

Peel Strength of Polyurethanes from Oxypropylene Polyols II. Effect of Additives, Isocyanate Structure, and Other Factors

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Synopsis

The study of factors influencing the adhesion properties of polyurethane coatings to aluminum has been continued. The data indicate that the addition of additives to polyurethanes can affect their peel strengths. The addition of epoxy resins, chlorinated paraffins, or sulfonamide-formaldehyde resins results in increased peel strengths; the use of a mixture of fatty acids resulted in reduced values. The isocyanate structure can also play an important role; those producing more flexible films (such as *m*-xylylene diisocyanate) result in higher peel strength values. Other factors found to be of importance included the concentration of aromatic and aliphatic groups, the type of solvent used in casting the films, the crystallinity of the polyether glycols and the presence or absence of certain substituents, such as fluorine, in the polyurethane chain. Tracer studies have indicated that the mechanism of adhesion failure involves the breaking of polymer-polymer as well as polymer-substrate bonds.

INTRODUCTION

In Part I of this study the effect of polyol structure and fillers on the peel strength of polyurethanes prepared from polyoxypropylene polyols was investigated.¹ The peel strength of coatings from aluminum was found to increase with increasing urethane and urea content. The peel strength decreased with increasing film rigidity, where rigidity resulted from increases in crosslinking density or isocyanate/hydroxyl ratio. Fillers were found to play an important role in the adhesion properties of polyurethanes; the peel strengths were dependent on the type and amount of fillers in the films.

The present investigation, an extension of the above work, reports the effect of the use of additive on the peel strength of polyurethanes and the influence of the type of diisocyanate (tolylene diisocyanate, TDI, or *m*-xylylene diisocyanate, XDI) used in their preparation. The effect of the concentration of aromatic and aliphatic groups in the polyurethane structure is also described as well as the influence of the type of solvent used in the preparation of the films. The influence of isotactic polyoxypropylene glycols as well as the effect of fluorine groups in the polyurethane structure on adhesion are reported. Some preliminary results from tracer studies, designed to determine the locus of adhesion failure, are also presented.

EXPERIMENTAL

Methods

The methods used were similar to those previously described.¹ The polyurethanes were formed by the reaction of glycols and polyols with prepolymers that were prepared from 1 equivalent of polyol and 2 equivalents of tolylene diisocyanate (TDI), 80:20 ratio of 2,4 and 2,6 isomers.

These prepolymers were isocyanate-terminated and extended to cross-linked polyurethanes by the glycols and polyols. The films were prepared from benzene solutions containing 0.1% dibutyltin dilaurate (DBTDL) as catalyst, deposited on the panels, dried for 2–2.5 hr. at room temperature, and cured at 55–60°C. for 15.5–17 hr. The solutions were uniform in viscosities (E on the Gardner-Holdt scale), usually requiring solids concentrations of 40–60%. The substrates were standard aluminum panels supplied by the Q Panel Co. of Cleveland, Ohio.

Cleaning of the panels was carried out by the following routine: (1) washing with detergent-water solution; (2) rinsing with water and drying; (3) rubbing with acetone-soaked paper towels (18 strokes); (4) rubbing with paper towels soaked in ethylene dichloride (8 strokes); (5) rinsing with ethylene dichloride.

Peel tests were carried out at an angle of 180° and were obtained on films of various thicknesses. Plots of peel strength versus thickness resulted in straight lines whose slopes appeared to be related to the rigidity of the films. The lines were extrapolated to zero thicknesses; these peel strength values were considered to be more significant for comparing different films than were the peel strength values at some finite thickness.

Materials

The glycols and polyols used in this investigation are products of Wyandotte Chemicals Corporation. A key to their nomenclature is as follows: P series = polyoxypropylene glycols; TP series = polyoxypropylene derivatives of trimethylolpropane; GP series = polyoxypropylene derivatives of glycerol. The numerical portions of this nomenclature are indicative of the glycol or polyol molecular weights. Thus, P-410 is a polyoxypropylene glycol of 400 molecular weight, TP-740 is a 730 molecular weight triol, prepared by the addition of propylene oxide to trimethylolpropane.

The PR-960 prepolymer was the isocyanate-terminated product from the reaction of 1 mole TP-1540 and 2 moles TDI.

RESULTS AND DISCUSSION

Effects of Additives

In an effort to determine the influence of including various molecular structures and functional groups on the adhesion properties of polyurethanes, a number of additives were used.

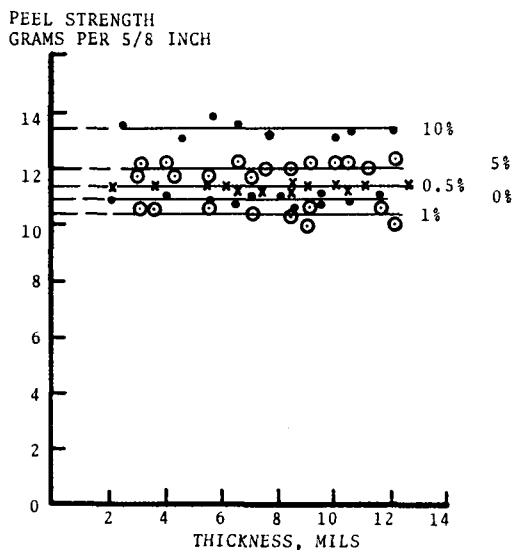


Fig. 1. Effect of Chlorez 70B on peel strength.

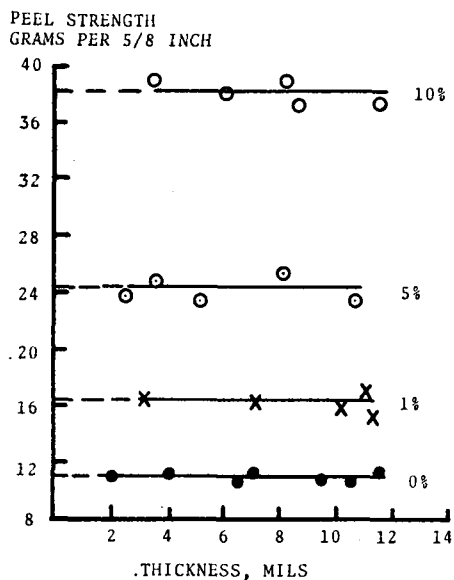


Fig. 2. Effect of PAROIL 170HV on peel strength.

The effect of chlorine-containing additives was determined by the use of chlorinated paraffins. Chlorez 70B and Paroil 170HV (70% chlorinated paraffins from Dover Chemical Co.) were compared. They differed mainly in their melting points, with Paroil 170HV a liquid at room temperature and Chlorez 70B melting at 90°C.

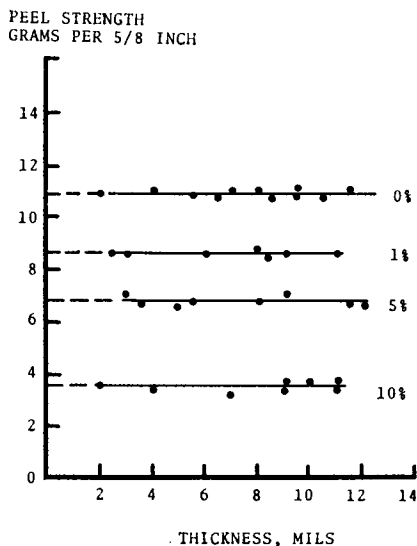


Fig. 3. Effect of tall oil fatty acids on peel strength.

Their effect on the peel strength of the polyurethane formed from P 2010 and the PR-960 prepolymer is shown in Figures 1 and 2. Both additives resulted in films with increased adhesion to aluminum. At low concentrations, the addition of Chlorez 70B resulted in almost no change in peel strength. The use of the lower-melting Paroil 170HV caused a more significant increase; it resulted in more flexible films than those prepared with Chlorez 70B. As noted previously,¹ flexible polyurethane films result in higher peel strengths than are obtained with more rigid films.

The effect of the inclusion of tall oil fatty acids (TOFA) into polyurethanes was investigated and significant reductions in peel strength were observed (Fig. 3).

The inclusion of unsaturated fatty acids, such as the linoleic and oleic that are found in TOFA, result in reduced adhesion of polyurethanes to aluminum. The effect of chlorine groups on paraffins in increasing peel strengths can be seen, therefore, to overcome the predominantly negative influence of the hydrocarbon chain.

The study of additives was continued with the evaluation of two epoxy resins and a sulfonamide-formaldehyde resin (Monsanto's Santolite MHP). The peel strengths from aluminum have been plotted against film thickness, in Figure 4, for the compositions containing Epon 834 (a low molecular weight epoxy resin from Shell Chemical Co.). Coatings containing 10% and 15% resin show a significant increase in peel strength. The slopes of these plots are all close to zero, indicating no increase in the rigidity of these coatings has resulted. In Figure 5 the data from those films containing Epon 1001 (a high molecular weight epoxy from Shell Chemical Co.) are shown. Only a moderate increase in peel strength is noted in those

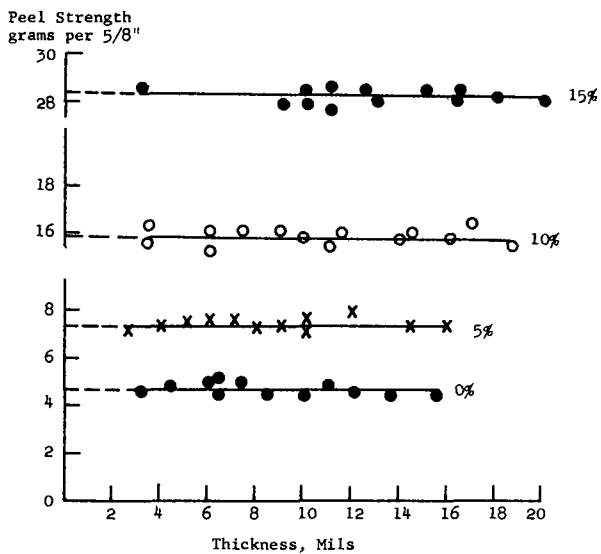


Fig. 4. Effect of Epon 834 on peel strength.

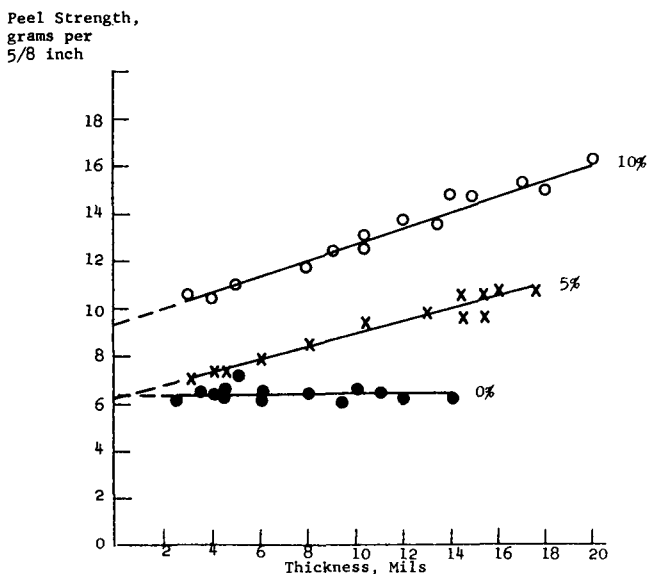


Fig. 5. Effect of Epon 1001 on peel strength.

compositions containing 10% resin. These results indicate that lower molecular weight epoxides are more effective than higher molecular weight epoxides in improving the adhesion of polyurethanes. The increase in slope that occurs with addition of Epon 1001 is evidence of the increased rigidity of these coatings. Thus, the influence of film rigidity on the adhesion properties of polyurethanes was again observed.

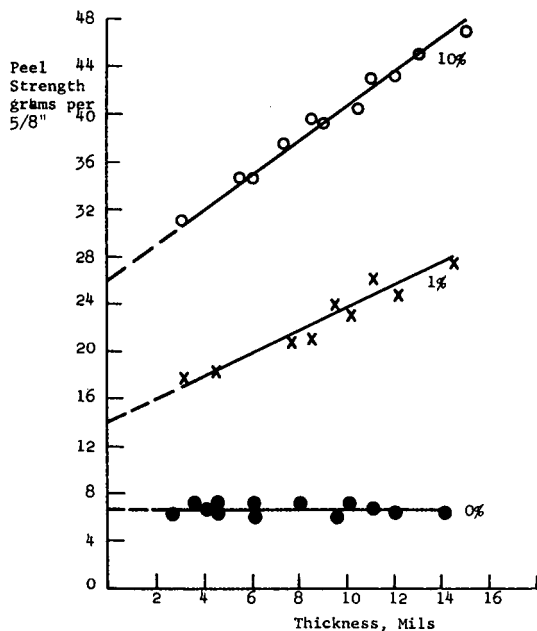


Fig. 6. Effect of Santolite MHP on peel strength.

The data from those coatings containing the sulfonamide-formaldehyde resin are plotted in Figure 6. Significant increases in peel strengths have been obtained, as well as increased film rigidity. The rigidity did not counteract the effect of the sulfonamide groups in producing increased adhesion properties.

Effect of Type of Isocyanate

A comparison was made of the adhesion properties of polyurethanes made from XDI (*m*-xylylene diisocyanate) and TDI prepolymers. Coatings were prepared on aluminum panels by the reaction of P-2010 with a GP-3030-XDI prepolymer and with a GP 3030-TDI prepolymer, at NCO/OH ratios of 1.3:1. The peel strengths that were obtained have been plotted against film thickness (Fig. 7), and it can be seen that a slight increase in adhesion results with the use of XDI prepolymer, as compared to the TDI prepolymer. Although no reduction in rigidity can be detected from these plots, since both exhibit zero slopes, an increase in the elongation properties of these films was observed with the use of XDI. These results seem to follow the general pattern, described earlier, of more flexible films providing improved adhesion properties over less flexible materials.

An attempt was also made to compare these data with those obtained by using polyphenyl polymethylene polyisocyanate (PAPI, the Upjohn Co., average NCO functionality of 2.8). The coatings that resulted were, as expected, considerably more rigid than those using the prepolymers described above. The cohesive strengths were not high enough to allow deter-

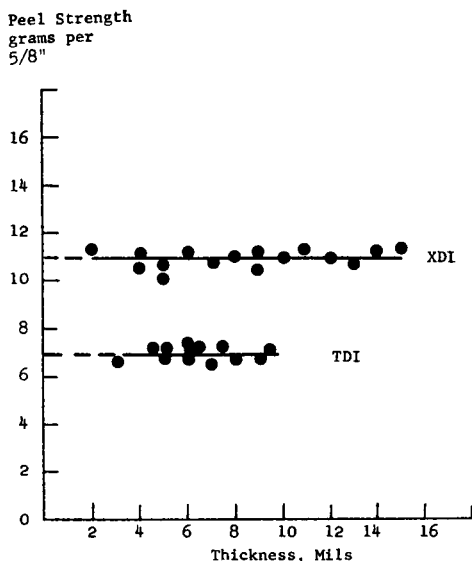


Fig. 7. Effect of XDI vs. TDI on peel strength.

mination of peel strengths at 180°, as the coatings broke before peeling could be accomplished. However, in a qualitative manner, it was apparent that the PAPI polyurethanes showed significantly greater adhesion to aluminum than those from either the TDI or XDI prepolymers. These results are especially noteworthy, due to the ability of PAPI to provide coatings of both increased modulus and adhesion. Similar results were observed with the use of diphenylmethane diisocyanate.

Effect of Aromatic and Alkyl Groups

An evaluation was made of the effect of the concentration of aromatic and alkyl groups on the peel strength properties of polyurethanes. This was done by the substitution of hydroquinone and 1,4-butanediol for P-2010 in the reaction with PR-960.

Plots of peel strength versus thickness are shown in Figure 8, and they indicate that increases in adhesion occur when either hydroquinone or butanediol is substituted for P-2010; when 50% of the alcohol groups came from either of the low molecular weight glycols, the increases in peel strengths over P-2010 were greater than when 33% of the alcohol groups came from these glycols. The increases obtained with the aliphatic butanediol were greater than those observed with the aromatic hydroquinone, which might indicate the relative effectiveness of alkyl and aromatic groups.

These results also indicate that increasing urethane concentration by substitution of these low molecular weight glycols for P-2010 results in improved adhesion properties. Apparently, for these systems, the ability

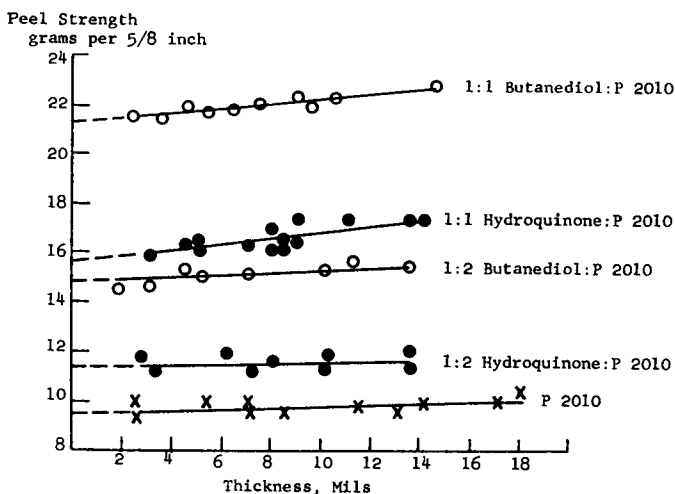


Fig. 8. Effect of aromatic-aliphatic groups.

of higher crosslink densities to reduce peel strengths is overcome by the influence of higher urethane concentrations.

Effect of Solvents

An evaluation was carried out to determine the influence of the type of organic solvent, used to obtain solution of glycol and prepolymer, on the peel strength characteristics of the resultant polyurethanes. Engel and Fitzwater² have reported that the peel strength of poly(methyl methacrylate) films prepared from solutions are related to the cohesive energy densities of the solvents employed.

A number of solvents (benzene, xylene, chloroform, ethylene dichloride, acetone, dioxane, and cyclohexanone) were used in the preparation of films from P-410 and PR-960. The peel strengths are plotted, in Figure 9, against film thickness; the cohesive energy density (CED) values for these solvents³⁻⁶ are shown in Table I.

It can be seen that the adhesion of these films to aluminum is related to the CED of the solvent from which it was cast; the higher CED value sol-

TABLE I
Cohesive Energy Density Values of Solvents

Solvent	CED
Xylene	77
Benzene	85
Chloroform	86
Ethylene dichloride	96
Acetone	98
Dioxane	98
Cyclohexanone	98

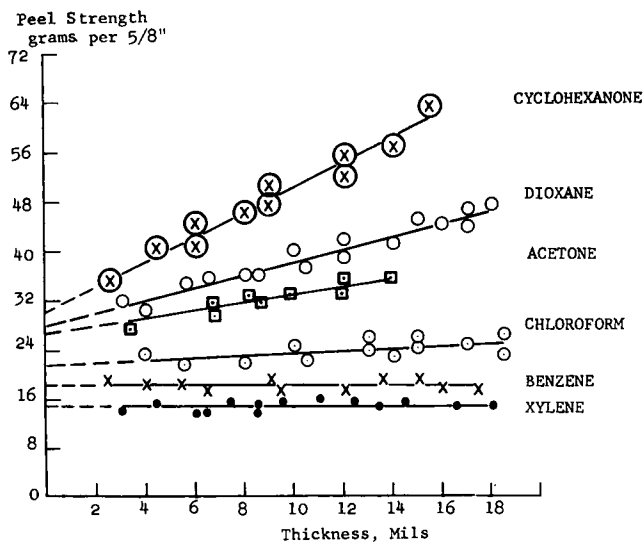


Fig. 9. Effect of solvent.

vents produced higher extrapolated peel strength values. Thus, cyclohexanone and dioxane result in the best adhesion values. It is possible that the solvents have an influence on the orientation of the polar groups in the polymer, making them more available for van der Waals or hydrogen bonding with the metallic substrate. Another factor may be the difference in retention properties, after baking, of the coatings for each of the solvents. Preliminary work with ^{14}C -containing solvents (in cooperation with Mr. J. Hensley) indicate this latter factor to be an important one.

Effect of Isotactic Glycols

A sample of stereoregular polyoxypropylene glycol was prepared, with 40% isotacticity. Its preparation will be described in a subsequent paper. With the use of a 3000 molecular weight stereoregular glycol (40% isotacticity) coatings were prepared on aluminum panels by reaction with PR-960. Their peel strengths have been determined and compared with coatings prepared from the same prepolymer reacted with atactic P-2010 and P-3010 glycols. The results are plotted against film thickness in Figure 10. The polyurethane from the isotactic P-3000 shows a significantly higher adhesion to aluminum than the products from P-2010 or P-3010. In addition, the slope of the peel strength-thickness plot indicates that the crystallinity of this glycol has resulted in a more rigid polyurethane.

An explanation for the effect of isotacticity on adhesion may be found in the tendency of isotactic polymers to crystallize in helical structures. Thus, it is possible that polar groups (urethane or ether) may be found on the outer surfaces of these helices and thus be more available for van der

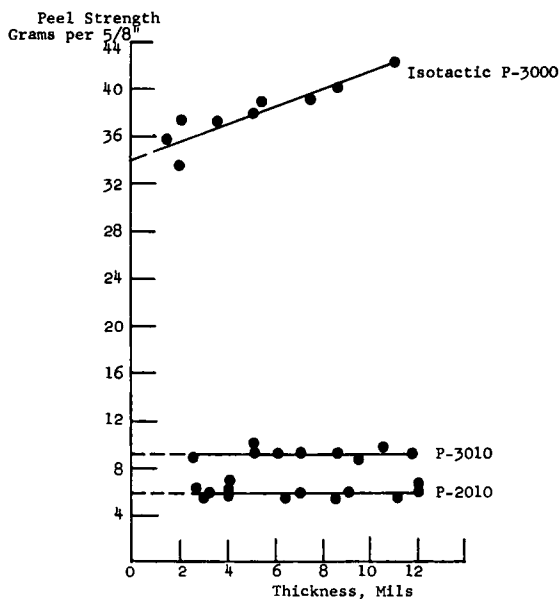


Fig. 10. Effect of isotactic glycol.

Waals or hydrogen bonding with the aluminum (or aluminum oxide) substrate.

This effect can be considered similar to that observed with poly(methyl methacrylate). Saponification of the ester groups was found to proceed at faster rates and to higher degrees of completion for the isotactic polymer than for the atactic samples.⁶⁻⁸ This has been explained as being due to the greater availability of the ester groups for hydrolysis when on the surface of helical structures.

Effect of Fluorine Groups

A study was carried out on the effect of the presence of fluorine groups on the adhesion of polyurethanes to aluminum. A fluorinated alcohol, 1,1,5-trihydroperfluoropentanol ($\text{CHF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$) was reacted with a TP-740-TDI prepolymer (at 1:1 mole ratio) to form a difunctional prepolymer with a fluorinated alkyl branch. When reacted with TP-740, this prepolymer produced a polyurethane film. A similar reaction was carried out with the TP-740 prepolymer and amyl alcohol, then cross-linking with TP-740, resulting in a polyurethane with an alkyl branch. The peel strengths of these films were determined and plots of thickness versus peel strength are shown in Figure 11. These data show that the introduction of fluorine groups into the polyurethane structure results in a decrease in adhesion values. Little difference in film rigidities could be detected between the two samples. The explanation for the behavior of fluorine-substituted polyurethanes probably lies in the more electropositive character of these polymers.

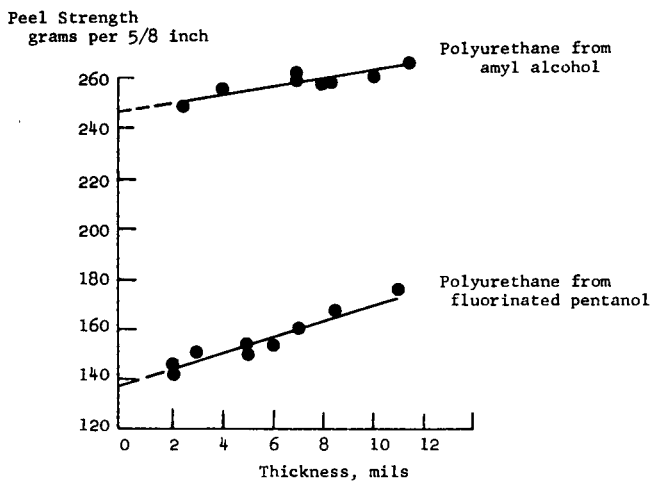


Fig. 11. Effect of fluorine groups.

Tracer Studies

There has been a great deal of controversy among research workers in the field of adhesion as to whether failure is ever obtained at the interface between adhesive films and metal substrates, some claiming that cohesion failure always occurs in the adhesive layer.⁹⁻¹² Studies were carried out in an effort to determine whether peel tests result exclusively in adhesion failure. Polyurethane films were prepared from ¹⁴C-labeled diols. After peeling, the residual film on the aluminum panels was measured by the count of β -particles. Using a film from the reaction of the glycols with PR-960 isocyanate adduct, it was determined that 2.34 μ g. of film remained per square centimeter of substrate. This calculates to an average of 45 layers of polyurethane film over this area (assuming 5 A. per unit layer). Apparently, at least some of the failure was of a cohesive nature, the bond breaking being a polymer-polymer layer.

Further work was carried out with coatings prepared from ¹⁴C-labeled glycerine, P-1310, and PR-960 from ethyl acetate solutions. Counts of β -rays were taken on the aluminum panels after removing the coatings. Three aluminum panels of different roughness (as measured with an end-window gas-flow counter) were used in these tests, and the data obtained are shown in Table II.

TABLE II
Effect of Roughness on Amount of Film Residue

Aluminum panel roughness, μ in.	Count/min. (1 $\frac{1}{4}$ in. dia.)	Residue, μ g./cm. ²
30-40	720	2.30
15-20	430	1.38
5-10	290	0.93

These results indicate that some residual film remains on the aluminum substrates. It is also apparent that larger amounts of film residues are obtained with increasing metal roughness. This could indicate that residues are probably due to mechanical entrapment in holes on the metal surface rather than the result of true adhesion to the metal being greater than the cohesion of the polymer. On the other hand, the larger residues might be due to the greater surface areas found on the rougher metal surfaces.

Appreciation is expressed to Mr. J. W. Hensley of this laboratory for supplying samples of ^{14}C -labeled diols, carrying out, and interpreting the tracer studies.

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Résumé

On a continué l'étude des facteurs influencant les propriétés adhésives de revêtements de polyuréthane sur l'aluminium. Les résultats indiquent que l'addition d'additifs au polyuréthane peut affecté leur force de résistance à l'écaillage. L'addition de résines époxy, de paraffines chlorées et de résines sulfonamide-formaldéhyde entraîne une résistance plus élevée à l'écaillage; l'utilisation d'un mélange d'acides gras, par contre, amène à des valeurs plus faibles. La structure isocyanée peut également exercer un rôle important; celle produisant des films plus flexibles (telle le diisocyanate de *m*-xylylène) donne également des résistances à l'écaillage plus élevées. D'autres facteurs également importants sont la concentration en groupes aliphatiques et aromatiques, le type de solvant utilisé pour couler les films, la cristallinité du glycol polyéther et la présence ou absence de certains substituants, tel que le fluore dans la chaîne polyuréthannique. Des études utilisant des traceurs ont indiqué que le mécanisme de manque d'adhésion comporte la rupture de liens polymère-polymère aussi bien que de liens polymère-substrat.

Zusammenfassung

Die Untersuchung der Faktoren, welche das Adhäsionsvermögen von Polyurethanüberzügen auf Aluminium beeinflussen, wurde fortgesetzt. Die Ergebnisse zeigen, dass der Zusatz von Additiven zu Polyurethanen ihre Abziehfestigkeit beeinflussen kann. Der Zusatz von Epoxyharzen, chlorierten Paraffinen oder Sulfonamid-Formaldehydharzen führt zu einer Erhöhung der Abziehfestigkeit; die Verwendung einer Fettsäuremischung ergibt eine Herabsetzung der Werte. Auch die Isocyanatstruktur kann eine wichtige Rolle spielen; Isocyanate wie *m*-Xylylendiisocyanat, die stärker flexible

Filme liefern, geben höhere Werte der Abziehfestigkeit. Andere wichtige Faktoren sind die Konzentration an aromatischen und aliphatischen Gruppen, der Typ des beim Giessen des Films verwendeten Lösungsmittels, die Kristallinität der Polyätherglykole und die Gegenwart oder Abwesenheit gewisser Substituenzen, wie Fluor in der Polyurethankette. Markierungsversuche zeigten, dass der Mechanismus des Verklebungsbruches sowohl eine Spaltung von Polymer-Polymer- als auch von Polymer-Substrat-Bindungen einschliesst.

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