Catalysis of Blocked Isocyanates with Non-Tin Catalysts

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Introduction

The use of “blocked” polyisocyanates has many advantages in the coating industry. It permits the formulation of stable one package coatings which on heating deblock and lead to the formation of the highly reactive polyisocyanate. Applications for these systems are in diversified areas such as powder coatings, electrocoating, wire coatings and in textile finishing. The nature of the blocking agent[1] has a significant effect on the deblocking temperature of the isocyanate. Typical blocking agents used include malonates, triazoles, ε-caprolactam, sulfite, phenols, ketoxime, pyrazoles and alcohols. For many blocked isocyanates an elimination-addition mechanism[2] as indicated in Eq. (1) is proposed.

$$\mathrm{RNHCOO\text{-}Bl} \quad \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} \quad \mathrm{RNCO} + \mathrm{Bl\text{-}H} \uparrow \qquad \text{EQ. (1)}$$

$$\mathrm{RNCO} + \mathrm{RNH_2\ (ROH)} \xrightarrow{k_2} \mathrm{RNHCO\text{-}NHR\ (OR)}$$

This traditional view of blocked isocyanates as an isocyanate precursor has already been challenged by Wicks[3,4,5] . He showed that for malonate blocked aliphatic isocyanates transesterification is the predominant reaction step.

For alcohol blocked isocyanates the decomposition to the isocyanate is a rather high temperature reaction step. In the presence of a catalyst, alcohols are effective blocking groups for isocyanates. Transesterification reaction according to EQ. 2 is the most likely reaction mechanism. The overall reaction rate can depend on the volatility of the alcohol[6].

$$\mathrm{RNHCOOR'} + \mathrm{R''OH} \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} \mathrm{RNHCOOR''} + \mathrm{R'OH} \uparrow \qquad \text{Eq. (2)}$$

For both the elimination-addition and the displacement mechanism, dibutyltin dilaurate (DBTDL) has been found to be an effective catalyst. Depending on the alcohol used non-tin metal compounds[7] and chelates were also found to be effective catalysts. In this study we were interested to determine if other metal catalysts can be used to catalyze the reaction of ketoxime, alcohol, pyrazol and caprolactam blocked isocyanates.

Experimental.

The blocked isocyanates were prepared from the polyisocyanate and the blocking agent.

An oxime blocked isocyanate was synthesized from the reaction of 2-butanone oxime and a commercially available HDI trimer[8] at NOH/NCO ratio of 1.05. FT-IR spectrum of the product showed no residual isocyanate. The product has a theoretical equivalent weight of 270 and was diluted with 2-methoxypropyl acetate to a 92 % solids content for use.

A pyrazole blocked isocyanates was obtained by reacting the above HDI trimer with 3,5-dimethylpyrazole at NH/NCO ratio of 1.0. After over 90% conversion (checked by FT-IR), the residual isocyanate groups were capped with alcohol. The final product had a theoretical equivalent weight of 279 and was diluted with 2-methoxypropyl acetate/t-butanol to 85 % solids for use.

A caprolactam blocked isocyanate was synthesized by reacting ε-caprolactam with IPDI trimer[9] at CONH/NCO ratio of 1.05. After over 90% conversion, the residual isocyanate groups were capped with isopropanol. The final product had a theoretical equivalent weight of 356 and was diluted with 2-methoxypropyl acetate/xylene to a 67% nonvolatile content with an equivalent weight of 532.

A glycolether blocked isocyanate was prepared by reacting 2-methoxyethoxyethanol with a polymeric aromatic isocyanate[10] (MDI) at 1.02 OH/NCO ratio. The final product has an nonvolatile content of over 99 % and equivalent weight of 254.

The phenol blocked isocyanate was prepared by reacting slight excess of phenol with a polymeric aromatic isocyanate (MDI) at temperatures of 80-120°C in the absence of any catalyst. The reaction mixture was diluted as the viscosity increased with DBE[11] dibasic ester, xylene and n-methylpyrollidinone. The resulting crosslinker had a nonvolatile content of 50 % and a calculated equivalent weight based on the solids of 255.

The uretdione blocked isocyanate[12] was a commercially available IPDI blocked crosslinker

The blocked isocyanates were blended with a commercially available acrylic resin[13] at a hydroxyl/blocked NCO ratio of 1/1. The catalyst levels shown in the result section are based on total resin solids, i.e. both acrylic and blocked isocyanate resin.

Films were prepared by draw down of the formulations on iron phosphate pretreated steel panels and baked in a forced draft air oven.

Results

Solvent resistance as measured by methyl ethyl ketone rubs (MEK) was found to be a simple and fast technique for determining crosslinking and was used for the screening studies.

Table 1: Catalyst Screening in Oxime blocked HDI-Trimer

Substrate Bonderite B1000, Dry film thickness: 22 µ (0.85 mils), cure 20minutes at 130^0C

Catalyst	Metal % on solids	Film Appearance	MEK 2x rubs
No catalyst	0	Clear	0
Dibutyltin dilaurate	0.05	Clear	43
Dibutyltin dilaurate	0.09	Clear	46
Dibutyltin diacetate	0.18	Clear	38
Bismuth tris(2-ethylhexanoate)[14]	0.065	Clear	51
Aluminum dionate complex[15]	0.04	Clear	19
Cobalt bis(2-ethyl hexanoate)	0.05	Hazy	51
Zr bis(2-ethyl hexanoate)	0.18	Clear	12
Zn bis(2-ethyl hexanoate)	0.048	Clear	35
Ti tetra(ethyl acetoacetato)	0.50	Yellow	52
Calcium bis(2-ethyl hexanoate)	0.05	Clear	24
Chromium tris(2-ethyl hexanoate)	0.255	Hazy	43

Table 2: Catalyst Screening in Pyrazole Blocked HDI-Trimer

Substrate Bonderite 1000, Dry film thickness: 22 µ (0.85 mils), cure 20minutes at 130^0C

Catalyst	Metal % on solids	MEK 2 x rubs
No Catalyst		23
Dibutyltin dilaurate	0.09	79
Bismuth tris(2-ethylhexanoate)	0.04	50
Bismuth tris(2-ethylhexanoate)	0.065	61
Zr bis(2-ethyl hexanoate)	0.09	27
Zn bis(2-ethyl hexanoate)	0.09	34
Cobalt bis(2-ethyl hexanoate)	0.10	57*
Chromium tris(2-ethyl hexanoate)	0.51	43
Ti tetra(ethyl acetoacetato)		46
Calcium bis(2-ethyl hexanoate)	0.10	29
Bismuth tris(2-ethylhexanoate)	0.04	50

* = Some Wrinkling

Table 3: Catalyst Screening in Caprolactam Blocked IPDI Trimer

Substrate Bonderite 1000, Dry film thickness: 22 µ (0.85 mils).

Catalysts Cure schedule, 20 min at	% Metal on solids	MEK 2x rubs 155 ^{0} C	MEK 2x rubs 165 ^{0}C
No catalyst	0.00	10	15
Dibutyltin dilaurate	0.10	77	200
Dibutyltin diacetate	0.18	98	200
Bismuth tris(2-ethylhexanoate)	0.10	58	200
Zn bis(2-ethyl hexanoate)	0.18	115	200
Cobalt bis(2-ethyl hexanoate)	0.30	73	200
Ti tetra(ethyl acetoacetato)	0.22		117

Table 4: Catalyst Screening in Carbitol Blocked MDI

Substrate Bonderite B1000,

Dry film thickness: 0.85 mils :0.18% metal catalyst on total resin solids

Catalyst Cure schedule 20 minutes at	MEK 2x rubs 150^o C	MEK 2x rubs 170^o C
No catalyst	2	2
Dibutyltin dilaurate	10	130
Bismuth tris(2-ethylhexanoate)	120	200
Zn bis(2-ethyl hexanoate)	24	200
Aluminum dionate complex	20	
Ti tetra(ethyl acetoacetato)	13	
Cobalt bis(2-ethyl hexanoate)	100	

Table 5: Catalyst Screening in Phenol Blocked MDI

Substrate Bonderite B1000,

Dry film thickness: 0.85 mils : 0.22% metal catalyst on total resin solids

Catalyst Cure schedule 20 minutes at	MEK 2x rubs 130^o C	MEK 2x rubs 150^o C
No catalyst	5	
Aluminum dionate complex	5	
Zirconium dionate complex	5	
Cerium naphthenate	5	
Ti tetra(ethyl acetoacetato)	5	
Zirconium bis(2-ethyl hexanoate)	10	
Calcium bis(2-ethylhexanoate)	30	
Chromium (III) tris(2-ethylhexanoate)	45	
Dibutyltin dilaurate	150	200
Bismuth tris(2-ethylhexanoate)	180	200
Zinc bis(2-ethyl hexanoate)	200	
Manganese naphthenate	200	

Table 6: Catalyst Screening in Uretdione Blocked IPDI crosslinker
Substrate Bonderite B1000,
Dry film thickness: 1.0 mils : 0.28% metal catalyst on total resin solids, DBU 0.5 % on resin solids

Catalyst	MEK 2x rubs	MEK	MEK	MEK
Cure schedule 20 minutes at	170° C	180° C	190° C	200°
No catalyst	50	60	60	70
Zinc bis(2-ethyl hexanoate)	70	80	95	110
Tin (II) bis(2-ethyl hexanoate)	70	75	80	100
DBU	80	80	90	100
Dibutyltin dilaurate	100	140	155	170
Bismuth tris(2-ethylhexanoate)	120	130	150	180

Discussion and Conclusions

Many metal salts and chelates can substantially reduce the cure temperature of blocked isocyanates. Besides dibutyltin dilaurate which is being used in many formulations other metal compounds are effective catalysts. Not all the metals tested performed equally well with all blocked isocyanates.

Of the many metal compounds and chelates screened in this study bismuth carboxylates show consistent catalysis in ketoxime, pyrazol, caprolactam, glycol ether, phenol and uretdione internally blocked isocyanates crosslinked coatings. On a metal basis bismuth is at least as effective as dibutyltin compounds. At this stage of our investigation it is not clear how bismuth catalyzes the reaction of blocked isocyanates with hydroxyl compounds.

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[2] S.P. Pappas, E.H.Urruti, 13th Annual Water-Borne and Higher Solids Coatings Symposium, New Orleans, LA 1986

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[8] HDI-trimer hexamethylene diisocyanate isocyanurate trimer, Desmodur N-3300; isocyanate equivalent weight 183, Bayer Corporation, Pittsburgh PA.

[9] Isophorone diisocyanate isocyanurate trimer commercially available as Desmodur Z-4370 from Bayer Corporation, Pittsburgh PA.

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[10] Polymeric aromatic isocyanate with an equivalent weight of 130 Modur MRS 5 from Bayer Corporation, Pittsburgh PA.

[11] DBE dimethylester of glutaric, adipic and succinic acid available from E. I. Dupont de Nemours. Wilmington, DE

[12] Uretdione blocked IPDI crosslinker Crelan VPLS 2147, equivalent weight 300 based on solids content, available from Bayer Corporation, Pittsburgh PA.

[13] Acrylic polyol with a nonvolatile content of 70 % and a hydroxy equivalent weight on a solids basis of 460; Paraloid AU-946 B available from Rohm and Haas Company, Philadelphia PA.

[14] K-KAT® 348 bismuth catalyst a product of King Industries Inc. Norwalk, CT 06852

[15] K-KAT® XC-5218 aluminum chelate catalyst a product of King Industries Inc. Norwalk, CT 06852