

## Peel Strength of Polyurethanes from Oxypropylene Polyols. I. Effect of Polyol Structure and Fillers\*

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### Synopsis

A study has been made of some of the factors that influence the adhesion properties of polyurethane coatings to aluminum. The peel strength (at angles of 180 and 90 degrees) has been plotted against film thickness (from 1.5 to 20 mils) and extrapolated to zero thickness; these intercept values have been found to have more significance than peel strengths at finite thicknesses. It has been found that, for polyether-urethanes prepared from polyoxypropylene glycols and polyols, the peel strength increases with increasing urethane and urea content. It has also been found that peel strength decreases with increasing film rigidity, where rigidity is caused by increasing the crosslinking density or isocyanate/hydroxyl ratio. Fillers play an important role in peel strength; at concentrations up to 15% in the glycol component the adhesion of polyurethanes increases with the addition of iron oxide and calcium carbonate. The use of chromic oxide causes only a decrease in peel strength.

### INTRODUCTION

The increasing use of polyurethanes in many applications, including elastomers, plastics, and oriented films or fibers, has resulted in many studies correlating mechanical properties with chemical and physical structures. Properties such as impact resistance, tensile strength, elongation, modulus, fatigue, stress relaxation, as well as heat, oxidation, and ultraviolet resistance have been shown to be influenced by urethane concentration, crosslink density, NCO/OH ratio, and many other variations in polymer structure.

Little work has been reported<sup>1</sup> attempting to define, either qualitatively or quantitatively, the factors influencing the adhesive properties of polyurethanes, even though applications, either potential or already commercialized, include at least a minimum degree of adhesion to various substrates in their specifications.<sup>2</sup>

This work is an effort to add to the knowledge of polyurethane behavior by providing information on some of the factors that influence their adhesive characteristics on metals.

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## METHODS

The adhesion characteristics of polyurethanes have been determined by measuring the peel strengths of films from metal (mainly aluminum) panels. These polyurethanes were formed by the reaction of glycols and polyols with prepolymers that were prepared from 1 equiv. of polyols and 2 equiv. of tolylene diisocyanate (TDI), 80:20 ratio of 2,4 and 2,6 isomers.

These prepolymers are isocyanate-terminated and are 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 usually carried out at an angle of 180° (Fig. 1).<sup>1</sup> Where a 90° angle peel was studied, use was made of a fixture fitted on the lower jaw of the Instron tester that allowed the manual horizontal movement of the test panel, maintaining a constant peel angle.

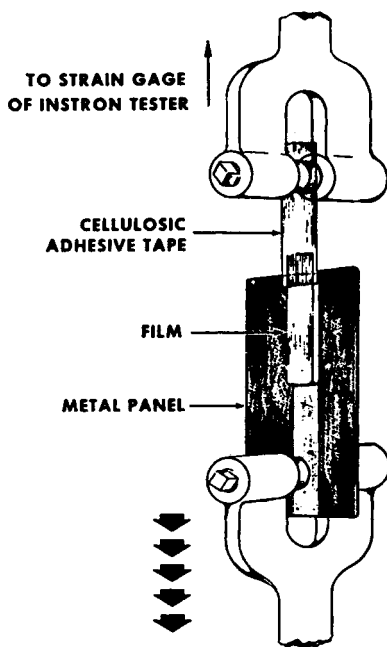


Fig. 1. Peeling test.

## EXTRAPOLATION

Peel strength data at an angle of  $180^\circ$  have usually been obtained on films of various thicknesses. It has been noted that plotting peel strength versus thickness results in straight lines whose slopes range from zero to 20–30 g./mil. These slopes appear to be related to the rigidity of the films being peeled; the higher modulus films result in plots with higher slopes, lower modulus films produce lower slopes. It has been necessary, therefore, to eliminate the influence of slope when comparing the adhesion properties of a group of films; this has been done by extrapolating the plots to zero thickness. These intercept values are considered to be more significant for comparing different films than are 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 = polypropylene 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 polypropylene glycol of 400 molecular weight; TP-740 is a triol, prepared by the addition of propylene oxide to trimethylolpropane, of 730 molecular weight.

## RESULTS AND DISCUSSION

### Effect of Crosslinking Density

An effort was made to study the influence of film stiffness and rigidity on peel strength by varying the degree of crosslinking density. This was done by comparing films prepared from the linear P-410 glycol with those from the branched TP-740 glycol, as well as 1:1 equivalent mixtures of the two polyols. Films were prepared by reacting the polyols with the TDI (80:20, 2,4:2,6) prepolymer from TP-1540 in the presence of dibutyltin dilaurate catalyst at an NCO/OH ratio of 1.1, from benzene solutions. The peel strength data at  $180^\circ$  angle are plotted in Figure 2 against film thickness. They show that the highest peel strengths were obtained from the linear P-410 glycol, the lowest from the branched TP-740 which forms the polyurethane with the highest crosslink density. The 1:1 mixture of P-410:TP-740 produced films with intermediate peel strengths.

Figure 2 also shows the data that were obtained when these films were peeled at an angle of  $90^\circ$ . These tests were carried out at a crosshead speed of 0.1 in./min. as compared to 0.2 in./min. for the  $180^\circ$  tests. In this way the actual peel speeds in both cases were maintained at 0.1 in./min. It can be seen that the highest peel strengths were again obtained with polyurethane films from the P-410 glycol, the lowest from TP-740,

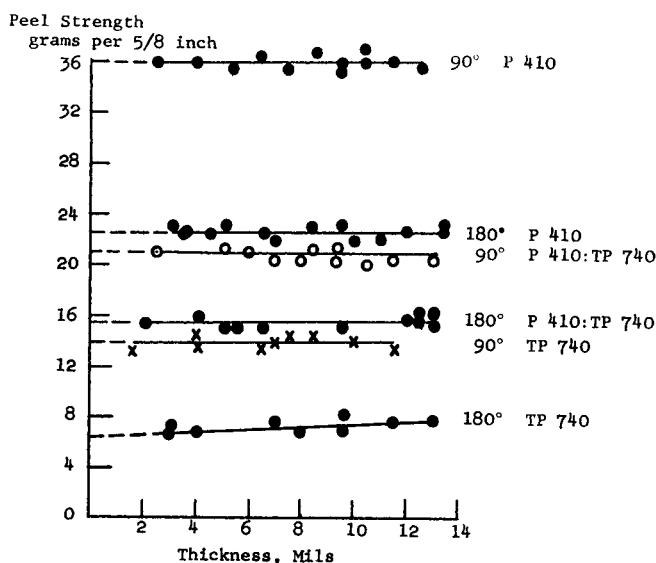


Fig. 2. Effect of crosslink density and peel angle.

and intermediate values for the mixture of P-410 and TP-740. It is of interest to note that higher peel strengths were consistently obtained at 90° peels than at 180°. These results agree with previously published data on the effect of angle on the peel strengths of poly(vinyl acetate)<sup>3</sup> from glass.

An attempt was also made to correlate the peel strength data with the physical properties of the films. These properties are listed in Table I.

TABLE I  
Physical Properties of Films with Variable Crosslink Densities

Glycol or polyol used to prepare film*	Breaking tensile, psi	Breaking elongation, %	Tensile at 100% elongation, psi
P-410	307	276	118
P-410 + TP-740 (1:1)	208	125	164
TP-740	336	106	304

\* After reaction with TP-1540 prepolymer.

It can be seen that the films with higher peel strengths possess the highest breaking elongations and lowest tensiles at 100% elongation (which is indicative of modulus). No correlation could be made between adhesion and breaking tensile. It is possible that those films with less rigidity (such as the one from P-410) are able to conform more easily to the rough surface of the aluminum substrate (roughness index = 15–20  $\mu$ in.) after drying and gelation takes place during the baking operation; they would

also be able to resist permanent shrinkage which tends to reduce the contact area with the substrate.<sup>4,5</sup>

### Effect of NCO/OH Ratio

Work has been carried out to determine the influence of the NCO/OH ratio on the peel strength of polyurethane films. Variations in the amount of TDI in polyurethane compositions are one of the primary means of changing their physical properties and it was of interest to determine the influence on adhesion characteristics. TP-740 polyol was reacted with the TDI prepolymer from TP-1540 at NCO/OH ratios of 1.0, 1.1, 1.2, and 1.5.

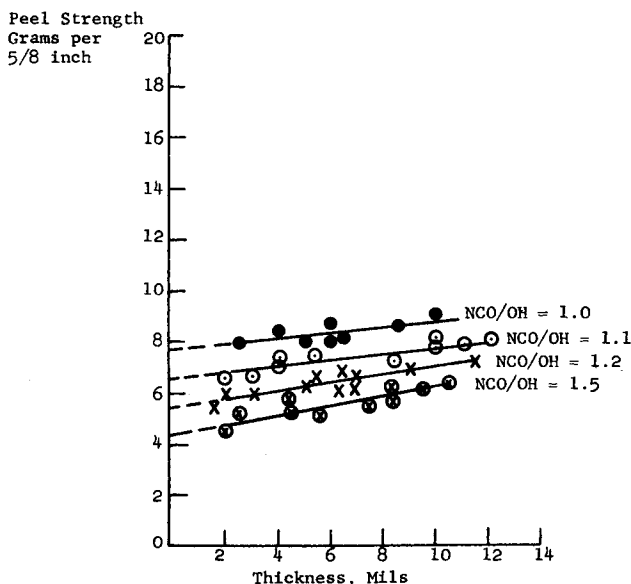


Fig. 3. Effect of NCO/OH ratio.

The peel strengths of these films from aluminum panels are plotted against film thickness in Figure 3. It can be seen that only slight changes in peel strengths were effected by these variations; the extrapolated values range from 4.4 to 7.8 g. per  $\frac{5}{8}$  in. However, they appear to increase with

TABLE II  
Physical Properties of TP-740 Polyurethanes at Various NCO/OH Ratios

NCO/OH ratio <sup>a</sup>	Breaking tensile, psi	Tensile at 100% elongation, %	Tensile at 100% elongation, psi
1.0	308	108	290
1.1	336	106	304
1.2	327	104	306
1.5	384	86	—

<sup>a</sup> TP-1540 prepolymer used as isocyanate component.

decreasing NCO/OH ratios. The physical properties of these films have been determined and are listed in Table II.

A comparison of these physical properties with the peel strength data in Figure 3 shows that the small increase in the adhesion values of these films occurs simultaneously with small increases in breaking elongation and reductions in tensile at 100% elongation. Once again it can be seen that less rigidity in films resulted in corresponding increases in peel strength.

### Effect of Urethane and Urea Concentration

One of the primary means of changing the chemical composition and physical characteristics of polyurethane products is to alter the concentration of urethane and urea groups. Linear polyurethane-ureas were formed by the reaction of glycols, isocyanates, and diamines.

Films were prepared from these polymers out of 1:1 ethyl acetate-MIBK solutions on aluminum panels and peel strengths determined after aging for 16 days at 21°C. and 55% R.H. Their peel strengths have been plotted against film thickness in Figure 4; it can be seen that only 3-5 points are given for each. This was due to difficulty in obtaining peel strengths from films less than 10-15 mils thick; the peel strengths were

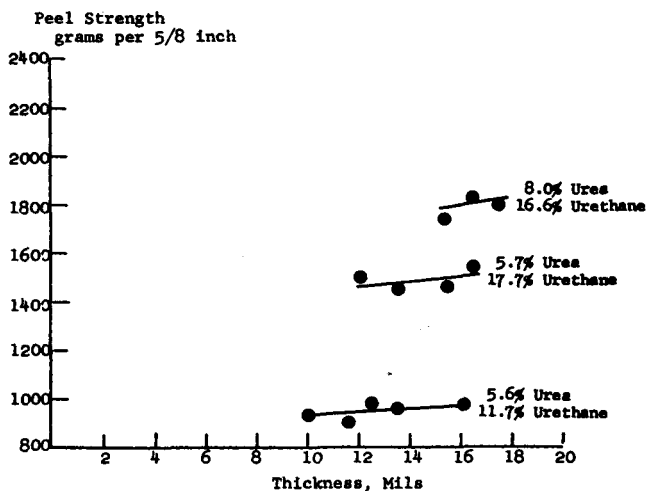


Fig. 4. Effect of urethane-urea concentration.

high compared to the cohesive strengths of the films and they repeatedly broke when tests were attempted at lower thicknesses. Even with these limited data, however, it is apparent that the presence of both urethane and urea groups results in increased adhesion to aluminum; urea groups are somewhat more effective than urethanes in producing high adhesion.

It should be noted that the peel strength data in Figure 4 are considerably higher than those obtained from polyurethanes containing no urea (900-1800 g. as compared to 40-200 g.), showing the importance of including

these latter groups in compositions where superior adhesion properties are required.

### Effect of Urethane Concentration and Crosslink Density

It has been shown previously that the peel strengths of polyurethane films can be raised by increasing the concentration of urethane groups; the peel strengths can be reduced by increasing crosslink density. It was of interest to determine the effect of increasing both simultaneously. Polyurethanes can be prepared with varying concentrations of urethane groups and crosslink densities; the higher the hydroxyl number (or the lower the molecular weight) of a polyether diol, the higher will be the concentration of urethane groups and the higher will be the crosslink density, when reacted with trifunctional prepolymers. This study was carried out by comparing the peel strengths of polyurethanes prepared from linear polypropylene glycols (P-410, P-1310, and P-2010) and the TDI prepolymer from TP-2540 at an NCO/OH ratio of 1:1.2. These results are plotted in Figure 5

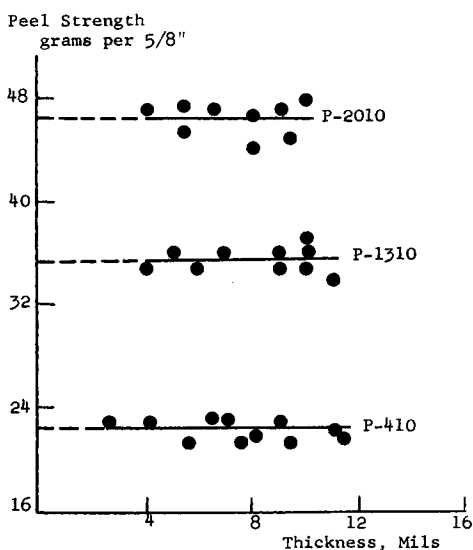


Fig. 5. Effect of urethane concentration and crosslink density.

against film thickness. It is apparent that polyurethanes from higher molecular weight diols possess better adhesion properties than do those from lower molecular weight diols. Thus, P-2010 produces the highest peel strength, P-410 results in the lowest peel strength.

The study of the influence of urethane groups and crosslink density was extended to include polyurethanes formed from branched polyols. These polyols (TP-740, TP-1540, and TP-2540) form more highly crosslinked polyurethanes than those from the linear polypropylene glycols; by reacting with the TDI prepolymer of TP-1540 instead of TP-2540, the crosslink

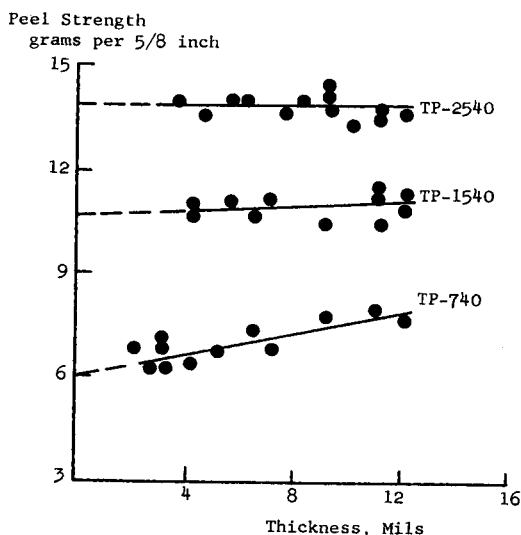


Fig. 6. Effect of urethane concentration and crosslink density (branched polyols).

density was further increased. In Figure 6 the results are plotted against film thickness. Again, it can be seen that the adhesion of polyurethanes decreases as both urethane concentration and crosslink density increase simultaneously.

Apparently, in the case of branched polyols, as well as linear glycols, the influence of the urethane groups in providing increased attraction to the metal surface has been overcome by the increased rigidity of the resulting polyurethanes that was caused by the higher crosslink densities. This increased rigidity can be noted in Figure 6, resulting in higher slopes in the plots of peel strength versus thickness.

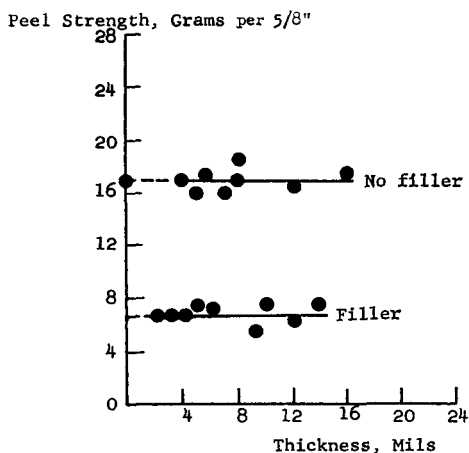
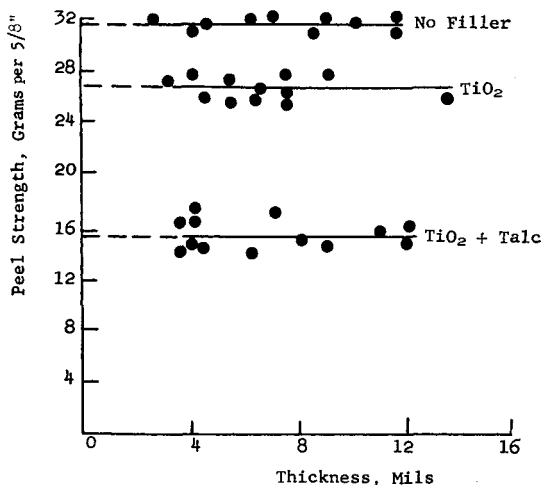
The physical properties of the films from branched polyols have been obtained and are shown in Table III.

A comparison of these physical properties with the peel strength data in Figure 6 indicates that higher adhesive properties can be correlated with higher breaking elongations and lower moduli (tensiles at 100% elongation). As noted in previous tests, no correlation between breaking tensiles and peel strengths can be detected.

### Effect of Fillers on Peel Strengths

Included in the polyurethane compositions used in many applications (such as caulking or sealing compounds) are fillers that provide certain desirable physical properties. An effort was made to determine the effect of fillers on adhesion and, in preliminary studies, the peel strength of a polyurethane from P-1310, containing 25% by volume filler (1 part  $\text{TiO}_2$  and 1 part talc), and the TDI prepolymer from TP-2540 was compared with the same polyurethane containing no filler. The data from aluminum



Fig. 7. Effect of filler (TiO<sub>2</sub> + talc).Fig. 8 Effect of filler on peel strength (TiO<sub>2</sub>, TiO<sub>2</sub> + talc).

panels are plotted against thickness in Figure 7. The filler has an appreciable effect on peel strength, reducing it to 40% of the unfilled polyurethane.

A comparison was then made of a filler system containing talc and TiO<sub>2</sub> (1:1) with one containing only TiO<sub>2</sub>. The peel strengths of polyurethane films from P-1310 and the TDI prepolymer from TP-1540 (PR-960), containing these fillers, were determined from steel panels and are plotted against film thickness in Figure 8. The films containing no filler exhibit the highest values; the introduction of TiO<sub>2</sub> and talc caused a loss of more than 50% in peel strength. When only TiO<sub>2</sub> was used as the filler (at an equal volume concentration) the loss was cut to 15%. These results indicate the desirability of eliminating talc from compositions that should provide good adhesion characteristics.

TABLE III  
Physical Properties of Polyurethane Films

Polyol used to prepare film <sup>a</sup>	Breaking tensile, psi	Breaking elongation, %	Tensile at 100% elongation, psi
TP-2540	344	152	257
TP-1540	370	131	278
TP-740	312	107	301

<sup>a</sup> After reaction with TP-1540 prepolymer.

The study of the effect of fillers on the peel strength of polyurethane films was then expanded to include barium sulfate, calcium carbonate (acicular and cubic), zinc oxide, and titanium dioxide. The peel strengths of polyurethane films from P-2010 and PR-960, containing these fillers, were determined from aluminum panels; in each case the pigment volume concentrations in the glycols were maintained at 18%. The peel strengths have been plotted against film thickness in Figure 9. The unfilled coating exhibited a zero slope, with an extrapolated peel strength of 18 g. for a  $\frac{5}{8}$ -in. strip; the addition of barium sulfate or titanium dioxide caused a slight reduction in the extrapolated peel strength and a sharp increase in slope. The change in slope is indicative of the rigidizing effect of fillers on polyurethanes. With the addition of calcium carbonate to the poly-

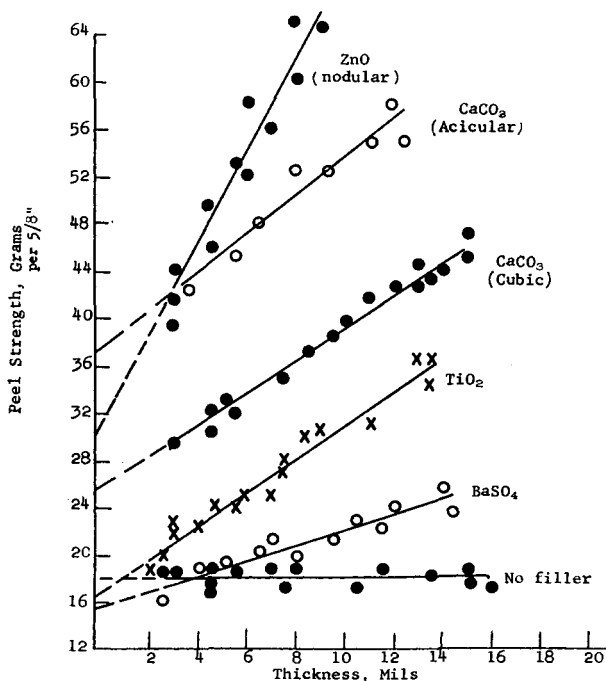


Fig. 9. Effect of filler (BaSO<sub>4</sub>, TiO<sub>2</sub>, CaCO<sub>3</sub>, and ZnO).

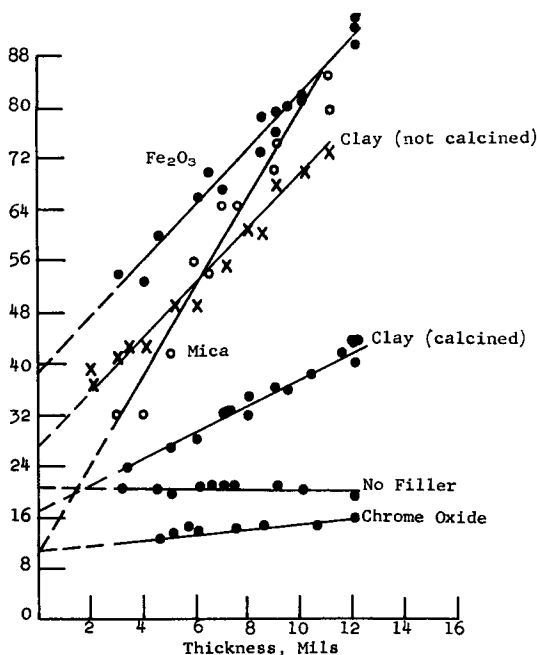


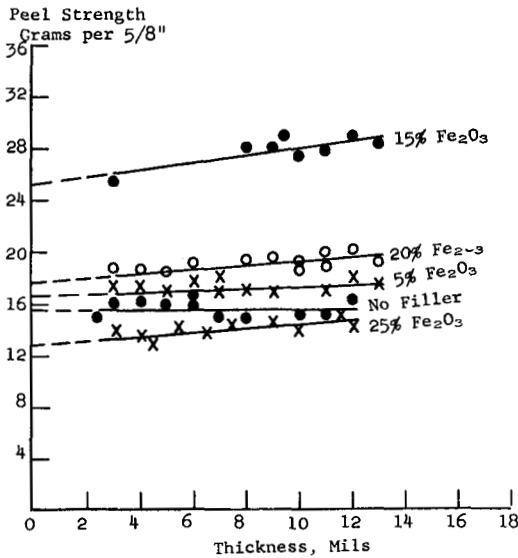
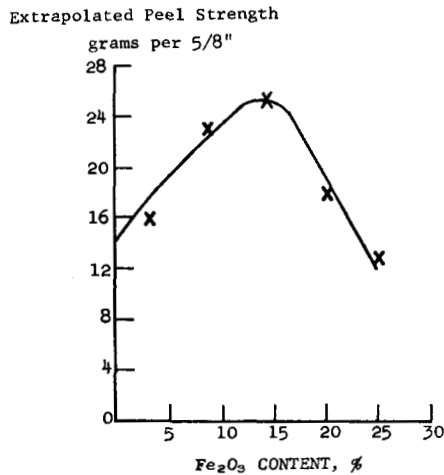
Fig. 10. Effect of fillers (chromic oxide, clay, mica,  $\text{Fe}_2\text{O}_3$ ).

urethane a substantial increase in peel strength is noted; the effect is somewhat greater for the acicular type than for the cubic type. In both cases the slopes are equivalent to that obtained with titanium dioxide, indicating that the bending moduli of these films are the same.

The addition of zinc oxide to the coating also results in a substantial increase in the extrapolated peel strength value; it is interesting to note that this filler also produces the most rigid film as indicated by the slope of the peel strength versus thickness plot.

A comparison of the slopes in Figure 9 emphasizes the importance of determining peel strength data at a substantial number of thicknesses and extrapolating to zero thickness in order to obtain more meaningful data. If only one thickness had been used for comparisons, such as 8 mils, a misleading indication of the effect of various fillers on adhesion would have resulted.

The comparison of the effect of various fillers on the adhesion of polyurethanes was continued with the study of iron oxide, mica, chromic oxide, and clay (calcined and not calcined). The peel strengths of polyurethane films from P-2010 and PR-960, containing these fillers, were determined from steel panels. The pigment volume concentrations in the glycols were maintained at 18%. The peel strengths have been plotted against film thickness in Figure 10, and it can be seen that the unfilled coating exhibited an extrapolated peel strength of 21 g. for a  $\frac{5}{8}$  in. width. The addition of iron oxide or clay (not calcined) resulted in increased values which are

Fig. 11. Influence of  $\text{Fe}_2\text{O}_3$  content.Fig. 12. Influence of  $\text{Fe}_2\text{O}_3$  content on extrapolated peel strength.

especially noteworthy for the case of iron oxide. Films containing mica are interesting, in that high peel strengths were observed at high film thickness, but a relatively low extrapolated value (10 g.) was obtained. Low values were also obtained for films containing chromic oxide and calcined clay.

It was next of interest to determine the influence of filler concentrations (volume) on peel strength with an investigation of iron oxide-filled polyurethanes resulting from the reaction of P-2010 and PR-960 at an NCO/OH ratio of 1.5. Coatings were prepared with filler concentrations of 5, 15,

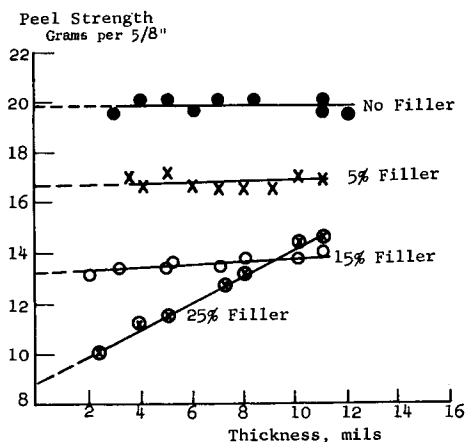


Fig. 13. Effect of hydrated chromic oxide.

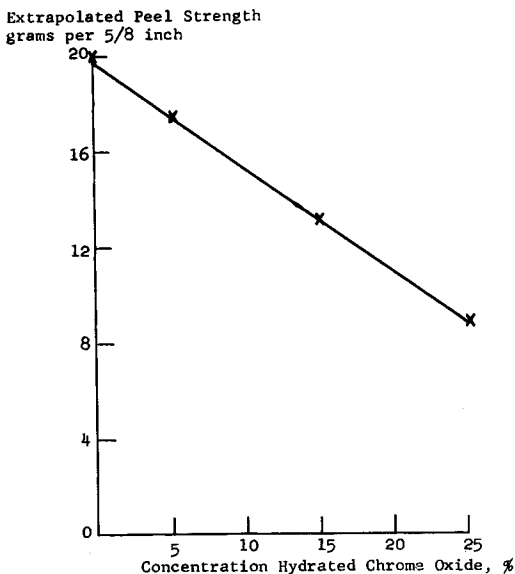


Fig. 14. Effect of hydrated chromic oxide on extrapolated peel strength.

20, and 25%; plots of peel strength versus film thickness are shown in Figure 11. In Figure 12 the values of extrapolated peel strengths have been plotted against iron oxide concentration. It is interesting to note that the latter curve exhibits a maximum value at about 15% iron oxide; at higher volume concentrations there is a sharp drop in adhesion until, at about 25%, it is below the unfilled coating.

These results suggest that fillers cannot be compared at one concentration; it would be expected that the position of maxima might vary from one to another filler.

The effect of addition of hydrated chromic oxide to polyurethanes resulting from the reaction of P-2010 and PR-960 was also evaluated. Coatings were prepared with filler concentrations of 5, 15, and 25%; plots of peel strength versus film thickness are shown in Figure 13. In Figure 14 the

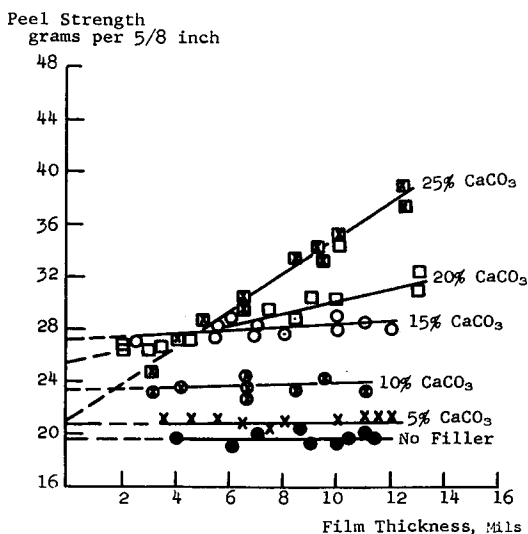


Fig. 15. Effect of CaCO<sub>3</sub>.

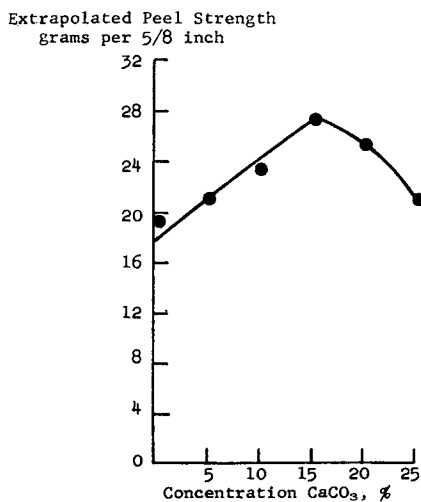


Fig. 16. Effect of CaCO<sub>3</sub> on extrapolated peel strength.

values of extrapolated peel strengths have been plotted against filler concentration. The addition of this form of chrome oxide to polyurethane films results in a decided decrease in peel strength; this behavior is quite different from that exhibited by iron oxide.

The study of the effect of fillers was continued with an examination of the influence of various concentrations of acicular calcium carbonate. Coatings from the reaction of P-2010 and PR-960 were prepared with 0, 5, 10, 15, 20, and 25% filler. Plots of peel strength versus film thickness are shown in Figure 15. The values of the extrapolated peel strengths have been plotted against filler concentration in Figure 16. The latter curve shows that the addition of this form of calcium carbonate to the polyurethane film results in a maximum value at about 15% concentration.

The behavior of calcium carbonate in polyurethane films was similar to that observed with iron oxide, which also gave a maximum in the extrapolated peel strength-concentration curve; it is not similar to the results observed with chromic oxide (hydrous), which does not exhibit a maximum in that plot but shows only a steady decline in adhesion. Attempts have been made to explain these differences in behavior. It has been observed that the particle size of these fillers is approximately the same (5  $\mu$ ) but the particle shapes differ greatly. The chromic oxide is round and smooth, the ferric oxide is irregular and the calcium carbonate is needle-shaped. It is possible that this is a factor in the adhesion of polyurethane-filler systems, with round particles unable to fit into the holes present in most substrates while the more irregular filler particles are able to enter these holes and serve to anchor the films.

Another factor to be considered is the wetting properties of these fillers. Those fillers that improve the ability of the polyurethane compositions to wet the metal substrate would be expected to produce films with higher peel strengths; those fillers that reduce the wettability of the polyurethanes would result in lower peel strengths. It would be of interest to compare the surface tensions and contact angles of polyurethane compositions containing various fillers and correlate these data with peel results.

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### Résumé

On a fait une étude des facteurs qui influencent les propriétés d'adhésion des films de polyuréthane sur l'aluminium. La force d'écaillage (pour des angles de 180° et 90°) a été portée en fonction de l'épaisseur du film (de 1.5 à 20 mils) et extrapolée à épaisseur nulle. On trouve que ces valeurs à l'origine ont une plus grande signification que les forces d'écaillage à épaisseurs finies. On a montré que pour les poly éther-uréthanes préparés au départ de polyoxypropylène glycols et polyols, la force d'écaillage augmente en fonction de la teneur en uréthane et en urée. On a aussi montré que la force d'écaillage diminue pour une augmentation de la rigidité du film lorsque la rigidité est causée par une augmentation de la densité de pontage ou du rapport isocyanate/hydroxyle. Les charges jouent un rôle important dans la force d'écaillage;

pour des concentrations supérieures à 15% en glycol, l'adhésion des polyuréthanes augmente lorsqu'on ajoute de l'oxyde de fer et du carbonate de calcium. L'utilisation d'oxyde chromique provoque uniquement une diminution de la force d'écaillage.

### Zusammenfassung

Eine Untersuchung einiger Faktoren, die die Adhäsionseigenschaften von Polyurethanüberzügen an Aluminium beeinflussen, wurde angestellt. Die Abreissfestigkeit (bei Winkeln von 180 und 90 Grad) wurde gegen die Filmdicke (von 1,5 bis 20 mils) aufgetragen, und auf Dicke Null extrapoliert; diese Ordinatenabschnitte haben eine grössere Bedeutung als die Abreissfestigkeit bei endlicher Dicke. Es wurde gefunden, dass die Abreissfestigkeit für aus Polyoxypropylenglycol und -polyol hergestelltes Polyätherurethan mit zunehmendem Urethan- und Harnstoffgehalt ansteigt. Ausserdem wurde gefunden, dass die Abreissfestigkeit mit zunehmender Filmsteifigkeit abnimmt, wobei die Steifigkeit durch Zunahme der Vernetzungsdichte oder des Isocyanat-Hydroxylverhältnisses bedingt ist. Füllstoffe spielen bei der Abreissfestigkeit eine wichtige Rolle, bei Konzentrationen bis zu 15% der Glycolkomponente nimmt die Adhäsion des Polyurethans bei Zufügen von Eisenoxyd und Calciumcarbonat zu. Die Verwendung von Chromoxyd verursacht nur eine Abnahme der Abreissfestigkeit.

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