CROSS-LINKING WITH POLYURETHANES

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Introduction

Blocked isocyanate cross-linking agents are used in coatings where, a one package system is required, heat cure is possible and the performance of a polyurethane coating is called-for. Blocked isocyanates are thermally labile and undergo a deblocking reaction to the isocyanate before reaction with a nucleophile. Recent studies indicate that an elimination and addition reaction is the major pathway for both caprolactam and ketoxime blocked isocyanates (1). As an alternate mechanism the nucleophilic substitution of the blocking group has to be considered.

We were interested in the use of alcohol blocked thermally stable polyurethanes as cross-linker for hydroxyl functional polymers and the pathway for reaction of these materials.

Experimental

As model compounds for the polyurethane cross-linker difunctional materials were prepared by reacting of 1 mol of a diisocyanate with 2 mol of the alcohol. As blocking groups one diol and two alcohols, 1,2-propanediol (PG), 2-methoxypropoxypropanol (DPM) and 2-ethylhexanol (2EH), materials with similar boiling point, 187°C, 188°C and 185°C respectively were selected. For comparison purposes a ε-caprolactam blocked 1,6-diisocyanatohexane was used.

Commercial materials without any further purification were employed. The preparation of the model compounds was carried out uncatalyzed at 50-70°C under anhydrous conditions. The progress of the reaction was followed by FT-IR. After 80 % completion the reaction temperature was raised to 120°C to bring the reaction to completion. The 1,2-propanediol blocked compound was prepared by a non isocyanate route. (2)

The above cross-linker were tested in clear coating formulations with a commercially available high solids hydroxyl functional acrylic resin (3). (Solids, % 79.0; OH Equivalent Weight 590; Viscosity, 25°C, mPas 9000). The formulations were tested uncatalyzed and catalyzed with dibutyltin diacetate (DBTDA), (0.34 % of Sn on polymer) and zinc octoate (ZnOCT), (0.18 % of Zn on polymer) and a proprietary metal catalyst XP-348, (0.24 % Me on polymer). A ratio of hydroxyl groups to blocked isocyanate groups of 1/1 was used.

Films of a dry film thickness of 20 μ were cast on iron phosphate pretreated steel and cured for 20 minutes in a forced air oven.

The clear films were tested for Tukon hardness, Gardner front and reverse impact, MEK double rubs, and for solvent swelling in methylene chloride.

Swelling experiments were carried out on free films under the microscope. Film fragments of a size of about 1 mm square were covered on a microscope slide with a cover glass and a drop of methylene chloride was wicked between the slide and cover glass.

Results

FT-IR analysis of the synthesized compounds confirmed the urethane structure and verified the absence of any residual isocyanate groups.

GPC analysis shows the urethane compounds with the exception of the 2-ethylhexanol addition product to be >93 % monomeric with only minor levels of higher molecular weight oligomers. The 2-ethylhexanol reaction product contained 8.6 % of a higher MW oligomer (Table 1). The unreacted impurities are basically less than 2 %.

Table 1
GPC Analysis

	Blocking Agent	Solids	Retention time(min)	Area %
PGHDI	1,2-Propane diol (PG)	96.5	9.57	94.8
DPMHDI	Methoxypropoxypropanol (DPM)	97.9	9.37	93.1
			8.96	2.0
			8.79	2.0
2EHHDI	2-Ethylhexanol (2EH)	96.2	9.45	88.2
			9.02	8.6
CAPHDI	ε-Caprolactam(CAP)	96.4	10.46	96.1
			9.73	1.3

The characteristics of the polyurethane cross-linker and the blocked isocyanate is displayed in Table 2.

Table 2
Characteristics of Blocked Isocyanate Cross-Linker

	Solids, %	Viscosity mPas, 20°C	Equivalent Weight, solids
PGHDI	96.5	150000	160
DPMHDI	97.9	730 *	232
2EHHDI	96.2	989 *	214
CAPHDI	96.4	**	197

* Under cooled liquid, crystallizes after 1-3 days at room temperature.
** Melting Point 90°C

Hardness and MEK solvent resistance (Figure 1 and 2) of uncatalyzed coatings cured for 20 minutes at 165 to 215°C in 10°C increments, show hardness development for CAPHDI at 175°C. PGHDI, DPMHDI and 2EHHDI develop hardness only at 205°C. There is evidence for film degradation for all coatings at the 215°C cure. Only CAPHDI cross-linked coatings develop any MEK resistance.

The use of a tin catalyst has a significant effect on the reactivity of the polyurethane cross-linker. DBTDA gives at the cure temperature of 175°C equal hardness and MEK resistance for all systems (Figure 3 and 4). At the lower cure temperature of 155°C only the PGHDI system exhibits adequate cure. At 165°C CAPHDI shows the least cure response. Impact resistance for these coatings is given in Figure 5. Flexibility of the coating is improved with increased cross-linking.

The effect of Zinc octoate on Knoop hardness and MEK resistance is shown in Figure 6 and 7. PGHDI and CAPHDI show evidence of cure at 155 and 165°C. DPMHDI starts to cure at 165°C. 2EHHDI does not cure even at the 175°C cure temperature.

A proprietary catalyst XP-348 (4) results in cure for PGHDI at 155 and 165°C, as manifested in Knoop hardness and MEK resistance (Figure 8 and 9). Both DPMHDI and CAPHDI begin to cure at 165°C. 2EHHDI does not cure to any extend at 165°C but indicates some response at 175°C.

Linear swelling experiments on free films cure at 175°C for 20 minutes are illustrated in Figure 10. Although there is a considerable scatter in results, PGHDI cross-linked films show the lowest degree of swelling, CAPHDI with the exception of ZnOCT catalysis is more prone to swell, indicating lower cross-linking density.

Discussion

The traditional view of "blocked isocyanate" cross-linker as isocyanate precursor which under the application of heat dissociate to the isocyanate and the blocking group has already been challenged by the work of Wicks (5,6,7), he showed that malonate and acetoacetate blocked isocyanates do not deblock to the isocyanate but rather in the presence of suitable catalysts undergo a nucleophilic substitution reaction of the malonate or acetoacetate ester groups.

Our work indicates that "stable polyurethanes" can be catalyzed with suitable metal catalysts to perform as "blocked isocyanates".

An addition /elimination mechanism is presumably the prime reaction passway.

The similar boiling points for the two leaving alcohols and the diol dispel any notion that the substantially different reaction rates are a result of a varied residence time of the alcohol in the film and as a result of a reversal of the cross-linking reaction.

$$RNHCOOR' + R''OH \longleftrightarrow RNHCOOR'' + R'OH$$

Further evidence against such a hypothesis is found in the PGHDI cross-linker. PGHDI a diol should be effectively compete with the functional groups of the resin and therefor lead to lower cross-linking rates and lower cross-linking density. Surprisingly PGHDI is the presence of a catalyst a superior cross-linker, with high reaction rates at lower temperature.

In a previous study of PGHDI (8) the authors claim lower thermal stability of ß-hydroxyalkycarbamates compared to other urethane groups.

Our work does not confirm this. In the uncatalyzed form PGHDI, DPMHDI and 2EHHDI have approximately the same stability and show reaction only above 205°C. Only in the presence of suitable catalysts does the PGHDI show superior reactivity.

Although the MEK resistance obtained with all the cross-linker is not outstanding the swelling experiments showed acceptable cross-link density. The failure mode in the MEK test for the coatings systems tested is not attack by the solvent but rather loss of adhesion to the substrate.

Conclusions

We have demonstrated that thermally stable polyurethanes can be catalyzed to be used as cross-linker for hydroxyl functional resins.

Surprising is the rate enhancement in presence of catalyst of the polyurethane cross-linker compared to the caprolactam blocked isocyanate. Is likely that the polyurethane cross-linker respond predominately to a substitution mechanism. The catalysts used are all known to be excellent transesterification catalysts.

The role of the leaving group on reaction rate and its interaction with the catalyst requires further studies.

Acknowledgment

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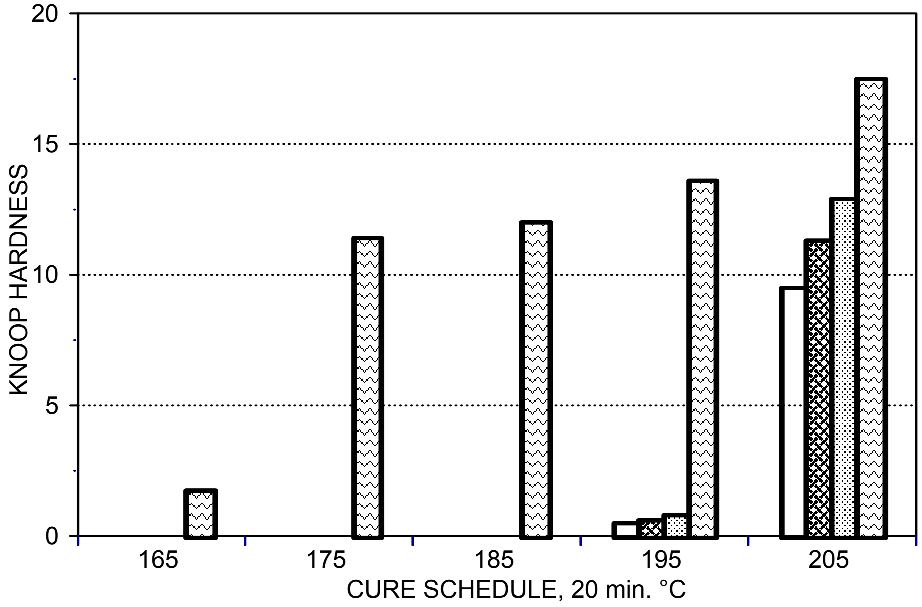

Figure 1. Acrylic/Blocked Isocyanate 1/1; Uncatalyzed

BLOCKING AGENT ☐ PG ▩ DPM ▒ 2EH ▨ CAP

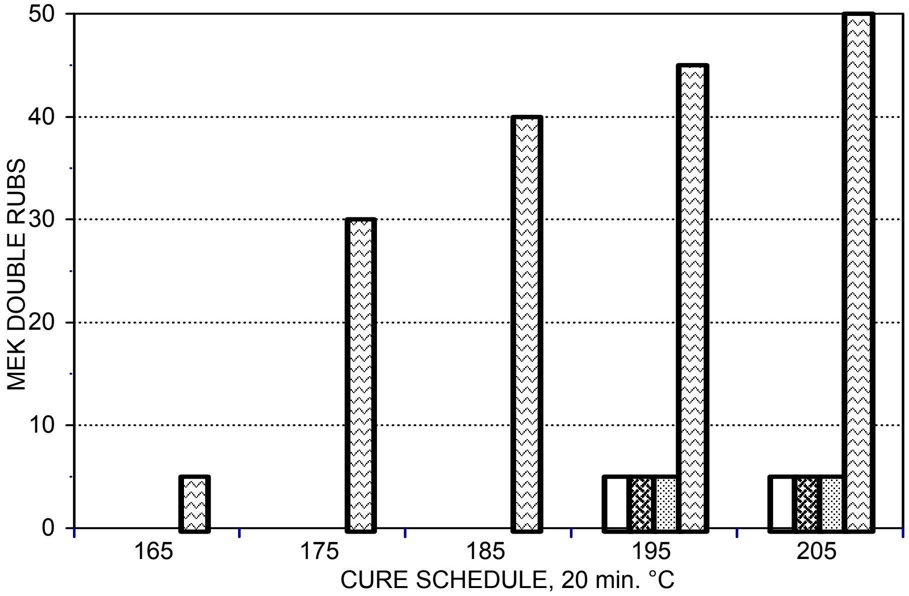

Figure 2 Acrylic/Blocked Isocyanate 1/1;Uncatalyzed

BLOCKING AGENT ☐ PG ▩ DPM ▒ 2EH ▨ CAP

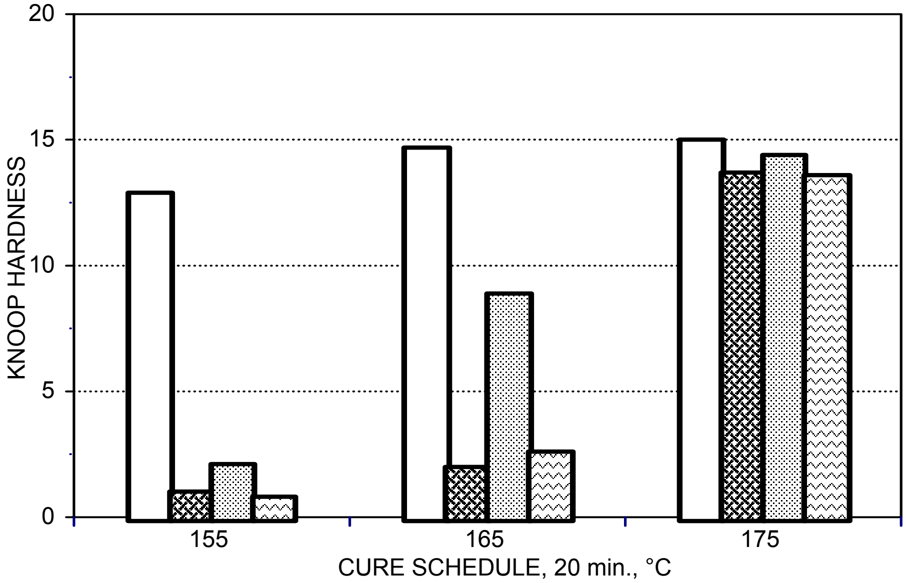

Figure 3 Acrylic/Blocked Isocyanate 1/1; DBTDA, Sn 0.34 %

Blocking Agent ☐ PG ▩ DPM ▨ 2EH ▤ CAP

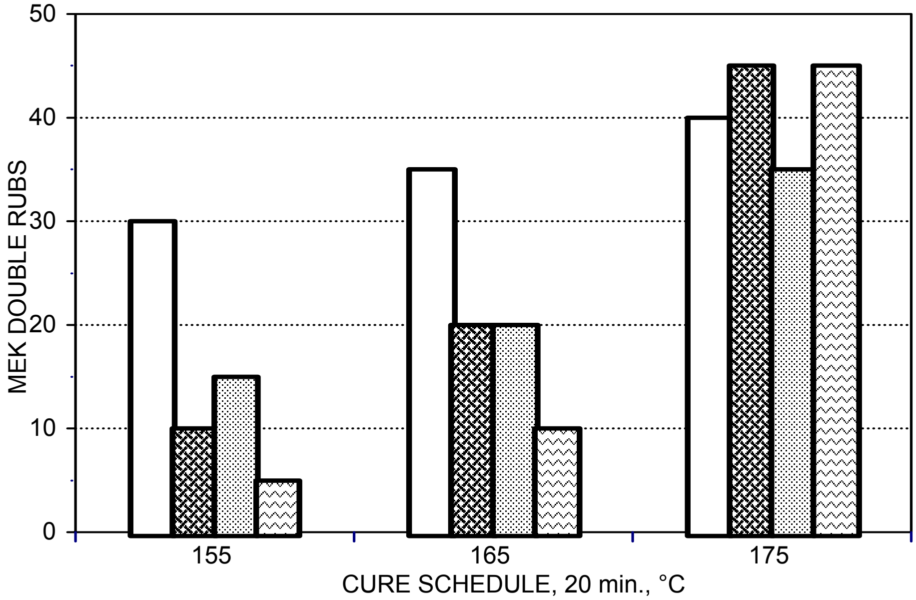

Figure 4. Acrylic/Blocked Isocyanate 1/:1 DBTDA, Sn 0.34 %

BLOCKING AGENT ☐ PG ▩ DPM ▨ 2EH ▤ CAP

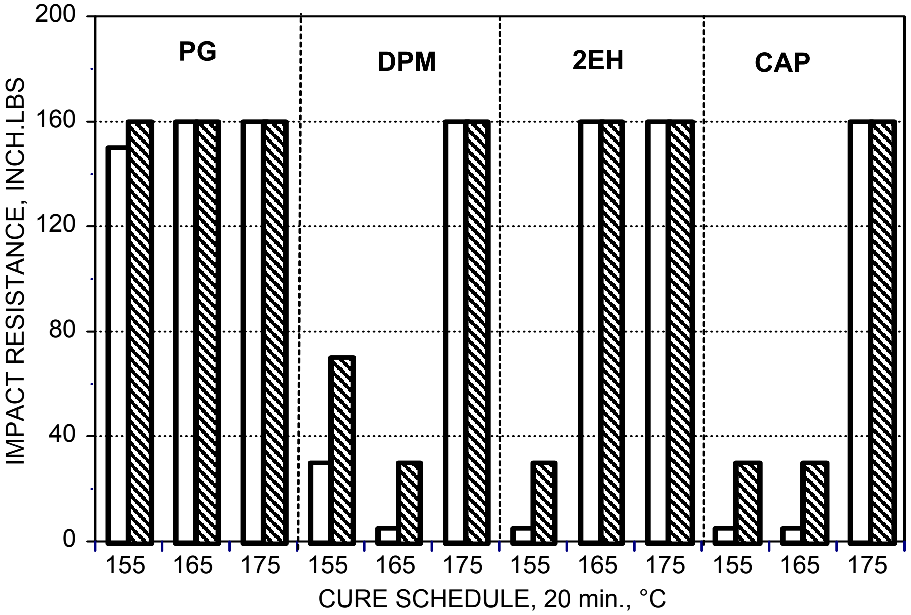

Figure 5 Acrylic/Blocked Isocyanate 1/1;Uncatalyzed

Impact Resistance ☐ REVERSE ▧ FRONT

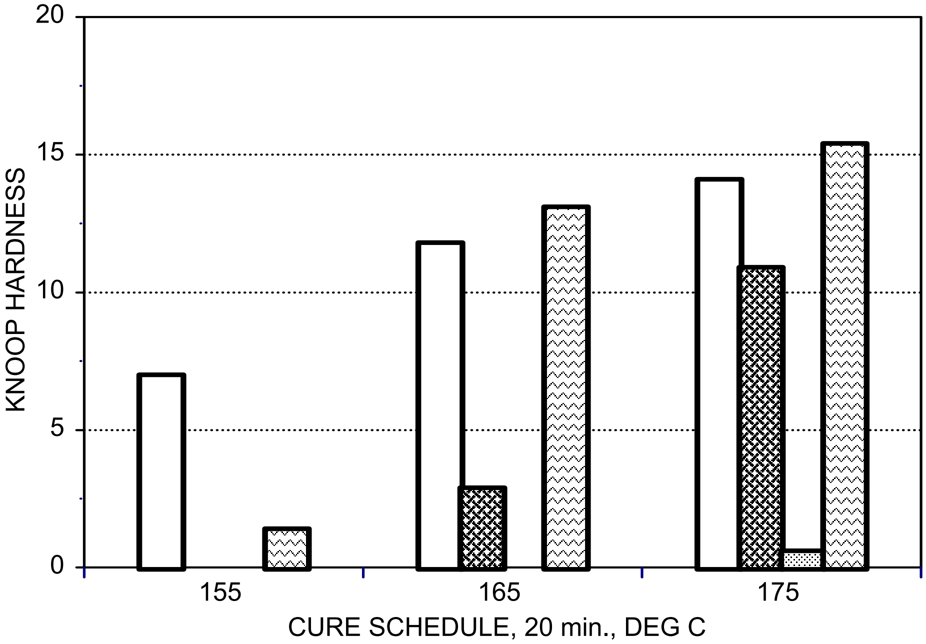

Figure 6. Acrylic/Blocked Isocyanate 1/1; ZnOct. Zn 0.18 %

BLOCKING AGENT ☐ PG ▩ DPM ░ 2EH ▧ CAP

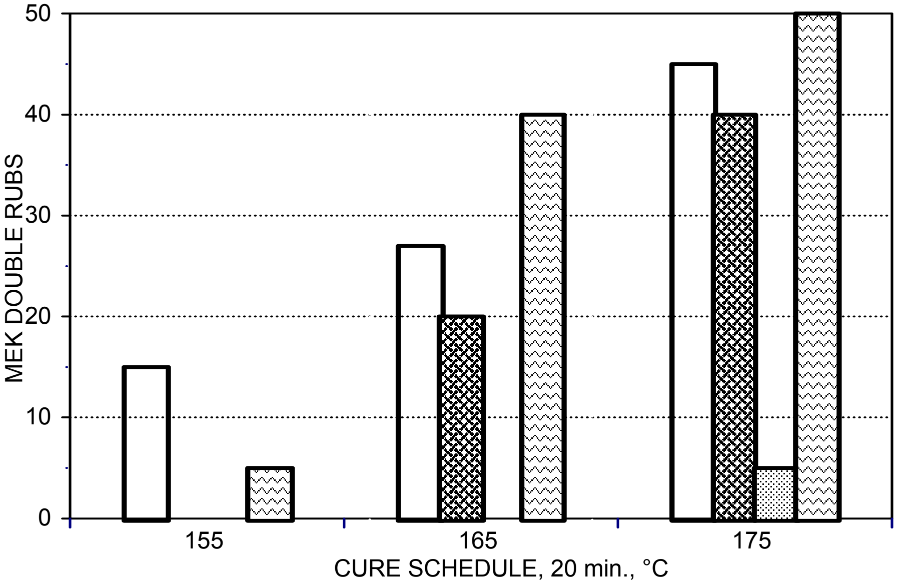

Figure 7. Acrylic/Blocked Isocyanate 1/1; ZnOct. Zn 0.18 %

BLOCKING AGENT ☐ PG ▩ DPM ▒ 2EH ▨ CAP

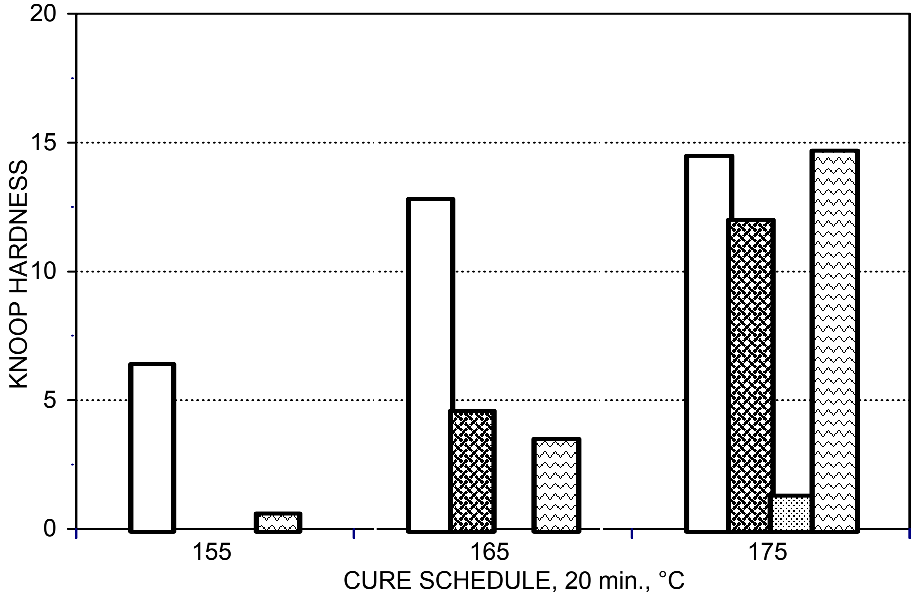

Figure 8. Acrylic/Blocked Isocyanate 1/1; K-348, Bi 0.24 %

BLOCKING AGENT ☐ PG ▩ DPM ▒ 2EH ▨ CAP

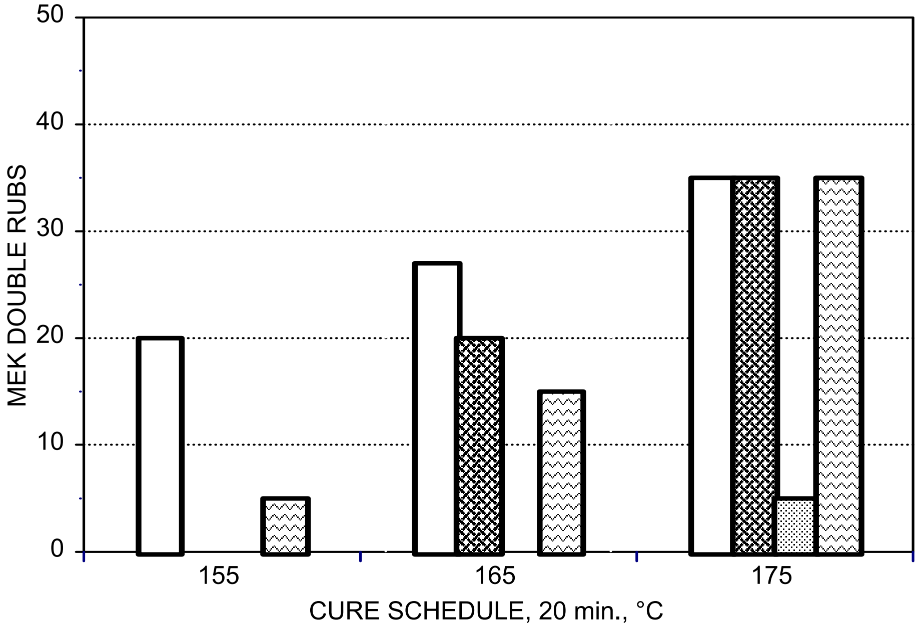

Figure 9.   Acrylic/Blocked Isocyanate 1/1; K-348, Bi 0.24 %

BLOCKING AGENT ☐ PG ▩ DPM ▨ 2EH ▧ CAP

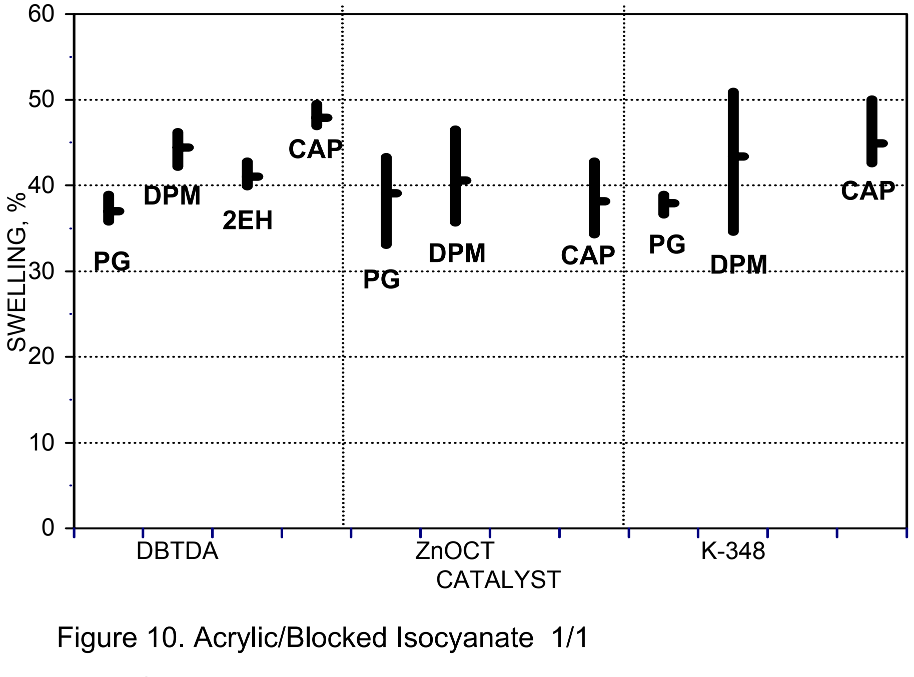

Figure 10. Acrylic/Blocked Isocyanate 1/1

Linear Swelling with Dichloromethane