

New Polyisocyanurate Catalysts for Rigid Polyurethane Foams

SPI Conference 1994

by
Susan M. Clift
Jobst Grimminger
Kruno Muha

© Air Products and Chemicals, Inc., 1994
Abstract Number: 112 Session: N



ABSTRACT

Rigid polyurethane (PUR) and polyisocyanurate (PIR) foams are among the most widely used and versatile insulating materials currently available. These foams have traditionally been expanded with chlorofluorocarbons (CFC's). CFC's combined good blow efficiency with excellent insulation properties and good processing performance. In response to global scale legislative pressure to reduce and eventually eliminate the production of CFCs, the rigid polyurethane industry has been forced to develop alternative blowing technologies. These alternative blowing or cblowing agents include carbon dioxide from the water-isocyanate reaction, hydrofluorocarbons like HCFC-22 and HCFC-141b, hydrofluoroalkanes, pentane and cyclopentane. Changes in blowing agent technology have also required other formulation modifications to maintain foam performance and processability.

HCFC-141b, n-pentane and cyclopentane have emerged as the leading alternatives to CFC-11 in applications such as appliances or laminate boardstock where insulation value is critical. Water blowing or cblowing has also become increasingly prevalent. Each of these alternatives provides its own challenges to the formulator. The use of water results in higher resin premix viscosities and often requires substitution of lower functionality polyols to maintain a workable viscosity. Decreasing polyol functionality will have negative effects on foam dimensional stability and flame resistance. Rapid migration of carbon dioxide from water blown or cblown foams also leads to dimensional stability problems. In pentane blown formulations, higher concentrations of flame retardants may be required to meet flammability standards, resulting in plastisized foams with poorer physical properties. The increased solvent effect of HCFC-141b leads to foams with poorer dimensional stability, strength and demold characteristics.

An effective way to compensate for many of these deficiencies is by increasing the stoichiometric excess of isocyanate used during foam formation. This provides additional three dimensional crosslinking due to allophanate, biuret and isocyanurate formation. Additional crosslinking compensates for lower polyol functionality and improves flame retardancy, as well as other physical properties such as compression strength and dimensional stability. Key to the success of this approach is an understanding of the role of catalysis in controlling relative reaction rates and foam morphology. Trimerization or isocyanurate catalysts have become increasingly important. Their use has extended beyond traditional high index (150+) PIR applications into more typical PUR applications, where intermediate indices (110-150) are being used successfully to overcome demoldability and dimensional stability issues.

In this paper, we present the results of a study investigating both performance and reactivity for a series of trimerization catalysts. Isocyanurate yields, rise profiles and foam performance were evaluated for each catalyst. The effect of foam index and water level on catalyst activity were also investigated. Isocyanurate yields were determined using FTIR and NMR techniques and results correlated to selected physical properties. Catalysts included in this study are traditional trimer catalysts such as potassium acetate and potassium octoate, several quaternary ammonium salts from the Air Products' DABCO® TMR catalysts series, and two new generation trimerization catalysts that offer further processing advantages.

INTRODUCTION

Rigid polyurethane foams are unique products with regard to insulation performance, mechanical properties and processing advantages. They are used in applications such as:

- * rigid bunstock or block production for construction and insulation
- * continuous lamination of insulation panels with rigid and/or flexible surfaces
- ‡ spray foam insulation of buildings and tankers
- * insulation of appliances such as coolers and freezers
- * pour in place door panels
- * high density structural rigid foams for housings, wood imitation and other applications
- * packaging foams for high valued goods such as VCR's, computers etc.



These foams have traditionally been expanded with chlorofluorocarbons (CFC's). Global legislative pressure to reduce and eventually eliminate the production of CFC's has forced the rigid polyurethane industry to develop alternative blowing technologies. These changes have also required other formulation modifications to maintain foam performance and processability which include:

- * increased use of water as a coblowing agent
- * reduced polyol functionality to maintain workable viscosities
- * increased use of unreactive flame retardants to meet flammability standards

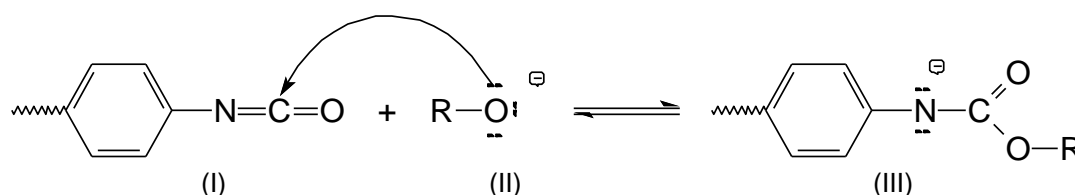
All of these modifications impact final foam performance, particularly dimensional stability and demoldability. An effective way to compensate for many of these deficiencies is through the use of excess isocyanate in the presence of trimerization catalysts to provide additional three dimensional crosslinking due to allophanate, biuret and isocyanurate formation. Additional crosslink density improves mechanical properties such as compression strength and dimensional stability, and increased isocyanurate content generally results in better fire retardancy [1]. Key to the success of this approach, however, is an understanding of the role of catalysis in controlling relative reaction rates and foam morphology.

This paper presents the results of a study investigating both the performance and reactivity of a series of seven trimerization catalysts. Isocyanurate yields, rise profiles and key performance properties were evaluated for each catalyst. The effect of foam index and water level on catalyst activity were also examined. Catalysts included in the study were traditional isocyanurate catalysts such as potassium acetate and potassium octoate, several quaternary ammonium salts from the Dabco® TMR series, and two new generation catalysts that offer further processing advantages.

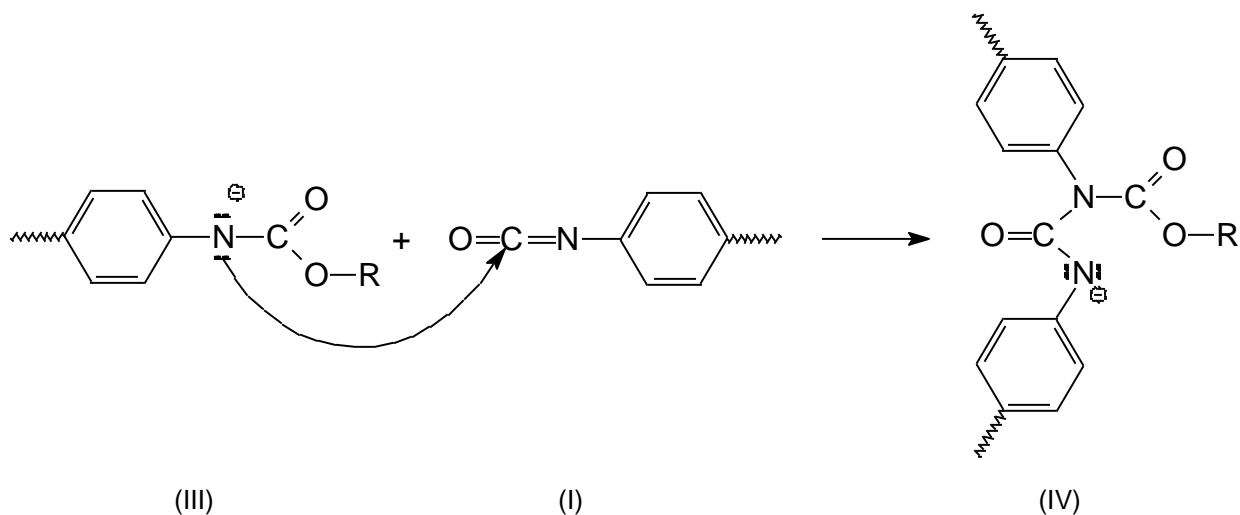
THEORETICAL BACKGROUND

Isocyanurate Formation

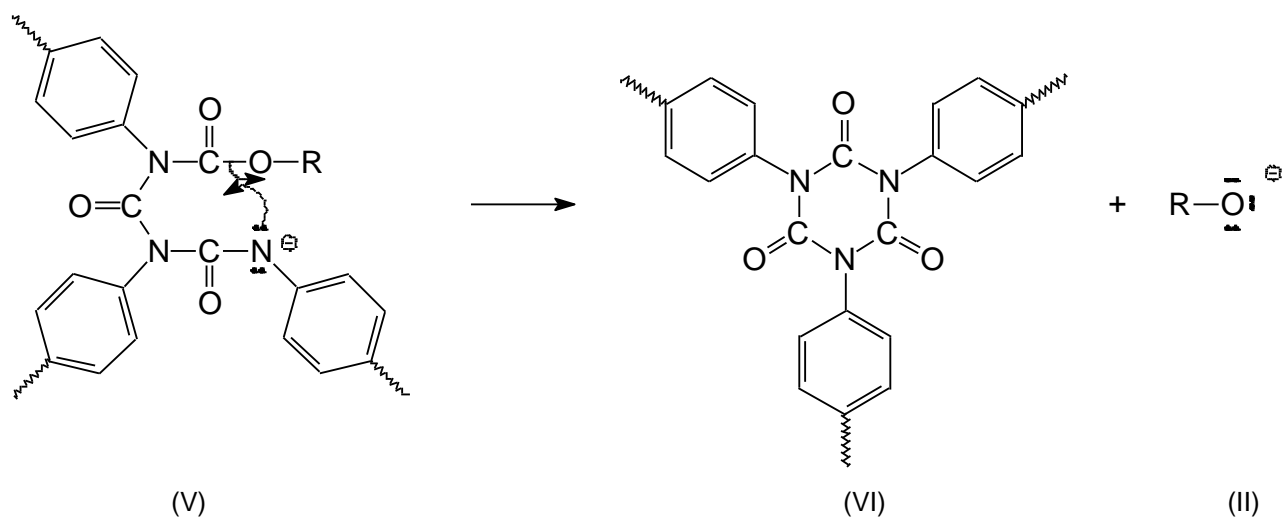
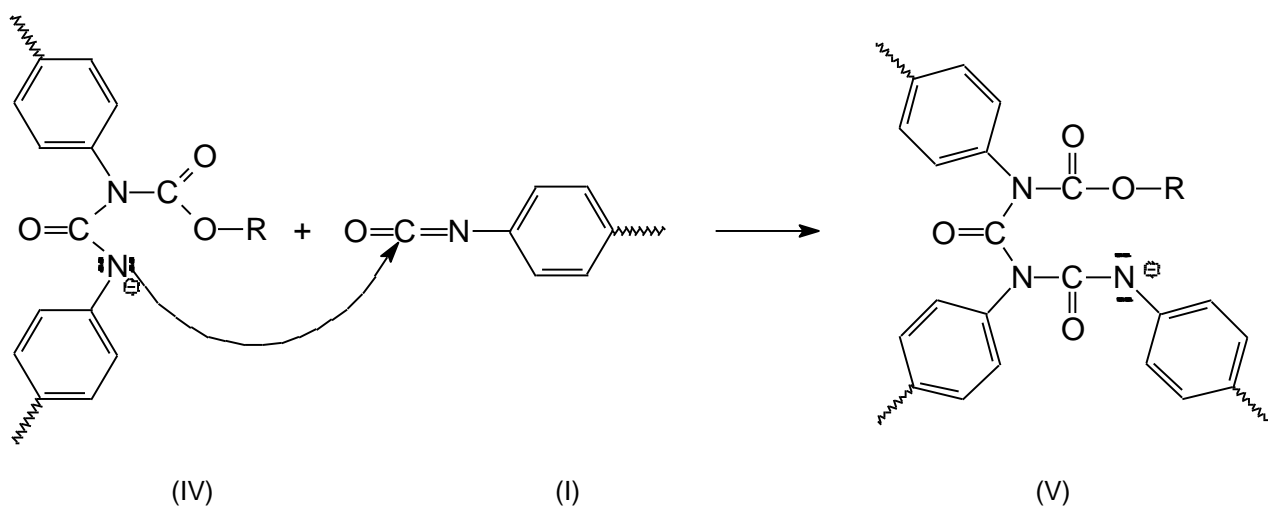
The mechanisms of the isocyanurate formation are not completely understood. However the general mechanism for base catalyzed isocyanate trimerization is shown in the following scheme.



The catalyst (II) adds across the isocyanate (I) carbon nitrogen double bond to form an active complex (III). This complex (III) has a nucleophilic center at the nitrogen atom which attacks the carbonyl carbon of a second isocyanate to form adduct (IV).



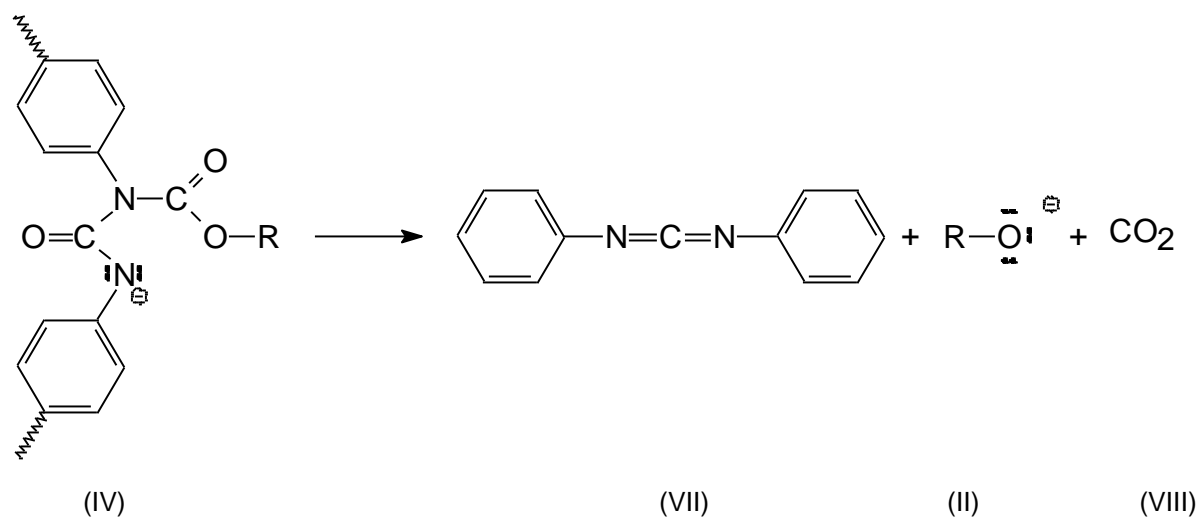
Adduct (IV) has a similar nucleophilic center at one of its nitrogen atoms which attacks a third isocyanate forming adduct (V). Adduct (V) subsequently collapses into the stable isocyanurate (VI) and regenerates catalyst (II). In the presence of alcohol, an alternative route to trimer may be via the allophanate (VII) which results from interception of complex (III) by alcohol, followed by sequential isocyanate addition [2].





Byproduct Formation

Under certain reaction conditions carbodiimide formation competes with the cyclotrimerization of isocyanate. At high temperatures or with sterically hindered catalysts and/or isocyanates [2], complex (IV) may decompose to carbon dioxide and carbodiimide (VII).



TRIMERIZATION CATALYSTS

While a variety of acids, bases, and organometallic compounds can catalyze isocyanate trimerization, only three types have shown practical importance to date [2]: (1) alkali metal carboxylates like potassium acetate or 2-ethylhexanoate, (2) N-hydroxyalkyl quaternary ammonium carboxylates and (3) selected amines containing at least three tertiary amine sites, or two amine sites plus one or more hydroxyl groups.

The catalysts included in this study are listed in Table 1. They include the potassium salts, Polycat 46 and Dabco K-15, quaternary ammonium salts Dabco TMR, Dabco TMR 2 and Dabco TMR 5 and two experimental products, XF I10 85 and XF J10 04. Dabco TMR 5, a relatively new trimerization catalyst developed by Air Products, is based on a nonfugitive amine, providing reduced odor versus standard quaternary ammonium salt catalysts. XF I10 85 and XF J10 04 offer further reductions in odor, while still maintaining good isocyanurate conversions and other performance benefits.

Table 1: Trimerization Catalysts

Product	Composition	Type	Remarks
Polycat® 46	KAc in MEG	Salt	15% Potassium
Dabco® K15	KOc in DEG	Salt	15% Potassium
Dabco TMR®	proprietary	Quaternary Ammonium Salt	
Dabco TMR 2	proprietary	Quaternary Ammonium Salt	delayed action
Dabco TMR 5	proprietary	Quaternary Ammonium Salt	low odor
XF I10 85	proprietary	Experimental	low odor
XF J10 04	proprietary	Experimental	low odor



FORMULATIONS

Two polyether polyol and two polyester polyol based formulations were employed in this study (Tables 2-5). The polyether polyol systems are more typical of European formulations, while the polyester polyol systems were based on North American lamination formulations. Table 2 shows the full HCFC-141b blown polyether system at three indices. It uses a low reactivity polyol, Arcol® 3544, to minimize the influence of polyol on system reactivity. The water content of this full HCFC blown formulation results from the water content of the polyol. Polycat 8 is used as a cocatalyst and was kept constant relative to the polyol and water concentrations for each index. Dabco DC5454 is a medium polarity silicone surfactant designed to stabilize HCFC-141b blown and water coblown systems. Silicone surfactant use levels were kept constant relative to the entire formulation, including isocyanate. HCFC-141b levels were adjusted to maintain a free rise density of 33 +/- 1Kg/m³ in conjunction with Polycat 46 as trimerization catalyst. Polycat 46 is a standard catalyst in polyether PIR formulations.

Table 3 represents the 50% water coblown version of the polyether formulation. HCFC-141b levels were once again adjusted to achieve a free rise density of 33 +/- 1Kg/m³. Polycat 8 levels were reduced relative to the no water formulation. Trimerization catalyst levels for all polyether formulations were adjusted to produce a 30 second cream time, since cream time is a limiting factor in the production of double band lamination and rigid bunstock.

Table 2: Polyether Polyol Based Formulations (HCFC-141b blown)

	OH Number	Index	Index	Index
	[mgKOH/g]	100	150	300
ARCOL® 3544	500	100.00	100.00	100.00
Dabco DC 5454	81	1.50	1.89	3.10
Water	6232	0.07	0.07	0.07
Polycat 8	-	3.00	3.00	3.00
HCFC-141b	-	39.00	48.00	80.00
Trimerization Catalyst		varied	varied	varied
Polymeric MDI	%NCO 32	118	178	356

ARCOL® 3544 : Polyether polyol supplied by Arco Chemical (Deutschland) GmbH

Table 3: Polyether Polyol Based Formulations (HCFC-141b/water coblown)

	OH Number	Index	Index	Index
	[mgKOH/g]	100	150	300
ARCOL® 3544	500	100.00	100.00	100.00
Dabco DC 5454	81	1.50	1.93	3.40
Water	6232	2.00	2.00	2.00
Polycat 8	-	0.70	0.70	0.70
HCFC-141b	-	15.00	18.00	56.00
Trimerization Catalyst		varied	varied	varied
Polymeric MDI	%NCO 32	146	220	440

The polyester formulations presented in Tables 4-5 are HCFC-141b coblown with low and high water levels. They use an aromatic polyester polyol. Polycat 5 was used as a cocatalyst; it strongly catalyzes the reaction of water with isocyanate to improve blowing efficiency. HCFC-141b levels were adjusted to maintain a free rise



density of 30 +/- 1Kg/m³ in conjunction with Dabco K-15 as trimerization catalyst, a standard catalyst used in North American high index PIR formulations. HCFC-141b and isocyanate compatible Dabco DC5098 silicone surfactant were partitioned between the polyol and isocyanate to improve mixing. Trimerization catalyst levels were adjusted to a standard 33 +/- 1 second string gel time.

Table 4 : Polyester Polyol Based Formulations (HCFC-141b/low water coblown)

	OH Number [mgKOH/g]	Index 280
Terate® 2541	240	100.00
Water	6232	0.50
Dabco DC5098	10	2.00
Polycat 5	-	0.20
HCFC-141b	-	41.00
Trimerization Catalyst		varied
Polymeric MDI	31.6 % NCO	191.05

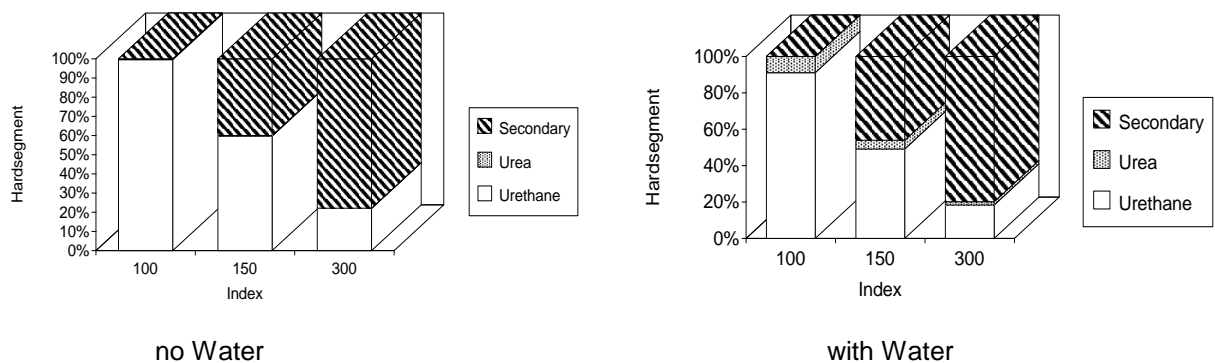
Terate® 2541 is an aromatic polyester polyol supplied by Cape Industries

Table 5 : Polyester Polyol Based Formulations (HCFC-141b/high water coblown)

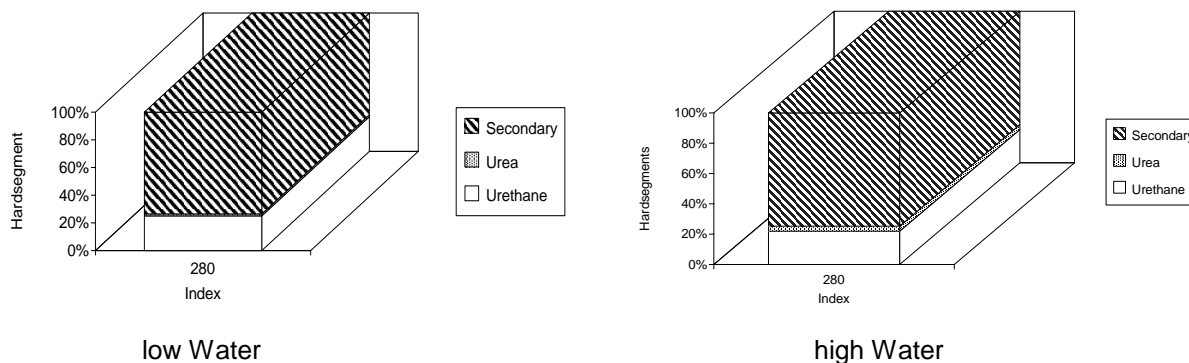
	OH Number [mgKOH/g]	Index 280
Terate 2541	240	100.00
Water	6232	1.72
Dabco DC5098	10	2.00
Polycat 5	-	0.20
HCFC 141b	-	33.00
Trimerization Catalyst		varied
Polymeric MDI	31.6 % NCO	232

THEORETICAL HARD SEGMENT DISTRIBUTION

The theoretical hard segment distribution for each formulation is shown in Figures 1 and 2. Distributions were calculated assuming that all hydroxyl groups produce urethane, all water results in urea and excess isocyanate is converted into secondary products, such as isocyanurates, biurets, allophanates etc..



Figures 1a and 1b: Calculated hardsegment distribution polyether polyol based formulations



Figures 2a and 2b: Calculated hardsegment distribution polyester polyol based formulations

EXPERIMENTAL PROCEDURES

Foam Preparation

All foams prepared during the course of this study were produced using standard handmix techniques. Following is a typical procedure.

A sufficient quantity of polyol preblend to produce 200 g of foam was preweighed into a 1 l plastic cup. The preblend consisted of polyol, HCFC-141b, water, catalyst and silicone surfactant. The corresponding amount of isocyanate was added to the polyol preblend and mixed for 6-10 s at 5000 rpm using a 4 cm, mixing blade. The reaction mixture was then poured into a 2.9 l paper bucket and allowed to rise freely under an ultrasonic height detector. The cream time is defined as the time when the foam reached 2% of its final rise height. Rise time is defined as the time at which the foam reaches 98% of its final height.

Rate of Rise Equipment

Height and temperature data were recorded using both Weidmüller (for polyether polyol formulations) and Time Tech DAPS QA Model 2500 (for polyester polyol formulations) rate of rise systems. These systems use ultrasonic sound waves to measure the height of a rising urethane foam. Foam temperatures were recorded using conventional thin wire type J thermocouples. In the polyether formulations, temperatures were measured 2 cm from the bottom of the cup at both the center and the edge of foam. For polyester formulations, temperature was measured 5 cm from the bottom in the center. A representative schematic is shown in Figure 3. The parameters used to describe the kinetic performance of each catalyst are defined in Table 6.

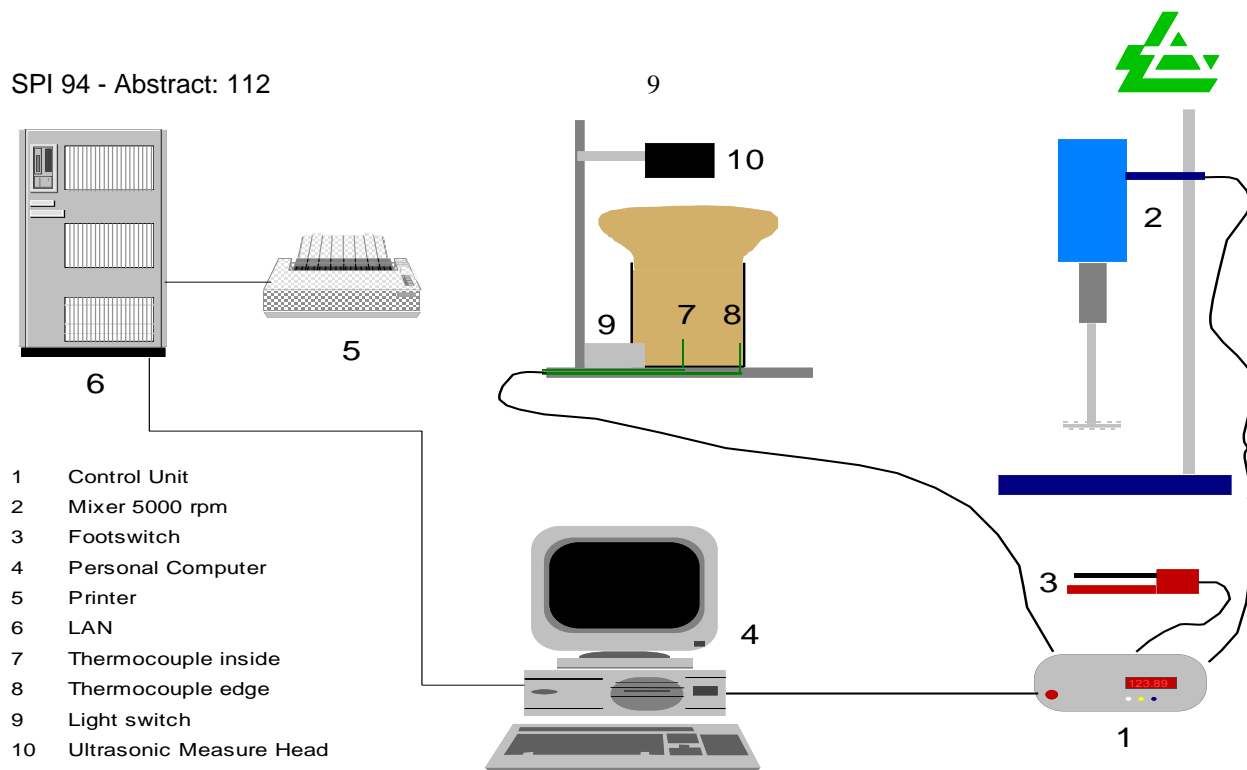


Figure 3: Rate of rise equipment to determine rise and temperature profiles

Table 6: Rate of Rise Parameter Definitions

Performance	Dimension	Description
level	[pph]	level of catalyst to achieve 30 +/-1 s cream time in polyether foam or 33 +/- string gel in polyester systems
cream time	[s]	time at which foam reaches 2% of its final rise height
rise time	[s]	time at which foam reaches 98% of its final rise height
max. rate of rise	[mm/s]	maximum rate of rise
max. rate of rise time	[s]	time at maximum rate of rise
inside max. temperature	[°C]	maximum temperature in the bulk of the rising foam
inside max. temperature time	[s]	time at maximum temperature
inside temperature at max. temperature rate	[°C]	temperature at maximum temperature rate
outside max. temperature	[°C]	maximum temperature at the edge of the rising foam

FT-IR Spectroscopy

FT-IR spectroscopy was used to determine the relative functional group concentrations within the PUR/PIR rigid foams. Because it is difficult to measure the IR absorption spectra of polyurethane foams due to their thickness and opacity, special techniques were required [1]. Polyether polyol based foams were analyzed using a Perkin Elmer 1605 FTIR spectrometer and the microfocus unit shown in Figure 4. Polyester polyol based foams were analyzed with an attenuated total reflectance (ATR) attachment also shown in Figure 4.

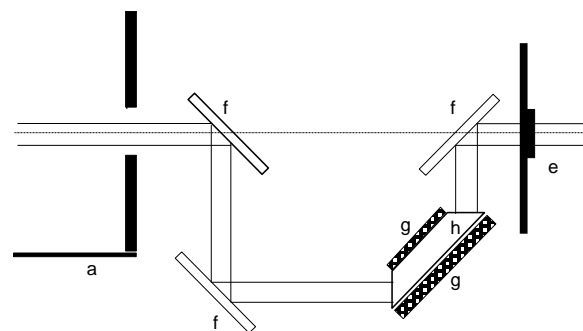
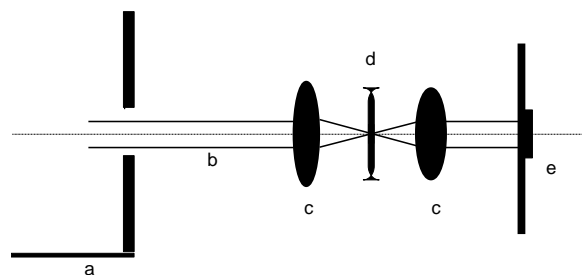


Figure 4: Microfocus unit and ATR attachment

a: Attachment holder
 b: Infrared beam
 c: Lenses
 d: Micro disc holder with foam sample

e: Detector
 f: Mirror
 g: Foam sample
 h: ATR crystal

1. The Microfocus Technique

The microfocus unit consists of two lenses and a micro disc holder. Sample preparation includes the densification of a small piece of foam using two polished anvils and a 10 ton press. A small fiber of this pressed foam is placed in the 50 μm split of the micro disc holder which is then placed in between the lenses. The infrared spectrum was obtained from 64 scans (4000 cm^{-1} -700 cm^{-1} ; resolution 4 cm^{-1}). Transmission data were converted into absorbance, which is directly related to the concentration of the functional group by Beer's law. A baseline correction was made using the absorbance at 1950 cm^{-1} , due to constant absorption in all spectra, and data normalized using the aromatic ring deformation absorbance at 1595 cm^{-1} . A typical FTIR spectrum is presented in Figure 5.

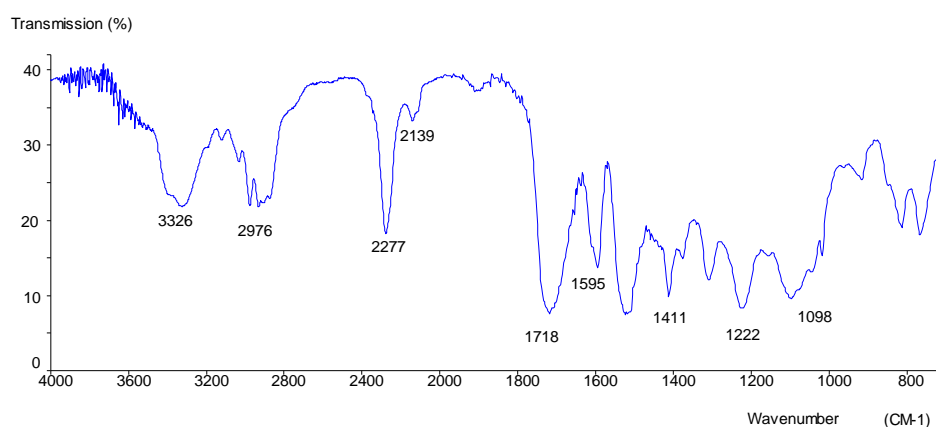


Figure 5: FTIR spectral profile of PUR/PIR rigid foam

Frequency assignments are given in Table 7. Relative trimer content was determined using the absorbance at 1411 cm^{-1} , carbodiimide content by the stretch at 2139 cm^{-1} and unreacted isocyanate by the absorbance at 2277 cm^{-1} .



Table 7: Frequency Assignments for Polyurethane Foams

Wave number	Chemical structure	Interpretation
3326 cm ⁻¹	N-H	Nitrogen-hydrogen stretch
3030 cm ⁻¹	Ar-H	Aromatic carbon-hydrogen stretch
2939 cm ⁻¹	C-H	Aliphatic carbon-hydrogen stretch
2277 cm ⁻¹	N=C=O	Isocyanate stretch
2139 cm ⁻¹	N=C=N	Carbodiimide stretch
1718 cm ⁻¹	C=O	Carbonyl stretch
1595 cm ⁻¹	Ar-H	Aromatic ring deformation
1512 cm ⁻¹	N-H	Nitrogen-hydrogen deformation
1411 cm ⁻¹	PIR	Isocyanurate deformation
1222 cm ⁻¹	C-N	Carbon-nitrogen stretch
1098 cm ⁻¹	C-O	Carbon-oxygen stretch

2. Attenuated Total Reflectance

Attenuated total reflectance (ATR) data on polyester polyol based foams were acquired on 10mm thick cross-sections taken from the center of bucket-cured handmix foams. Spectra were obtained using a Spectra-Tech Contact Sampler™ that holds the crystal horizontally above the instrument sample compartment cover. A 45° incident angle ZnSe crystal (1 x 10 cm rectangular sampling area) was used because it provided the greatest available sampling depth. The foam disc was centered over the crystal and covered with an aluminum plate. Four steel weight discs massing a total of 13.4 kg were placed on the aluminum plate to provide uniform pressure of the sample on the crystal. The infrared spectrum was obtained by co-adding 128 scans of 4.0 cm⁻¹ resolution with a Nicolet 20DXB interferometer. The crystal was cleaned with acetone after each spectrum was measured. Each sample disc was rotated 90° and a second spectrum was obtained. Results represent the averages of these two sample orientations.

The main sampling variable was the contact area between each foam sample and the ATR crystal. Shifts in absorption intensities and spectrum baselines are a result of contact variability. The effects of the baseline shifts were removed by computing the second derivative of each spectrum by the Savitsky-Golay convolution method with 11 convolution points [3].

Spectral assignments were similar to those given in Table 7. Data were normalized to the second derivative band intensity at 1595 cm⁻¹ after determining that the aromatic polyester absorption in that area was negligible. Absorbance intensity ratios acquired by this method should not be compared to those acquired by different methods, including the microfocus technique detailed above.

NMR Spectroscopy

In addition to FTIR, solid-state NMR was used to determine the isocyanurate content in selected foams [4]. This determination is made by quantifying the isocyanurate-carbonyl signal in the ¹³C NMR spectrum of the foam. Complicated by the similar chemical shift values of other components and broad signal linewidths, this technique requires computer lineshape procedures to obtain accurate peak integrals for quantitative purposes.

The Bruker ASX-200 NMR spectrometer, magnetic field of 4.7 Tesla, was used to perform the ¹³C cross-polarization magic-angle spinning (CPMAS) experiments. The CP experiment was used to maximize sensitivity and reduce recycle delay limitations typically associated with ¹³C NMR experiments. The Hartmann-Hahn match was set using glycine, which additionally served as an external chemical shift reference. A pulse sequence recycle delay of 1.5 seconds and a CP time of 1ms were used in all cases. Approximately 20,000 transients were collected for each sample. Samples were spun at 3kHz using a Bruker double air bearing MAS probe tuned to ¹³C (50.32MHz). The data were collected at room temperature.

The resultant 16k data point spectra were Fourier transformed using 30Hz of line broadening, prior to lineshape analysis. The corresponding ASCII files were then transferred to a VAX 8799 computer, where a curve fitting



procedure involving an Air Products developed program was used to determine areas for the peaks of interest. The program utilizes a standard FORTRAN subroutine from the MINPACK math package. A least squares iterative process is used to obtain the best calculated fit to the experimental data.

The range of ^{13}C NMR chemical shifts for the carbonyl resonances of urethane, urea, allophanate, biuret and isocyanurate groups is approximately from 149-156ppm. Isocyanurate is distinctive because it uniquely appears below 150ppm. The isocyanurate content can be readily determined by comparing the peak area of the urethane/urea carbonyl (153ppm) to the isocyanurate (149ppm). The wide linewidths typically encountered in solid state NMR require a linefitting routine to accurately determine the area represented by the two peaks. Due to some overlap with urea/urethane and the aromatics used in the system, the lower detection limit for the carbonyls in an isocyanurate environment is estimated at one molar percent.

Foam Properties

Foam friability was determined according to a modified ASTM C-241 test by measuring the weight loss after tumbling of the foam for 10 and 20 minutes.

Compression strengths were measured according to DIN 53421, both parallel and perpendicular to the direction of foam rise. Isotropy was calculated by dividing the perpendicular by the parallel compression strength.

RESULTS AND DISCUSSION

Rate of Rise Data

Typical examples of relative rise profiles are presented in Figures 6 and 7. The data depicted here were obtained using Dabco TMR as the trimerization catalyst, but similar trends were observed with all trimerization catalysts from Table 1. Rise profiles were obtained by dividing foam height at a given time by the final height. The strong impact of water in the polyether polyol based formulations can be seen from the differences between the rise profiles of formulations that contain 0 and 2 parts water. Water generally caused a delay of reaction with significantly longer rise times at higher indices. Formulations without water showed little rise time/index sensitivity.

In the polyester polyol based systems, higher water levels resulted in similar or even faster rise profiles, as shown in Figure 7. The cocatalyst used in these formulations, Polycat 5, aggressively catalyzes the reaction of isocyanate with water and generates early heat [5,6]. The larger amount of heat and carbon dioxide produced early in the reaction of the high water systems resulted in faster rise profiles.

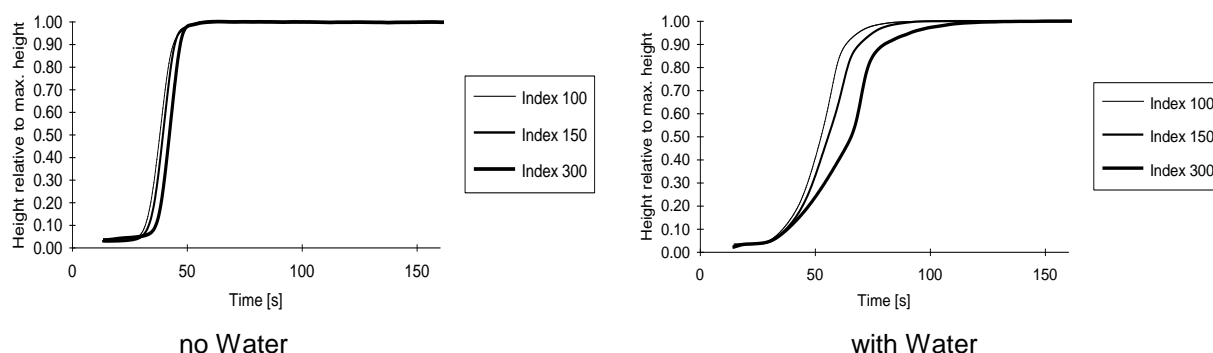


Figure 6a and 6b: Rise profiles comparing polyether polyol based formulations catalyzed with Dabco TMR, with Polycat 8 as cocatalyst

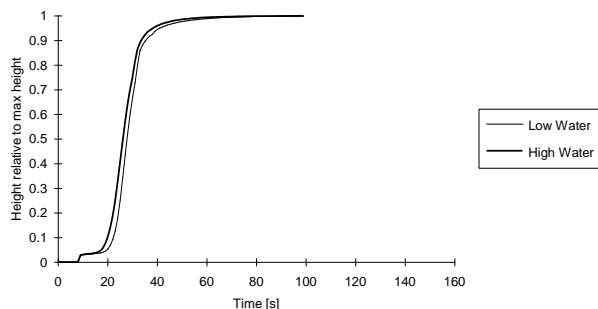


Figure 7: Rise profiles comparing polyester polyol based formulations catalyzed with Dabco TMR. with Polycat 5 as cocatalyst

Generally an increase in formulation water levels, requires the use of higher amounts of trimerization catalysts to maintain reactivity. The catalyst levels required to maintain a 30 s cream time for the polyether polyol based systems and a 33 s string gel time for the polyester formulations are presented in Figures 8 and 9.. When water is used as a coblowing agent, catalyst levels are increased as much as 100%. The catalysts appear to be partially deactivated by the water present in the formulation. Since the trimerization catalysts investigated during this study are organic salts, complex formation with the water may be responsible for this effect. As water is consumed during the course of the polymerization, catalyst does become increasingly available. However, at a later stage in the reaction, catalyst mobility is decreased due to molecular weight buildup and decreased isocyanate concentrations, resulting in overall reduced catalyst activity.

As seen in Figures 8a and 8b, trimerization catalyst levels decrease with increasing index. The amount of Dabco TMR 5 required to produce a constant cream time is relatively independent of index, since this catalyst also catalyzes the reaction of isocyanate with water.

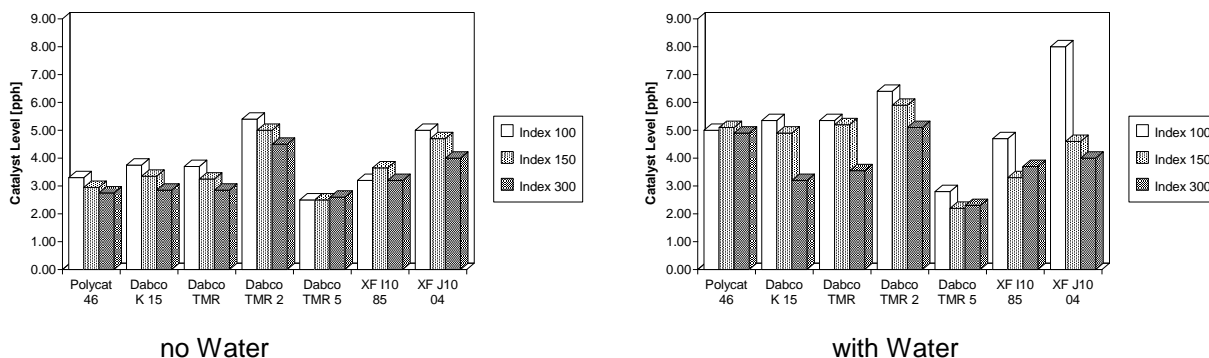


Figure 8a and 8b: Trimerization catalyst level comparison for polyether polyol based formulations with Polycat 8 as cocatalyst

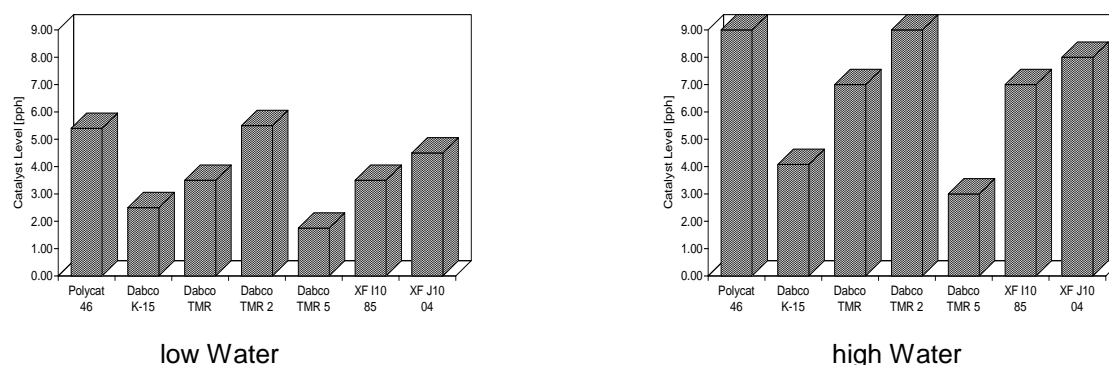


Figure 9a and 9b: Trimerization catalyst level comparison for polyester polyol based formulations with Polycat 5 as cocatalyst



The rise times (Figure 10) of the polyether polyol based formulations without water appear independent of isocyanate index, while the water containing systems show an increase in rise time with increasing index. Water containing polyether polyol based formulations exhibit substantially longer rise times versus the full HCFC blown formulations. With the exception of Dabco TMR 2 and Dabco TMR 5, faster rise times for the polyester polyol based systems are again observed with increased water levels.

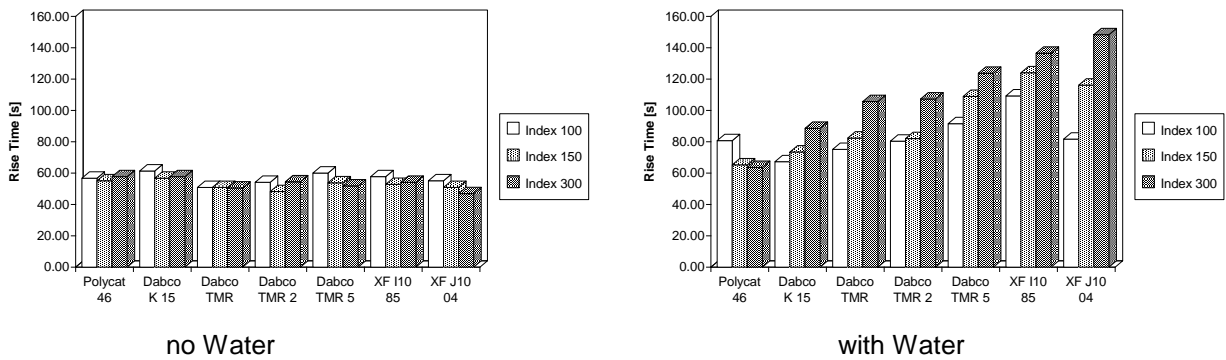


Figure 10a and 10b: Rise time comparisons of polyether polyol based formulations with Polycat 8 as cocatalyst

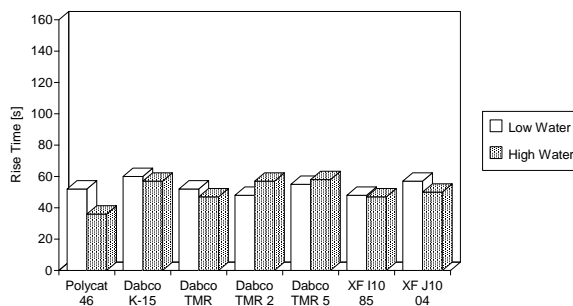


Figure 11: Rise time comparisons of polyester polyol based formulations with Polycat 5 as cocatalyst

Rate of rise profiles in Figure 12, show extremely steep profiles for full HCFC-141b blown polyether formulations, while the water coblown systems show more gradual rise rate curves. The maximum rate of rise (Figure 14) and the time of this maximum rise rate is lower and delayed in the water coblown formulations. Increasing index in the presence of water results in further delay. Figure 13, once again shows an acceleration in the rate of rise profiles with increased water levels in the polyester polyol based formulation due to the strong blowing activity of the Polycat 5 cocatalyst.

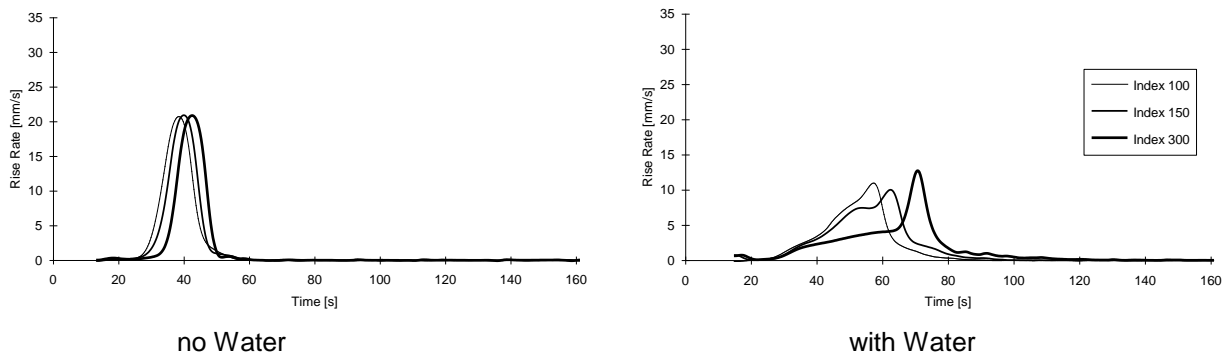


Figure 12a and 12b : Rise rate comparisons of Dabco TMR polyether polyol based formulations with Polycat 8 as cocatalyst

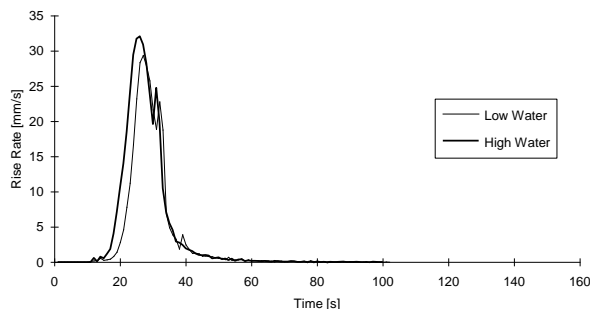


Figure 13: Rise rate comparison of Dabco TMR polyester polyol based formulations with Polycat 5 as cocatalyst

The maximum rise speed data in Figure 14 show little sensitivity to catalyst choice in the full HCFC blown polyether polyol based formulation. When water is used as a coblowing agent, both index and catalyst choice have large effects. Rise speeds with the potassium based catalysts are similar with both the full HCFC and water coblown formulations, but index sensitivity is reversed. Amine based products like the Dabco TMR series and the two experimental catalysts show lower maximum rise speeds in the presence of water. Of the amine based products, Dabco TMR 2 gives the highest maximum rise speed, comparable to those of the potassium salts.

In the high index polyester polyol based systems (Figure 15), maximum rise speeds vary with catalyst choice. In most cases, water has little effect. Dabco TMR 2 maximum rise speed was much greater than the other amine based catalyst tested in the low water formulation. As water level increased, maximum rise speeds were similar to that of other catalysts.

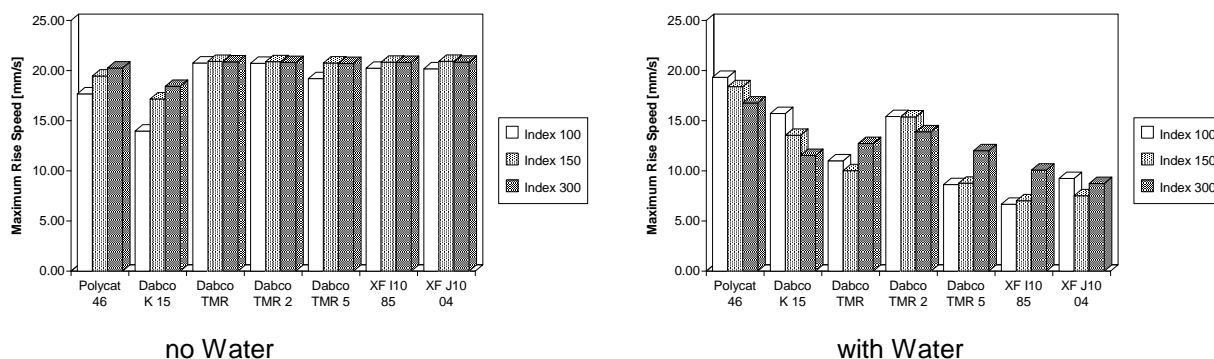


Figure 14a and 14b: Maximum Rise Speed comparisons in polyether polyol based formulations with Polycat 8 as cocatalyst

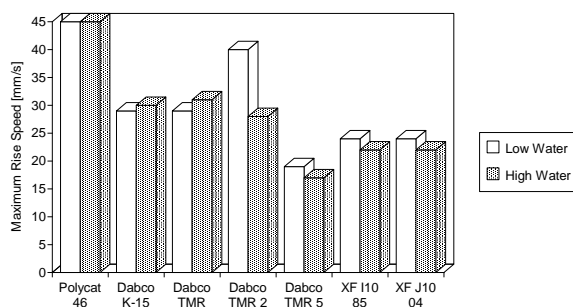


Figure 15: Maximum Rise Speed comparison in polyester formulations with Polycat 5 as cocatalyst

Temperature profiles of the rising foams are shown in Figures 16 and 17. Water coblown foams experience higher exotherms. This results from the exothermic reaction of water with isocyanate combined with reduced



cooling of the foam by vaporization of HCFC 141b. Higher index foams naturally reach higher maximum temperatures due to the formation of increased amounts of isocyanurate.

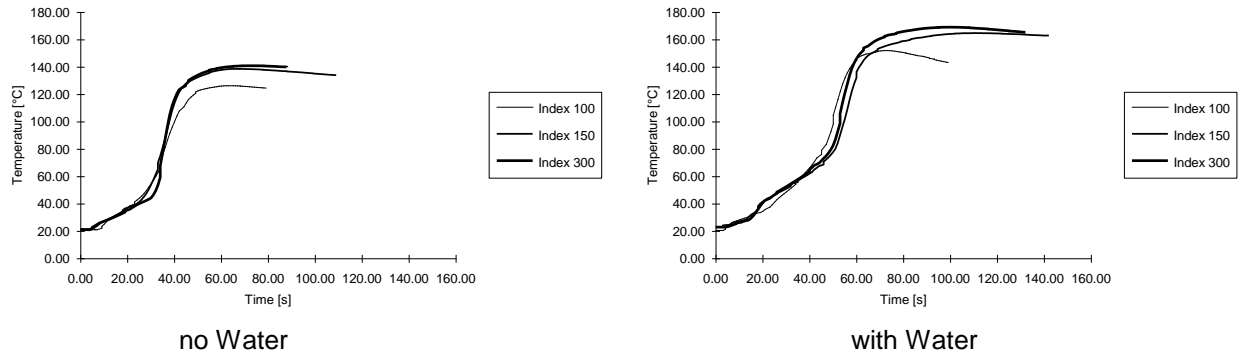


Figure 16a and 16b : Inside temperature profiles of Dabco TMR polyether polyol based formulations with Polycat 8 as cocatalyst

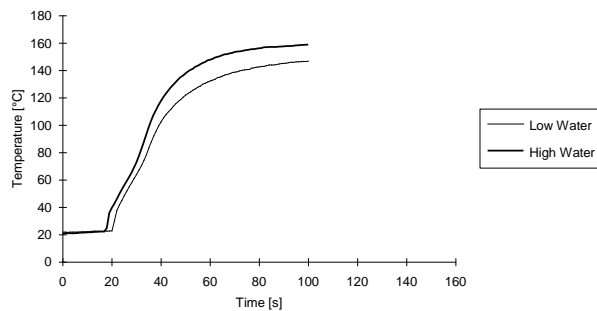


Figure 17: Inside temperature profiles of Dabco TMR polyester polyol based formulations with Polycat 5 as cocatalyst

A plot of temperature rate over time versus temperature (Figure 18) provides information about the temperature at which reactions occur. Higher temperature rates indicate higher conversion speeds. Without water as a coblowing agent there is an increase in the steepness of the temperature curve with increasing index, again a result of the high exothermic nature of the trimerization reaction. Comparing the plots with and without water, it is obvious that water shifts the main conversion towards higher temperatures. The activation temperature of the water containing formulation is as much as 20 °C higher than for the non water system. Higher activation temperatures are consistent with our anticipation of the formation of a catalyst-water complex which delays isocyanurate formation.

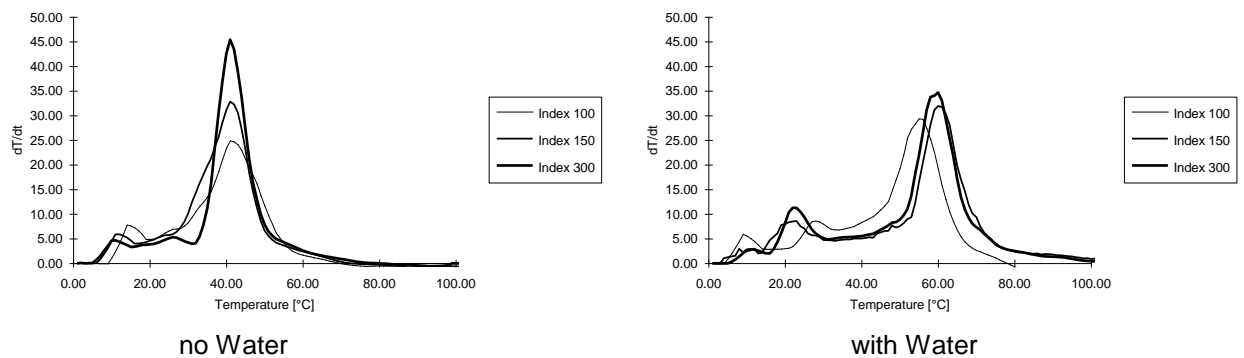


Figure 18a and 18b: Temperature rate versus temperature comparison of Dabco TMR polyether formulations with Polycat 8 as cocatalyst

Analytical Results



FT-IR Results

FT-IR results for the foams included in this study are presented in Figures 19-23. Relative functional group concentrations were determined by normalizing the assigned band intensity to the intensity of the MDI aromatic ring deformation at 1595 cm⁻¹ and are presented in dimensionless scale parts. Polyether foams were evaluated using a technique different from that used for the polyester foams, so only comparisons within a given polyol foam type are meaningful. In the absence of extinction coefficients, absolute concentrations could not be determined. Graphs show relative amounts only.

Foam core isocyanurate contents for the polyether and polyester polyol based formulations are shown in Figures 19 and 20. As expected, isocyanurate yields increase with increasing index. The presence of water lowers trimer conversions, especially at higher indices. In the no water polyether formulation, isocyanurate yields for amine based Dabco TMR series and two experimental catalysts equaled or exceeded that of the potassium carboxylates. When water is used as a cblowing agent isocyanurate yields at index 100 and 150 are similar for all trimerization catalysts. At index 300, Polycat 46 and Dabco K-15 yield higher conversions. Similar trends are seen in the polyester polyol based foams.

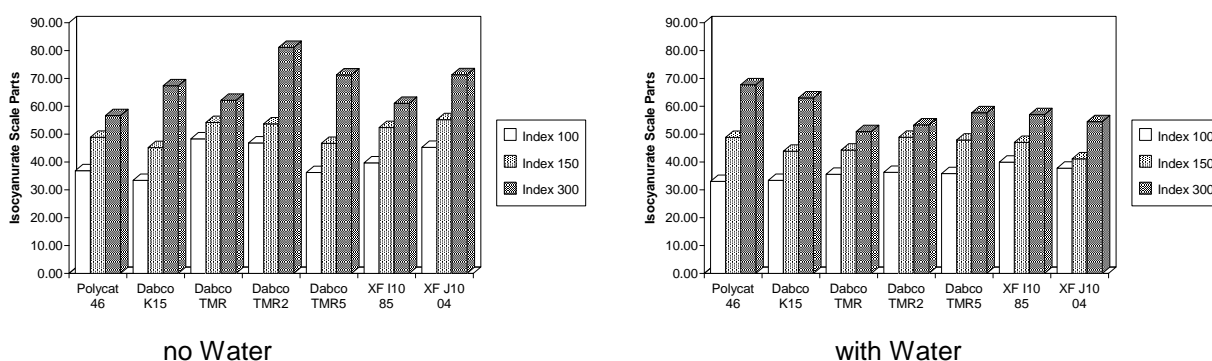


Figure 19a and 19b: Internal isocyanurate contents of polyether polyol based foams

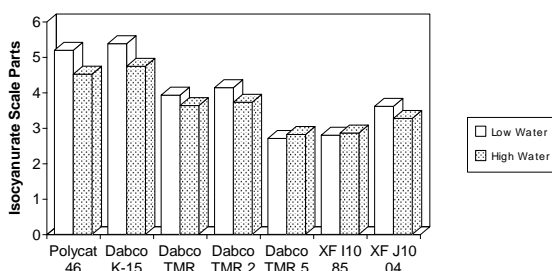


Figure 20: Internal isocyanurate content of polyester polyol based foams

Figure 21 shows the isocyanurate content at the edge of the polyether based foams. Isocyanurate content again increases with increasing index. With low and intermediate indices, edge isocyanurate content is similar for all catalysts tested. At high indices the Dabco TMR's and two experimental catalyst result in increased isocyanurate conversions vs. the potassium carboxylates at the edge of the full HCFC blown foams. Higher edge isocyanurate yields are again observed for the water cblown Dabco TMR, TMR 2 and TMR 5 catalyzed foams.

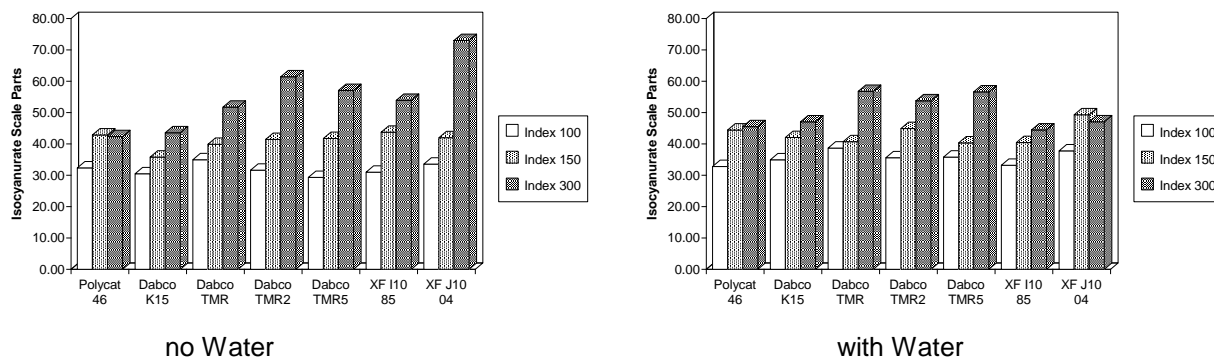


Figure 21a and 21b: Edge isocyanurate contents of polyether polyol based foams

As was noted earlier, under certain reaction conditions, carbodiimides may form during the cyclotrimerization of isocyanates. Carbodiimide was detected in the core of certain polyether and polyester polyol based foams. No carbodiimide was detected at the foam edge, probably due to lower temperatures in the foam edge zone. Carbodiimide concentrations of the water cblown polyether polyol based foams (Figure 22) are significantly higher compared with the full HCFC blown foams. Again, this is probably the result of the higher temperatures inside the foam of the water cblown formulations. Similar results are shown for the polyester polyol based system in Figure 23.

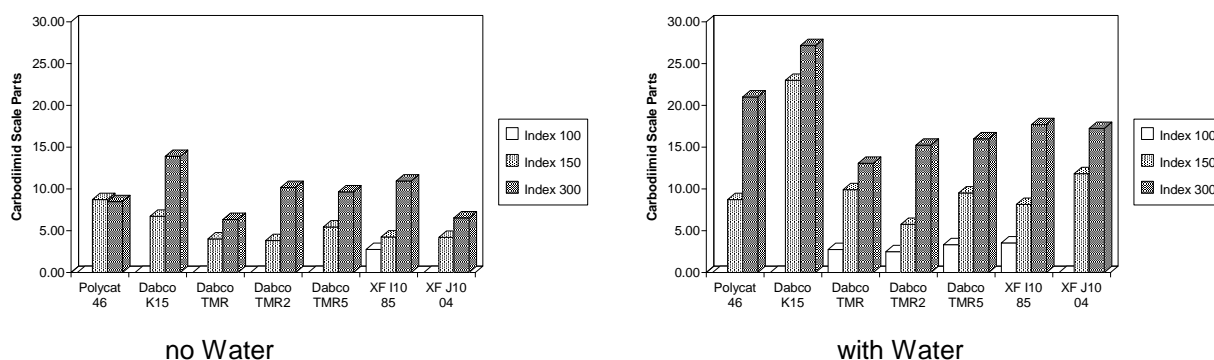


Figure 22a and 22b : Internal carbodiimide contents of polyether polyol based formulations

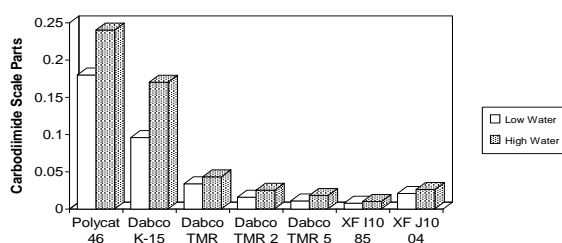


Figure 23: Internal carbodiimide content of polyester polyol based foams

Comparison of NMR and FTIR Results

Solid-state NMR has been used effectively to provide quantitative comparisons of the efficiency of isocyanurate catalysts [4]. This same technique was applied to selected foams from this study. A comparison of the NMR and FTIR (determined by the ATR technique) is given in Figure 24. NMR results are expressed as the relative percent conversion. This value represents the relative number percent of isocyanate carbons trimerized to isocyanurate carbons. FTIR results are in isocyanurate scale parts, as explained above. Results agree with regards to rank ordering of relative isocyanurate content in the 280 index polyester based foams. Isocyanurate



concentrations in the 150 index polyether based foams were below the sensitivity threshold of the NMR technique.

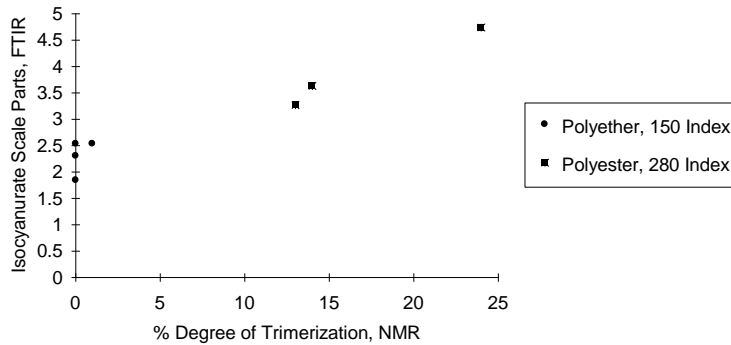


Figure 24: Comparison of FTIR and Solid State NMR Results

Physical Properties

1. Isotropy

The degree of foam cell isotropy or symmetry can be influenced by reaction kinetics and therefore the catalyst system. Isotropy is calculated by ratioing the perpendicular-to rise and parallel-to-rise compression strengths. Foams with lower isotropy exhibit lower compression strengths perpendicular to the direction of rise, resulting in shrinkage and poor dimensional stability. Figure 25 details the isotropy results for the polyether polyol based foams. In the full HCFC blown formulation, foams are more anisotropic, with index and catalyst having little effect. The water cblown foams are more isotropic and that isotropy is strongly influenced by index and catalyst choice. The Dabco TMR's and experimental catalysts produce more isotropic foams than those catalyzed with potassium carboxylates. The presence of water delays isocyanurate crosslinking and improves flow, so cells are less subject to stretching. The longer rise times associated with the amine based catalysts offer improved cell symmetry.

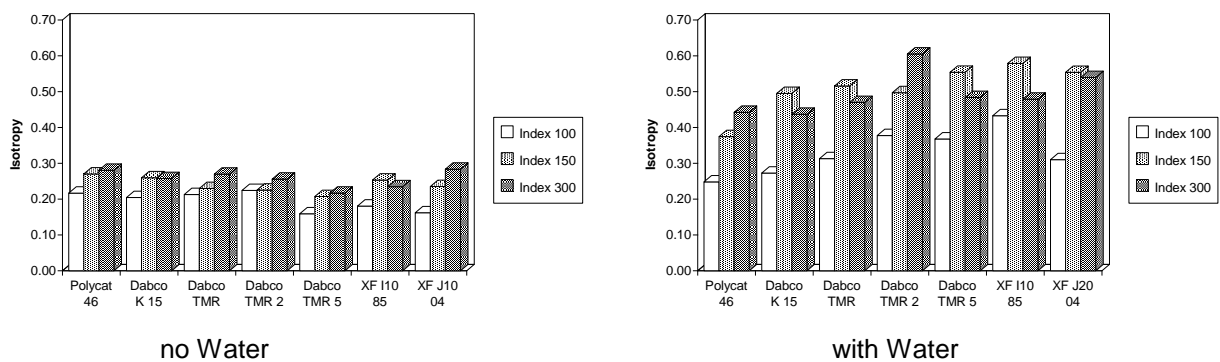


Figure 25a and 25b: Isotropy of polyether polyol based foams

2. Friability

Friability in high index foams continues to be a problem, adversely affecting foam strength and adhesion to facer materials. Increasing water levels generally aggravate this problem. Core friability weight loss results are given in Figure 26 for the 280 index polyester polyol based foam formulations at two water levels. As expected, the high water formulations show significantly greater weight loss for each of the catalysts tested. The two potassium based catalysts, Polycat 46 and Dabco K-15, produce the most friable foams. Friability is significantly improved for foams prepared using Dabco TMR, TMR 2 and TMR 5. Experimental catalysts XF I10



85 and XF J10 04, offer further improvements over the potassium carboxylates. Similarly, surface friability was qualitatively improved in both polyether and polyester high index foams using the amine based catalysts.

A good correlation is seen between maximum internal temperature during foaming and foam friability for a given formulation and water level. Foams with higher internal core temperatures were the most friable (Figure 27). It has been proposed that friability in high index foams results from excessive crosslinking which limits the extent of isocyanate conversion that can occur [7]. Our data suggest that other factors also contribute to friability, since there is little correlation between unreacted isocyanate levels and foam friability. In many cases the least friable foams are associated with the highest levels of unreacted isocyanate (Figure 28).

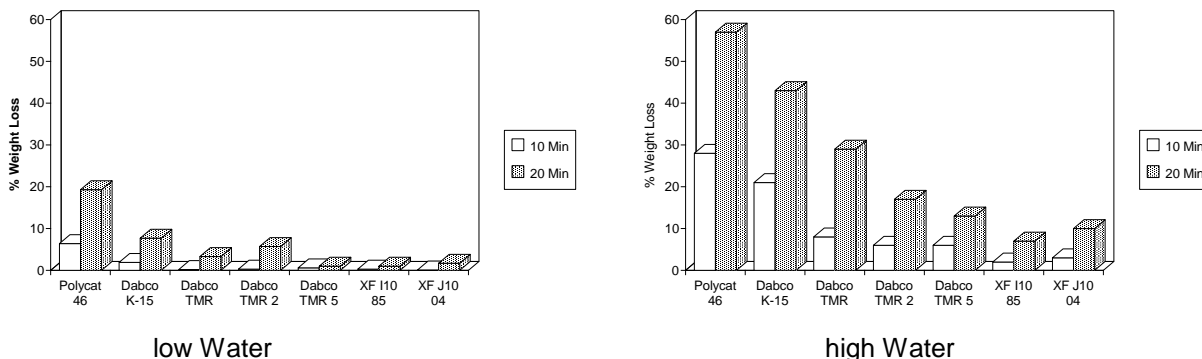


Figure 26a and 26b : Core friability of polyester polyol based foams

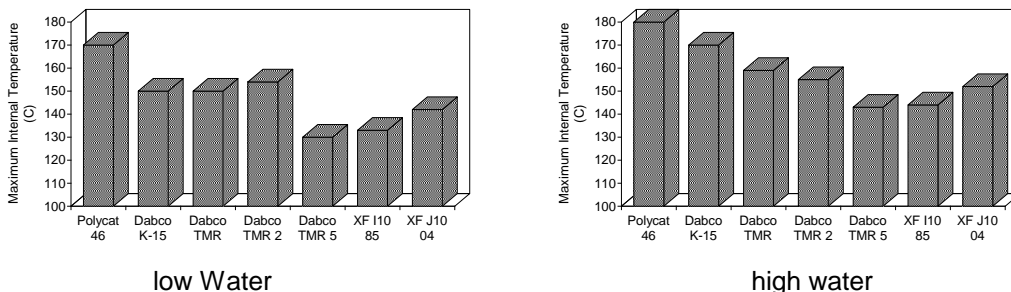


Figure 27a and 27b: Maximum internal temperature of polyester polyol based foams

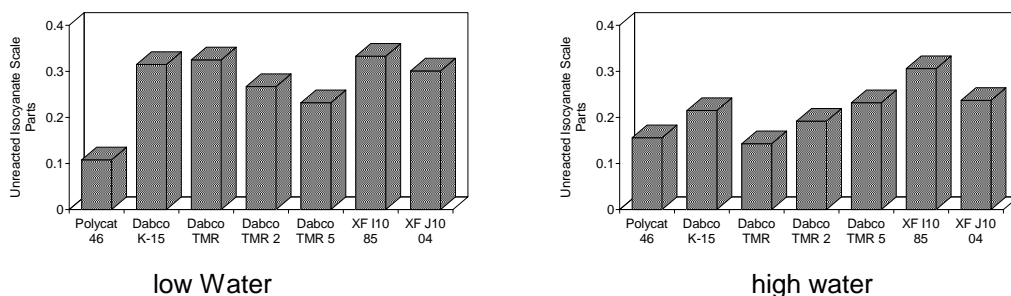


Figure 28a and 28b: Unreacted isocyanate content of polyester polyol based foams

SUMMARY AND CONCLUSIONS

The industry trend towards total CFC elimination necessitates reformulation of many rigid PUR/PIR systems. One way to overcome some of the performance deficiencies resulting from these changes is by the introduction of additional crosslinking through isocyanurate formation. In this study we evaluated the performance of seven trimerization catalysts in four formulations based on polyether and polyester polyols. Full HCFC 141b and water coblown systems were used. Foams were analyzed using FTIR and solid state NMR techniques to determine relative isocyanurate contents. Rise profiles and selected physical properties were evaluated for each catalyst.



The presence of water as a coblowing agent impacts foam reaction kinetics, resulting in delayed reaction with significantly longer rise times. Increased trimer catalyst use levels are required to match the reactivity profiles obtained without water. Complexation of water with the organic salt trimerization catalysts may be responsible for this effect. As water is consumed during the course of polymerization, catalyst becomes available. At this later stage in the reaction, however, reduced catalyst mobility due to increased polymer molecular weight buildup and decreased isocyanate concentrations result in overall reduced catalyst activity. Polycat 5, used as a cocatalyst, partially compensates for the delaying effect of water due to its high blow activity. Water cblown foams experience higher exotherms resulting in increased carbodiimide formation.

FT-IR is a useful method of determining the relative effectiveness of foam trimerization catalysts in cured foams. Results correlate with those obtained by solid state NMR techniques. The increased sensitivity of FTIR versus NMR, allow for detection of isocyanurate in low index foams.

Catalysts from the Dabco TMR series are effective isocyanurate catalysts. Experimental catalyst XF 110 85 and XF J10 04 produce similar isocyanurate yields combined with reduced odor. The amine based catalysts produce higher isocyanurate conversion on the foam surface versus potassium compounds.

The Dabco TMR catalysts series produces significantly smoother rise profiles in water cblown formulations, resulting in more isotropic foams where less shrinkage and better dimensional stability are anticipated.

Foams catalyzed with quaternary ammonium salts from the Dabco TMR series show significantly lower friability versus foams produced with potassium compounds such as Polycat 46 and Dabco K-15. Experimental catalysts XF 110 85 and XF J10 04 produce the least friable foams.

FUTURE WORK

The results of this study indicate there are opportunities to improve and control isocyanurate conversion in the presence of water. Future work will involve the synthesis and evaluation of new catalyst structures to accomplish this purpose. The effect of various cocatalysts on reactivity and performance will also be investigated. Additionally we plan to correlate FTIR results with other foam properties including dimensional stability, flammability and thermal conductivity.

ACKNOWLEDGMENTS

The authors would like to thank Frank Safari and Gary L. Johnson for the excellent support they provided in FTIR methods development and data acquisition as well as Paula L. McDaniel for her assistance in the solid state NMR analysis and interpretation. The authors would particularly like to thank Dolores A. Kloap and Ahmad Rweha for their valuable technical assistance.

Literature

- [1] Burns, S. B. and Schmidt, E. L. 1993. *Proceedings of the Polyurethane World Congress 1993*, pp. 234-240.
- [2] Reymore, H. E.; Carleton, P. S.; Kolakowski, R. A.; Sayigh, A. A. R. 1975. *J. Cell. Plast.*, 11:328 and references therein.
- [3] Savitzky, A. and Golay, M. J. E. 1964. *Analytical Chemistry*, 36:1627-1639.
- [4] Bartish, C. M.; Yue, H. J.; Seger, M. R.; Manis, P. A. 1989. *Proceedings of the SPI 32nd Annual Technical/Marketing Conference*, pp. 157-163.
- [5] Listemann, M. L.; Savoca, A. C.; Wressell, A. L. 1991. *Proceedings of the Polyurethane World Congress 1991*, pp. 524-544.
- [6] Listemann, M. L.; Savoca, A. C.; Wressell, A. L.; Lassila, K. R.; Klotz, H. C.; Johnson, G. L. 1993. *Proceedings of the Polyurethane World Congress 1993*, pp. 595-608.



[7] Van Gheluwe, P.; Cole, K. C.; Hebrard, M. J; Leroux, J., *J. Cell. Plast.* 1987, 23, 73.

BIOGRAPHIES

Susan M. Clift

Susan Clift is a Senior Principal Applications Chemist with the Polyurethane and Performance Chemicals Division of Air Products. She is responsible for North American technical service and applications development for the rigid foam market segment. Dr. Clift has been with Air Products since 1984. She holds a B.S. degree in chemistry from Ursinus College and a Ph.D. from Princeton University in organometallic chemistry.

Jobst Grimminger

Jobst Grimminger received his Dipl. Ing. (FH) diploma in 1983 from Fachhochschule Aalen, Germany. After 8 years of experience in development and technical service support in ZELU Chemie, a systems house in Germany, Jobst joined Air Products and Chemicals GmbH in Norderstedt in 1991. Mr. Grimminger is senior technical service chemist responsible for rigid polyurethane foam additives, additives for high density molding applications and polyurethane specialty products.

Krunoslav Muha

Krunoslav Muha is a technical manager in Air Products and Chemicals GmbH. He is responsible for technical service and application development regarding polyurethane additives, release agents and polyurethane specialty products. Other positions Krunoslav has held while at Air Products include senior chemist in the flexible cold cure molded area and flexible foams group manager. Krunoslav received his B.S. in chemical technology from the University in Ljubljana-Slovenia in 1981. Prior to coming to Air Products he was employed by Color Medvode-Slovenia as a polyurethane R&D group leader.