{-1}. Similarly, none contain an amide II band and only the alcohol soluble resin fraction displays any carbonyl stretch band. Furthermore, the

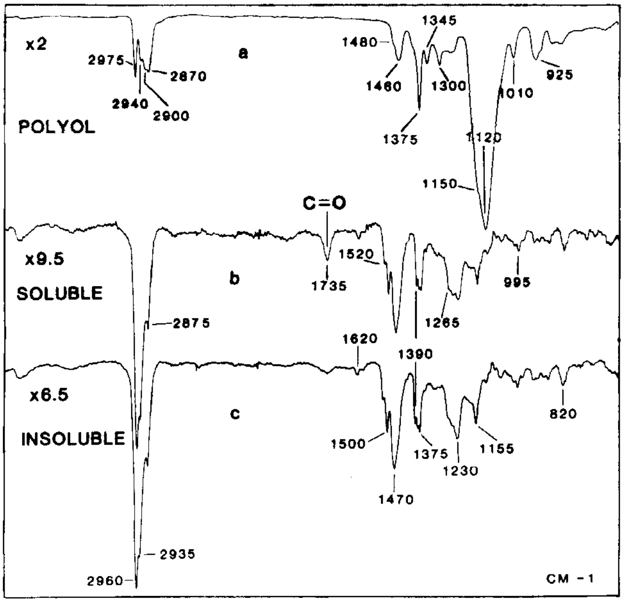

FIGURE 3 RAIR spectra from solution cast thin films of the major adhesive components: a) non-TDI reacted polypropylene oxide, b) alcohol soluble fraction of the terpene phenolic resin, c) alcohol insoluble resin fraction.

strength of this carbonyl relative to the 1470/1500 cm^{-1} bands in Figure 3(b) is very close to that displayed in Figure 2(b) from the transferred residue of the humidity/heat aged adhesive.

Hence, it is clear that the strong 1735 cm^{-1} carbonyl band, the 1533 amide II band and the 1602 cm^{-1} aromatic band in the total adhesive spectrum of Figure 2(c) are due to the TDI derived carbamate linkage only. Their total absence from spectrum 2(b) confirms that the transferred residue contains no TDI reacted polyol.

B. First *in-situ* thermal separation—insoluble resin fraction

In addition to establishing the absence of TDI reacted polyol, the resin film spectra of Figure 3(b, c) also imply, when compared to the transferred residue spectrum of Figure 2(b), the likely presence of the resin fractions in the residue. The residue could, of course, consist of all three components. To analyze the transferred residue film, an *in-situ* thermal desorption or separation experiment was performed. This

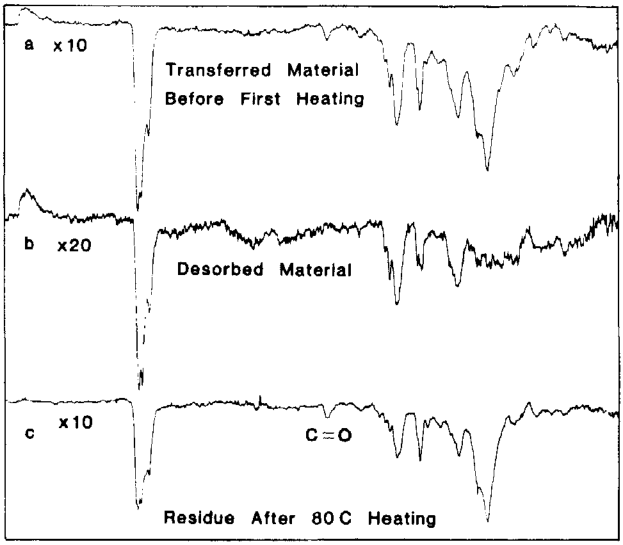

FIGURE 4 Comparison of the RAIR spectra from, a) the original surface residue transferred material (same as Figure 2(b)), c) the remainder of a) left on the sample mirror after heating to 80C, and b) the materials that desorbed from the mirror during the vacuum heating obtained by subtracting c) from a).

means the sample mirror with its residue film was heated in vacuum while on the RAIR sample holders. Because of the different thermal desorption properties of the film constituents, related *e.g.* to their different molecular weights, the component spectra can be isolated. That is, because the RAIR system is computer operated, and spectra can be saved, averaged, subtracted, etc., the spectra from the remaining film residue after a heating can be subtracted from the film residue before heating to obtain the spectrum of what desorbed.

The residue sample mirror was heated twice. The first heating to 80C produced the results shown in Figure 4, which compared the before and after heating residues with the desorbed material. In particular we observe that the desorbed spectrum 4(b) shows no evidence of any ether linkage (assymmetric C-O-C stretch at 1120 cm^{-1}) characteristic of the polyol and the complete absence of any carbonyl stretch. The small carbonyl band in the original residue has remained in Figure 4(c) with the post-heating residue.

Figure 5 compares this first heating desorbed spectrum with those of the two resin fractions, soluble and insoluble. The band positions

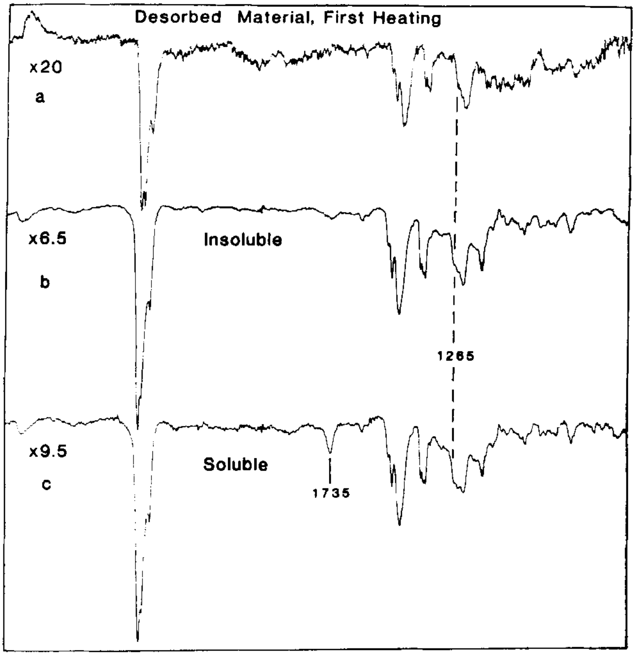

FIGURE 5 Comparison of the RAIR spectra previously shown in Figure 4(b), 3(b), and 3(c) to demonstrate that the material desorbed during the first *in-situ* residue is the alcohol insoluble resin fraction.

are labelled on Figure 3. The first thing to note is the unmistakable band correlation of the desorbed spectrum with the terpene phenolic resin signature. It should be noted as well that the many overlapping weak bands below 100 cm^{-1} in the two resin spectra are indeed bands and not noise. The two resin fractions are very similar as Figures 5(b, c) imply. Aside from the already noted weak carbonyl at 1735 cm^{-1} present in the alcohol soluble resin fraction, but essentially absent from the insoluble fractions, the only other difference is a slightly stronger side band at 1265 cm^{-1} in the soluble fraction (see Figure 3(b)). The unresolved triplet of bands in this large broad band between 1265 cm^{-1} and 1230 cm^{-1} is usually attributed to the single bond C-OR stretch of the phenol. Hence, the attenuation of the 1265 cm^{-1} side lobe could imply a chemical difference at this point between the alcohol soluble and insoluble fractions.

Turning now again to the desorbed spectrum of Figure 5(a) we observe that there is no carbonyl stretch band and the shape of the high frequency side of the 1230 cm^{-1} band resembles that of the insoluble fraction much more than the soluble fraction, implying the absence of the 1265 cm^{-1} band.

Hence, we can conclude that not only does the desorbed material from the first *in-situ* heating consist solely of the terpene phenolic resin, it is specifically the alcohol insoluble resin fraction.

C. Second *in-situ* thermal separation—soluble resin fraction and polyol

The second *in-situ* heating was not made immediately, but nearly three months after the first. A new spectrum from the "already heated once" sample was obtained just prior to the second heating which went to > 145°C. This second heating "*before*" spectrum is shown in Figure 6(a). Comparing it with Figure 4(c) it appears there may have been some shape change of the C = 0 band. This small change need not concern us here. Figures 6(c and b) show then respectively, the re-

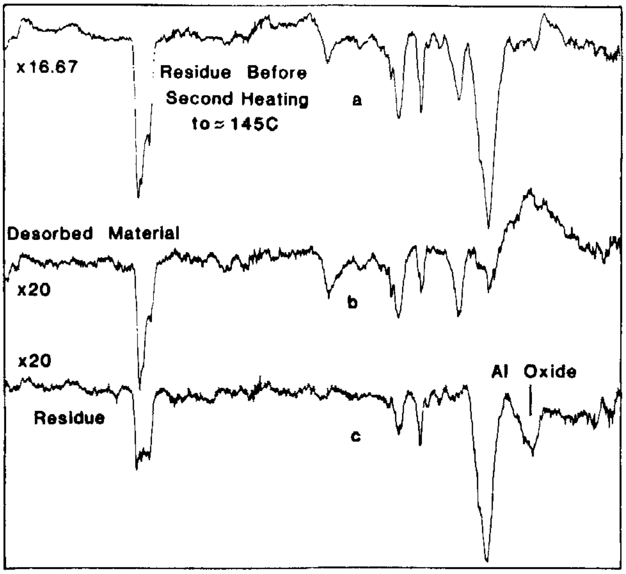

FIGURE 6 Comparison of the RAIR spectra from, a) the remaining surface residue on the mirror just prior to the second heating to ~ 145°C, c) the remaining residue after the heating and b) the material that desorbed obtained by subtracting c) from a).

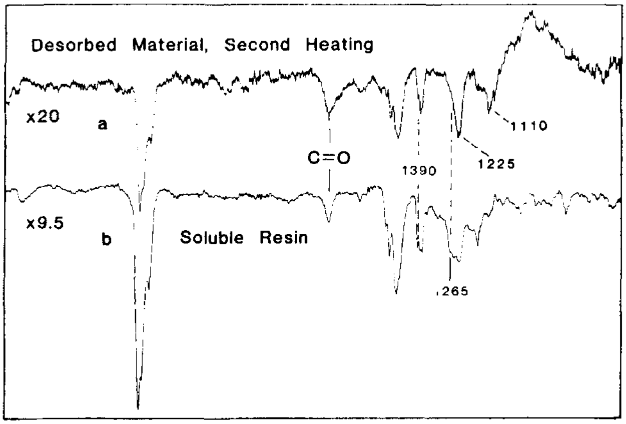

FIGURE 7 Comparison of the RAIR spectra previously shown in Figures 6(b) and 5(c) to demonstrate the strong resemblance of the second heating desorbed material to the alcohol soluble resin fraction.

maining residue after the second heating and the desorbed material spectrum obtained by subtracting Figure 6(c) from 6(a). This higher temperature heating in 4 x 10^{-7} Torr has resulted in further oxide growth of the aluminum substrate as testified by the very familiar 960 cm^{-1} band in Figure 6(c). It is also responsible then for the broad inverted band in Figure 6(b) below 1000 cm^{-1}.

We can compare the final two remaining separated spectra of Figure 6(b) and (c) now with the remaining major adhesive components to make a positive identification.

First, Figure 7 compares the second heating desorbed spectrum with that of the soluble resin fraction. The desorbed spectrum is undeniably the resin spectrum again, and the presence of the carbonyl band strongly implies that it is the alcohol soluble fraction—the only fraction remaining after the first heating. However, there are some subtle but important differences between Figures 7(a) and (b). (The broad inverted region below 1000 cm^{-1} in 7(a) can be ignored since as discussed above it is due to the oxide growth of the substrate appearing as a negative peak in the difference spectrum).

The most important are the apparent near total absence of the 1390 and 1265 cm^{-1} bands in the second desorbed spectrum of 7(a). Also, the carbonyl band intensity and the 1230 cm^{-1} band intensities have clearly increased relative to the other three major groups of bands. Finally, a new band at 1110 cm^{-1} seems to have appeared. Since the

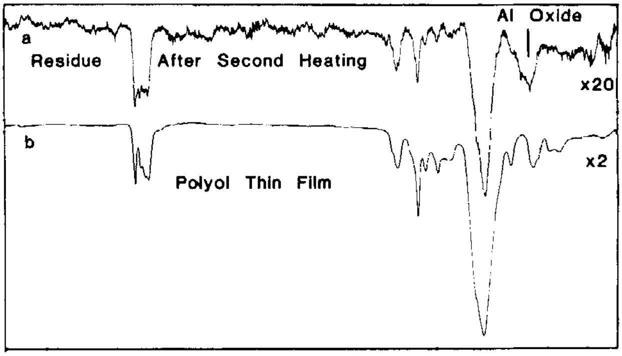

FIGURE 8 Comparison of the RAIR spectra previously shown in Figures 6(c) and 3(a) to demonstrate that the remaining residue after the second heating is non-TDI reacted polypropylene oxide.

1265 cm^{-1} side band is also absent in Figure 7(a) and 4(c) before the second heating, and the second heating residue of 6(c) has no significant band in this region, the apparent absence of the 1265 cm^{-1} (and presumably the other differences as well) is not a result of any thermal decomposition.

Apparently then, this alcohol soluble resin fraction component of the aged PSA surface residue is not exactly the same chemically as the bulk or starting soluble resin fraction. This is in contrast to the insoluble resin fraction which desorbed after the first heating. Its spectrum in Figure 5(a) does resemble almost perfectly the insoluble reference spectrum of 5(b), and in particular shows the 1390 cm^{-1} band missing in 7(a). The possible implications for chemical differences between the soluble resin fraction in the diffused residue and that in the starting material will be discussed later.

Secondly, the residue remaining after the second heating, Figure 6(c), is compared in Figure 8 with the RAIR spectrum from a plain non-TDI reacted polyol film as described in Table II. Despite the much reduced signal/noise ratio in 8(a) due to the small amount of material present, the second heating residue material is unmistakably the unreacted polyol. The aluminum oxide band at 960 cm^{-1} has of course obliterated the polyol 925 cm^{-1} band, but all the other bands are present with approximately the correct relative intensity as well.

In summary, we have established that the surface diffused residue of the humidity/temperature aged adhesive that transferred to the aluminum mirror did not contain any TDI related species, but did in fact consist of unreacted polyol and both terpene phenolic resin fractions. Furthermore, the polyol and alcohol insoluble resin fractions appear identical, from an IR chemical standpoint, to the original materials. The alcohol soluble fraction in the residue, however, displays several distinct differences in its RAIR spectrum which imply that it is chemically different from its bulk or original form. Finally, we note the order of desorption of the three components when heated in vacuum. Since the polyol molecular weight is much greater than the resins' it is not surprising that it remained on the sample substrate after the resins had desorbed. However, the fact that the soluble resin fraction remained after the insoluble fraction had desorbed implies either a higher molecular weight distribution for the soluble fraction or else some chemical interaction with the polyol or aluminum oxide substrate that kept it on the surface to a higher temperature. Further experiments to reflect on this are described next.

D. *In-situ* resin film desorption—soluble *vs* insoluble

The thin sample films of the two resin fractions whose spectra have already been discussed were also heated in vacuum, but under controlled conditions. While monitoring the temperature as it was increased in increments, RAIR spectra over the strong C-H stretch bands were retrieved, thus giving an absolute measure of the amount of material left on the mirror as a function of temperature. Figure 9 shows the C-H stretch band traces of the two fractions as the temperature increased. Both sample mirrors were heated simultaneously, *in-situ*, by identical substrate heaters since one was in the usual reference mirror position. The thermal mass of the mirrors is sufficient that during the scans the heating power could be turned off and the temperature remained approximately constant. Hence, the actual temperature for both sample mirrors should agree very closely, even though only one thermocouple was actually used for recording the temperature. There may be more uncertainty in the absolute accuracy of the temperature indicated due to differences between the real surface temperature and the thermocouple junction temperature, but the equivalence of the two surface temperatures should be reliable.

It is noteworthy then that the soluble resin fraction appears to be desorbing faster, *i.e.* at a lower temperature, than the insoluble fraction. This is shown clearly in Figure 10, which shows the 2960 cm^{-1} peak absorbances normalized to their 21C intensity. Here then is just the

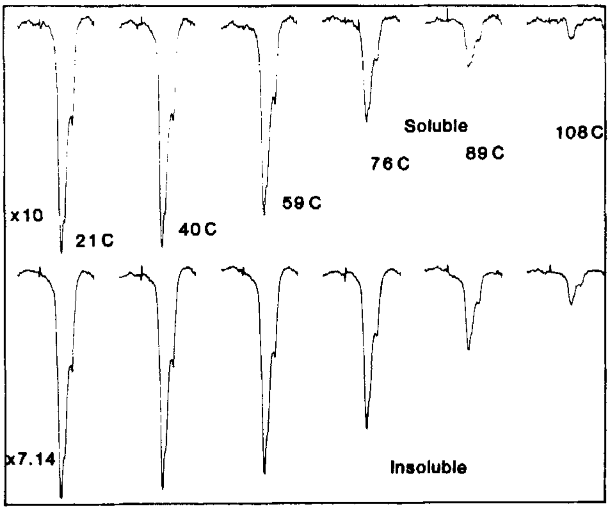

FIGURE 9 Series of scans over the 2960 cm^{-1} C-H stretch bands as a function of temperature while vacuum desorbing the solution cast thin films of both terpene phenolic resin fractions.

opposite effect of that seen in the residue thermal desorption experiments. In that case, as pointed out at the end of Section III. C, the alcohol soluble residue fraction desorbed *after* the alcohol insoluble residue fraction. As suggested there this implies either a higher molecular weight distribution for the soluble resin fraction or some chemical interaction with the polyol material and/or the substrate.

Concerning the latter possibility, of interaction with the air oxidized aluminum substrate of the sample mirror, Figure 11 compares the soluble resin fraction *thin film* spectrum (to be distinguished from the soluble resin fraction residue spectrum) before and after the heating discussed above. There we observe the interesting result that even though nearly all the C-H stretch bands have disappeared, and essentially all the resin signature bands below 1600 cm^{-1} have disappeared, the 1735 cm^{-1} carbonyl has shifted to 1745 cm^{-1} but is little if any reduced in intensity. Apparently, then, when alone on the aluminum oxide surface, the soluble resin fraction decomposed leaving the carbonyl function attached to the surface. This evidence would certainly seem to imply an interaction of the *thin film* soluble resin with the surface, even though it was observed to desorb at lower temperatures than the insoluble *thin film* resin sample. So since the

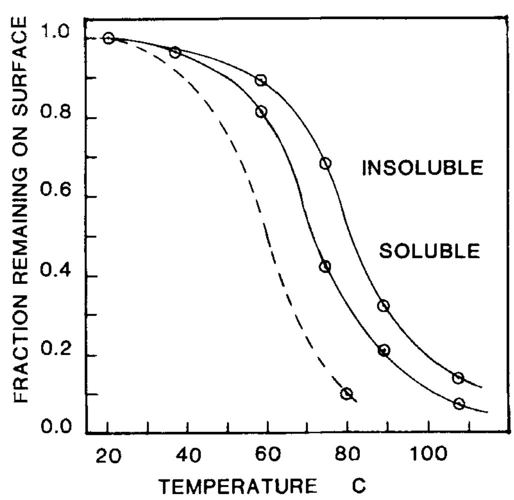

FIGURE 10 Variation with temperature of the normalized absorbances of the 2960 cm^{-1} bands shown in Figure 9. The band absorbance is taken to be proportional to the film thickness.

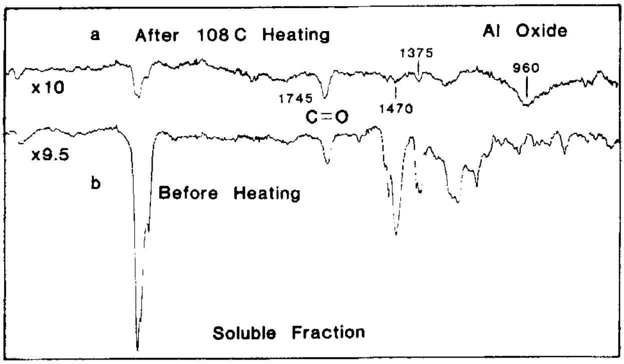

FIGURE 11 RAIR spectra from the solution cast thin films of the alcohol soluble resin fraction b) before heating in vacuo and a) after heating showing retention of the carbonyl on the surface and increased oxidation of the aluminum substrate. This demonstrates interaction of the soluble resin fraction with the substrate when polyol is not present.

soluble resin *residue* fraction desorbed cleanly in the residue thermal desorption experiments, *i.e.* the second heating residue (Figure 6(a)) shows no carbonyl remaining, we can conclude that the soluble residue fraction did not stay on the surface longer than the insoluble residue fraction because of some interaction with the oxide surface *via*, *e.g.*, its unique carbonyl.

Hence, the remaining possibilities are that the soluble fraction *residue* may be interacting more with the polyol, or have a higher solubility in it, or have a higher molecular weight distribution than the insoluble residue fraction. With respect to this last possibility, it is interesting to note that in the first residue heating the maximum temperature recorded was about 80C which was sufficient to remove, apparently, all the insoluble resin *residue*, whereas, on Figure 10 only *ca.* 50% of the insoluble resin *thin film* was removed at that temperature. Assuming the temperatures are correct this implies the insoluble resin *residue* is a low molecular weight form of the bulk or starting soluble resin as used in the thin film desorption of Figure 9. A model relating the observed thermal desorption data, such as in Figure 10, to the molecular weight distribution of the thin film material has been developed. From the model, and the known average molecluar weight of the insoluble resin fraction we estimate that the average molecular weight of the insoluble *residue* fraction is 570 as compared to 957 for the starting material. This is the only evidence that the insoluble resin *residue* fraction may be different in some way from the insoluble resin starting fraction, since from an IR spectral standpoint they are chemically the same.

E. Soluble resin fraction—residue chemical differences

The soluble resin *residue* fraction may also of course differ in molecular weight from the original material used in the adhesive. However, its situation is complicated by the presence of the carbonyl. To recapitulate, the following observations were made with respect to the soluble resin fraction:

1) In the residue thermal desorption experiment it desorbed after the insoluble residue fraction and without decomposing, *i.e.*, the carbonyl did not remain on the sample mirror

2) In the thin film thermal desorption experiment it desorbs before the insoluble thin film fraction and did decompose, leaving the carbonyl on the substrate.

3) In both the residue heating and thin film heating experiments, it desorbs at approximately the same temperature, *i.e.* $> 90\%$ gone at $T \geqslant 100$C.

4) The residue soluble fraction that diffused to the surface appears to be chemically different from the starting soluble material in the adhesive as indicated by the absence of IR bands at 1390 cm^{-1} and 1265 cm^{-1}, the addition of a new band at 1110 cm^{-1} and larger relative intensities of the carbonyl 1735 cm^{-1} and 1225 cm^{-1} bands.

From these observations we conclude that there is likely no significant molecular weight distribution difference between the soluble residue fraction and the starting soluble resin fraction, but there are some very definite chemical differences. We consider these now.

The 1390 cm^{-1} band and the 1375 cm^{-1} band in the resin spectra (see Figure 3) are usually attributed to the gem-dimethyl groups in terpene resins. Hence, its attrition in Figure 7(a) at the expense of the usually single methyl C-H deformation band at 1375 cm^{-1} is a strong indication that the α-pinene in the soluble *residue* fraction has been altered such that the symmetric pair of methyl groups has been separated.

The second major chemical difference we believe involved three of the other affected bands, *viz*, the 1735, 1225 and 1110 cm^{-1}. All appear more intense relative to the C-H stretch and C-H deformation bands. The 1110 cm^{-1} is new, of course, perhaps replacing the 1155 cm^{-1} in Figure 7(b). This combination of three bands is a strong indication of the presence of an ester, and quite possibly aromatic in nature.[13] In this case the 1125 cm^{-1} band is associated with the C-O stretch adjacent to the carbonyl and the 1110 cm^{-1} to the O-C stretch adjacent to the alcohol residue in the conventional ester formation.

Finally, the third spectral difference between Figure 7(a) and (b), the attenuation of the 1265 cm^{-1} band, may be related to the ester formation. Bands between 1225 and 1265 cm^{-1}, a triplet in Figure 7(b), are usually associated with the C-OR linkage of the terpene phenols.[14] Hence, its absence, or possibly its shift to 1225 cm^{-1} could signal a change occurring at this point in the soluble resin residue fraction.

At this time it is not possible to more specifically identify the chemical structure of the soluble fraction in the residue. Similarly, whether these chemical differences are in some way responsible for the out-diffusion properties of this resin fraction is something we can only speculate on. Until it is better understood what the chemical differences are between the soluble and insoluble fractions themselves, *e.g.* where the carbonyl is attached, these questions are likely to remain unanswered.

F. Quantitative relative composition of polyol and resins in the aged adhesive residue

Having completely separated by *in-situ* heating the total material transferred to the sample mirrors into unreacted polyol, soluble and insoluble resin fractions, the relative amounts of these materials can be estimated. This can be done by comparing certain band absorbances in the first *residue* heating desorbed spectrum, Figure 5(a), the second *residue* heating desorbed spectrum, Figure 6(b), the second *residue* heating residual spectrum, Figure 6(c), and the total transferred material spectrum, Figure 4(a).

In particular we note that the large 1120 cm^{-1} band due to the asymmetric C-O-C stretch in the polyol is unique to that material and is not overlapped by any significant band of the terpene phenolic resin. Similarly no significant polyol band interferes with the resin band at 1225 cm^{-1}. Table III lists the absorbances of these bands in the specific cases observed above, and also their ratio in the complete reacted adhesive in which the elastomer-to-resin fractions are 1.75:1. From Table III we can conclude several things. First, all the desorbed resin material is accounted for since the 1225 cm^{-1} band absorbance of 0.009 in the preheated transferred residue is very close to the 0.0095 absorbance sum in the two desorbed resin residue spectra. Some of the polyol in the original polyol residue may have been desorbed as well since after the two heatings the 1120 cm^{-1} band absorbance is about 20% smaller.

TABLE III
Comparison of the polyol and resin proportional band absorbances in the transferred residue and the bulk adhesive

Spectrum	A(1120 cm^{-1})	A(1225 cm^{-1})	$\frac{A(1120)}{A(1125)}$
Total transferred residue before heating	0.018	0.009	2
Insoluble fraction first heating desorption	N.A.	0.004	N.A.
Soluble fraction second heating desorption	N.A.	0.0055	N.A.
Polyol second heating residue	0.014	N.A.	N.A.
Total adhesive system elastomer to resin = 2:1	0.645	0.122	5.3

Secondly, the relative amounts of the two resin types in the original transferred residue are about equal, 0.0055 *vs* 0.004, but it must be remembered that these peak height absorbances assume no chemical differences between the two resin fractions. However, as concluded in the preceding section the soluble fraction's 1225 cm^{-1} band did appear more intense due to chemical changes. Roughly, then, the two fractions are present in the transferred residue in equal amounts.

Finally, and most importantly, if the ratio of the polyol proportional band at 1120 to the resin proportional band at 1225 cm^{-1} in the transferred residue is 2:1 compared to 5.3:1 in the complete adhesive for which the weight ratios are 1.75:1, then the weight ratios in the transferred material are $(2/5.3) \times (2/1) = 2/3$. Hence, the surface diffused residue of the humidity temperature aged PSA that transferred to the sample mirror has polyol to resin in the ratio of 0.67 parts to 1 part instead of 1.75 parts in 1 part as in the bulk.

IV. CONCLUSION

It has been demonstrated that RAIR can be used very effectively to study, indirectly, the surface of certain organic materials. More specifically, those systems in which the surface material can be transferred to another substrate by contact are amenable. In this way the surface material of interest has been isolated from the bulk making its characterization feasible.

The ability to interact *in-situ* with the sample (*e.g.* by heating *in vacuo* in this application), has also proven to be extremely useful. In regard to the more basic aspect of this study, characterization of the adhesive bulk-to-surface diffused residue, the following summary applies:

1) The humidity/temperature aged adhesive surface residue consists of three components, *viz*, the polypropylene oxide, alcohol soluble and insoluble terpene phenolic resin fractions. It very specifically does not contain any elastomer or TDI related species.

2) Quantitatively the unreacted polyol to total resin ratio is 0.67:1 in the residue compared to 1.75:1 in the bulk adhesive. The relative amounts of the two resin fractions are approximately equal.

3) Neither the polyol nor the insoluble resin fraction contained in the residue appears chemically any different from that in the original materials. That is, the IR spectra are unchanged. However, *in-situ*

vacuum thermal desorption implies the insoluble fraction's molecular weight distribution is lower in the residue than in the original material.

4) The vacuum thermal desorption results imply no significant change in the molecular weight distribution of the soluble resin fraction that is in the residue, but definite chemical changes are implied by the RAIR spectra. A total of five bands are affected, two are strongly attenuated, two are enhanced and one is new. The conclusions drawn based on an interpretation of the source of the bands is that the residue soluble fraction is characterized by elimination of the gem-dimethyl groups on the α-pinene and incorporation of an ester, possibly aromatic, near the hydroxyl end of the phenol.

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