

You are now at www.wernerblank.com

[HOME](#)

[NEWS](#)

[PUBLICATIONS](#)

[LECTURES](#)

[PATENTS](#)

[DOWNLOADS](#)

A SELECTIVE CATALYST FOR TWO COMPONENT WATERBORNE POLYURETHANE COATINGS

Z. Alex He, Werner J. Blank, Marie E. Picci
King Industries Inc.
Norwalk, CT 06852

Presented at the
International Waterborne, High-Solids, and Powder Coatings Symposium
February 10-12, 1999
New Orleans, LA, USA

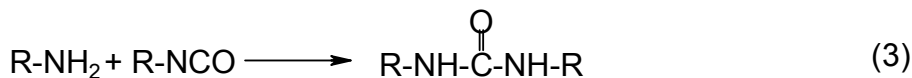
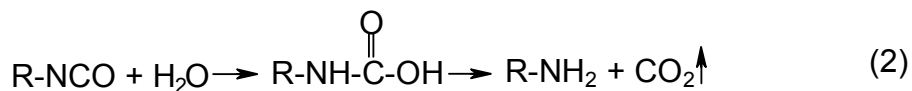
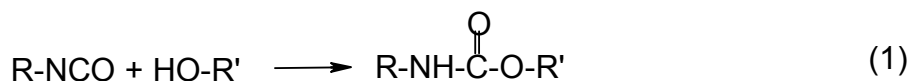
Symposium Sponsored by
The University of Southern Mississippi
Department of Polymer Science

Abstract

The potential for formulating low VOC, high performance, two component waterborne isocyanate crosslinked coatings has generated a great interest. The difficulties in formulating these coatings, however, are significant. A major problem associated with such systems is the isocyanate-water side reaction, which can lead to gassing/foaming, loss of isocyanate functionality, low gloss and a reduced pot life. To compensate for this side reaction, these formulations usually contain a large excess of isocyanate. One novel approach to control the water side reaction is the use of catalysts which selectively catalyze the isocyanate-polyol reaction and not the isocyanate-water reaction. The selectivity of a variety of metal catalysts to catalyze the preferred reaction was measured using an FT-IR method. A zirconium complex has shown unusually high selectivity for the isocyanate-polyol reaction in comparison to standard dibutyltin dilaurate catalyst. This zirconium complex catalyst has been evaluated in several water borne polyurethane formulations and has demonstrated less gassing/foaming, longer pot life and higher gloss than dibutyltin dilaurate at equal cure time. The mechanism of catalysis and formulating techniques of this novel zirconium catalyst will be discussed.

INTRODUCTION

The potential for formulating low VOC, high performance, two component (2K) waterborne isocyanate crosslinked coatings has generated a great deal of interest.^{1,2} Although some progress has been made in the past several years, formulating such water borne coatings remains a big challenge to coatings chemists. A major problem associated with such systems is the isocyanate-water side reaction (Scheme 1), which can lead to gassing/foaming, pinholes, loss of isocyanate functionality, low gloss and a reduced pot life. The generation of CO₂ also lowers the pH of the emulsion or dispersion which can reduce the stability of the WB formulations.¹ To compensate for functionality loss due to this isocyanate-water reaction, these formulations usually contain a large excess of isocyanate.^{1,2} Approaches to control the side reaction with water include plural spray gun application, thin film thickness and controlled low humidity levels during application. These physical constraints, however, will impose significant limitations on the application of this new technology.



Scheme 1. Isocyanate reactions with alcohol (1) and with H₂O (2,3)

The reactions of isocyanate, especially aliphatic isocyanate, with hydroxyl or water are relatively slow at ambient temperature in the absence of a catalyst. Organo metallic compounds or tertiary amines are normally needed to catalyze the crosslinking of isocyanate with hydroxyl groups for ambient cure applications.^{3,4,5} It is possible to control isocyanate-water reaction if one can selectively catalyze the isocyanate-polyol reaction and not the isocyanate-water reaction.

Several previous publications have reported the influence of catalysts on the selectivity of isocyanate reactions. The reaction rates with hydroxyl and water were determined in the presence of different tin catalysts in triethylene glycol dimethyl ether and in N-methyl pyrrolidinone.⁶ Dibutyltin dilaurate (DBTDL) was found to give selectivity (rate constant ratio of isocyanate-hydroxyl reaction vs. isocyanate-H₂O reaction) ranging from 1.8 to 3.8 depending on the solvents. Dibutyl tin dichloride gave the same selectivity for different solvents. The reaction rates of an aromatic isocyanate with water were studied in diglyme with tertiary amine, mercury and tin compounds as catalysts.⁷ DBTDL and 1,4-diazabicyclo[2,2,2]-octane (DABCO) were found to give

equal reaction rates. However, phenylmercuric acetate showed an exceptional high rate of isocyanate-H₂O reaction. It was also reported that the pK_a value of an amine catalyst had a big effect on the isocyanate-water reaction. The amine catalyst with a higher pK_a value showed more catalytic activity for the isocyanate-H₂O reaction.⁸

We were interested in a catalyst with high selectivity for the isocyanate-hydroxyl reaction and its applications in two component water borne polyurethane formulations. The relative selectivity of a variety of metal polyurethane catalysts were determined utilizing an FT-IR method. A zirconium diketonate catalyst with unusually high selectivity of the isocyanate-polyol reaction was tested with several water borne polyurethane formulations. The zirconium catalyst has demonstrated less gassing/foaming, fewer pinholes, longer pot life and higher gloss than DBTDL. The mechanism of catalysis along with formulating techniques for this novel catalyst will be discussed.

EXPERIMENTAL

Raw material

Two types of metal compounds were used in the study, metal carboxylates and metal β-diketonates. The commercial metal carboxylate products were used without further purification. The metal diketonates were obtained from commercial sources or prepared via ligand exchange reactions of the corresponding metal compounds with β-diketones. The diketone compounds were purchased commercially or synthesized via Claisen condensation reaction of a methyl ester and a ketone.⁹

Butyl isocyanate, purchased from Aldrich, was used without further purification. The reaction of this isocyanate with alcohol was slow in the absence of a catalyst, indicating a low level of catalytically active impurities. 2-Ethyl hexanol, THF and butyl amine used in the selectivity studies are reagent grade commercial materials. Deionized water was used as the water source. All other polyols and isocyanates used in the evaluation formulations were from commercial sources and their suppliers are indicated in the corresponding formulation tables.

FT-IR Selectivity studies

A homogeneous stock solution of H₂O and 2-ethyl hexanol in THF was added to a test tube. The metal catalyst (previously dissolved in THF) and butyl isocyanate were added at the same time to this stock solution. The solution was thoroughly shaken. The molar ratio of butyl isocyanate /alcohol/H₂O was maintained 1.0/1.0/2.0 for all the tests. The catalyst amount added was adjusted so that the isocyanate would be completely reacted in 5 hours under ambient temperature (ranging from 0.005 to 0.05 metal %). The uncatalyzed reaction took over 20 hours to complete under the same conditions. After the reaction was completed (disappearance of isocyanate checked by FT-IR in a sealed cell),

a drop of the reaction solution was taken to make a thin film on a ZnSe plate and the film was dried for 30 minutes under ambient temperature for each sample before recording the FT-IR spectrum. A Perkin Elmer Spectrum 2000 spectrometer was used for recording FT-IR spectrum. The urethane and urea peaks were integrated to calculate the relative selectivity. To minimize the experimental error, a calibration curve was determined using the standard urethane and urea made from the reactions of butyl isocyanate with 2-ethyl hexanol and butyl amine, respectively.

Coating formulations and film property evaluations

Standard procedures were used for coating formulations and evaluations. Cure studies were conducted on films drawn down with a wire applicator. The surface dry and through dry times were recorded with a Gardner circular dry time recorder.

RESULTS AND DISCUSSIONS

FT-IR spectroscopic studies of catalyst selectivity

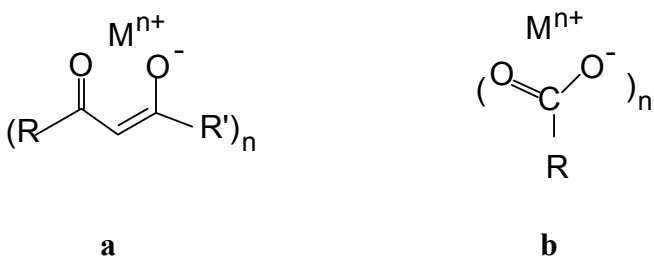
The reaction product ratio, urethane/urea, was used as a measure of the relative selectivity in this study (equation 4). The urethane to urea molar ratios were measured with full conversion of isocyanate groups at an isocyanate/hydroxyl/water ratio of 1.0/1.0/2.0 to differentiate the selectivity among catalysts. Although the reaction rate constant ratio as a selectivity measure was frequently used in the literature,⁶ the product ratio measurement is easier and more accurate since a number of factors affect rate constant measurements (such as solvents, temperature, catalyst deactivation, etc.).

$$S = [\text{urethane}]/[\text{urea}] \quad (4)$$

Butyl isocyanate and 2-ethyl hexanol were chosen as model compounds for their similarities to aliphatic polyisocyanate and hydroxyl resin and for the simplicity of their FT-IR spectra. Figure 1 shows the FT-IR spectra of urethane, urea and the mixture at a urethane/urea molar ratio of 1.0. Although there is some overlapping, the urethane and urea peaks around 1600-1750 cm⁻¹ are distinguishable. A calibration curve of urethane/urea molar ratio vs. urethane/urea peak area ratio gave a good correlation with urethane to urea peak area ratio ranging from 0.5 to 3.5 (Figure 2).

Two types of catalytically active metal complexes are screened in this study: metal carboxylates and β -diketonates (Scheme 2). Figure 3 shows some typical FT-IR spectra of reaction products of some catalyzed homogenous solutions of butyl isocyanate, 2-ethyl hexanol and H₂O. Zirconium diketonate showed predominant urethane formation and Zn octoate showed predominant urea formation, while DBTDL is somewhere in between. The relative selectivity (urethane to urea molar ratio) of a number of metal compound catalysts are summarized in Figure 4. The zirconium diketonate showed highest selectivity among the catalysts tested. The amount of urea product in the

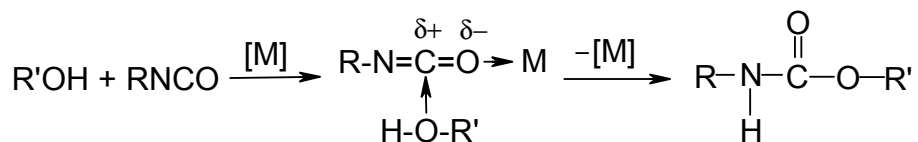
zirconium diketonate catalyzed formulation was too small to be determined accurately by FT-IR spectrum due to overlapping with the urethane peak. The product ratio for this catalyst in Figure 4 is an estimated value. Among the catalysts screened, only two catalysts have selectivity better than DBTDL, which may explain why this is a popular catalyst in polyurethane coatings. A number of metal complexes actually prefer to catalyze the water reaction (relative selectivity < 0.5 at NCO/OH/H₂O=1.0/1.0/2.0). Cobalt octoate catalyzes the water reaction almost exclusively (relative selectivity <0.1). This is not completely surprising since a similar high H₂O reaction rate was reported with phenyl mercuric acetate.⁷ It is also interesting to note that the selectivity of metal diketonates is always higher than that of metal carboxylates for the same metal (Figure 5). However, the number of metal compounds tested here may be too small to draw a general conclusion. There is also a big difference in the catalytic activity for these two types of metal complexes. For example, zirconium diketonates are highly active while zirconium carboxylates are virtually inactive.^{10,11}



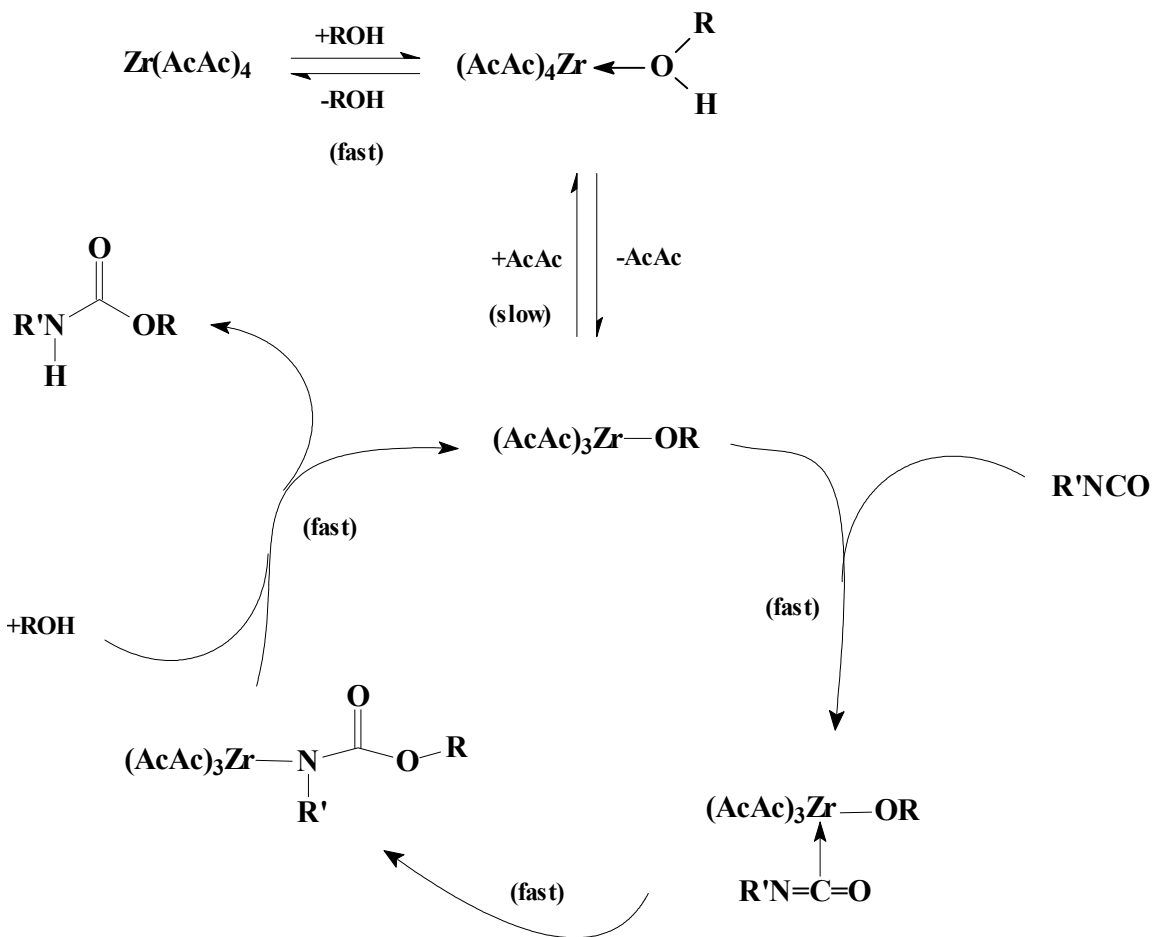
Scheme 2. Metal diketonates (a) and metal carboxylates (b)

The mechanism involving isocyanate-hydroxy catalysis is not yet fully understood. A Lewis acid mechanism (activating isocyanate) was proposed for commonly used organo-tin catalysts, such as DBTDL. The mechanism involves polarization of the carbonyl in isocyanate by the Lewis acid (organotin compound) and followed by nucleophilic attack of the hydroxyl groups (Scheme 3).^{4,12} It is also generally believed that amine catalysts function as Lewis bases to facilitate proton transfer (activating hydroxyl groups).^{3,4} The well known synergistic effect between organotin catalysts and tertiary amines is consistent with this mechanism. No significant catalytic synergy was observed between zirconium diketonate catalyst and tertiary amines.¹³ Our previous proton NMR studies found no evidence of any interactions between isocyanate and zirconium diketonate while the same NMR studies showed complex formation between hydroxyl and zirconium diketonate.¹¹ The proton NMR of butanol in the presence of a zirconium diketonate clearly showed peak broadening at room temperature and peak splitting at -50 °C, indicating a complex formation. The proton NMR of zirconium diketonate with water also showed some interaction at room temperature, but at a much lower degree than with butanol. An insertion mechanism which involves activation of hydroxyl by zirconium diketonate followed by insertion of isocyanate was proposed (Scheme 4).¹¹ Other metal diketonates may follow a similar mechanism to catalyze the

isocyanate-OH reaction. Alcoholysis of metal diketonate was suggested to be the first step in a ferric diketonate catalyzed urethane reaction.^{14,15} If this proposed insertion mechanism is indeed correct, the difference between the interactions of the zirconium diketonate with hydroxyl vs. water should lead to reaction selectivity of this zirconium diketonate. On the other hand, the reactivity difference between reactions of isocyanate with zirconium diketonate-OH complex and with zirconium diketonate-H₂O complex may also contribute to the high selectivity.



Scheme 3. Proposed mechanism of Lewis acid catalyzed isocyanate-OH reaction.



Scheme 4. Proposed insertion mechanism of Zr diketonate catalyst. AcAc = acetylacetone

Comparison of zirconium diketonate and DBTDL in water borne formulations

A commercially available zirconium diketonate catalyst (ZrCAT)¹⁶ was used in this part of the investigation. Its typical properties are shown in Table 1.

Table 1. Typical properties of a commercial zirconium catalyst (ZrCAT)

Appearance	Clear liquid
Nonvolatile, 60 min at 110 °C	95%
Gardner color	2
Viscosity, 25 °C, cps	100
Specific gravity, 25 °C, g/mL	0.98
Zr metal, %	0.38

One of the difficulties in catalyzing 2K water borne formulations is catalyst deactivation due to hydrolysis, pigment adsorption and/or interactions with other ingredients or impurities in the water containing component. Zirconium diketonate will hydrolyze over time in the presence of water. It is also sensitive to free carboxylic acid, phosphoric acid and sulfuric acid. To avoid catalyst deactivation, the zirconium diketonate catalyst can be blended into the isocyanate component. Figure 6 shows the stability of the zirconium diketonate catalyst in an HDI trimer. After 2 weeks at 50 °C, the viscosity, color and reactivity of the isocyanate solution remain virtually unchanged. The zirconium diketonate catalyst was also found to be stable in a number of other commercial isocyanate prepolymers including a hydrophilic modified version. The zirconium diketonate catalyst is completely compatible with polyisocyanate and only requires minimum agitation to be blended with low viscosity polyisocyanates. Some mechanical agitation might be required to blend it with some 100% solids isocyanate prepolymers due to their high viscosity at room temperature.

a) Catalyst comparison in a water reducible polyester dispersion/isocyanate formulation

The zirconium diketonate catalyst was formulated in a 2K waterborne polyurethane clear coating formulation based on a polyester dispersion (Table 2). DBTDL was used for comparison. This is a low VOC and high gloss formulation. The high solids of this formulation allows thicker film build up. The amount of isocyanate on total resin solids is high and regular HDI trimer without hydrophilic modification was used. This formulation dries very slowly in the absence of a catalyst. The zirconium diketonate catalyst not only improves the dry time substantially, but also reduces gassing/foaming and extends the pot life. It was previously reported that the viscosity change of 2K water borne polyurethane formulations does not correlate with its pot life.¹⁷

Even though the viscosity of this formulation increases with aging, gloss reduction on aging is a better indication of the pot life. The coatings were applied at different time intervals after the two components were mixed and the film gloss was determined as a measure of pot life. As the data in Table 2 show, the DBTDL catalyzed formulation had a pot life of less than 1/2 hour while Zr diketonate catalyzed formulation had a pot life of over 3 hours. The zirconium diketonate catalyzed formulation even had less gassing/foaming in the pot than the uncatalyzed control.

The coatings were also applied at different levels of relative humidity (RH) to see the effect on film properties. When the relative humidity is low (23%), the films with different catalysts applied immediately after mixing did not show much difference. However, at high humidity (70%), the film catalyzed with zirconium diketonate catalyst showed much better gloss. At extremely high humidity (90%), all the films were virtually flat and catalysts made no difference. The higher humidity also affects the cure response, especially for uncatalyzed formulations.

Table 2. Catalyst comparison in a 2K waterborne polyester dispersion/isocyanate coating
2a. Formulation

Weight, %	Control	ZrCAT	DBTDL
Part A			
Polyester dispersion ¹⁸	41.3	41.3	41.3
Water	9.3	9.3	9.3
Wetting agent ¹⁹	0.2	0.2	0.2
DBTDL	0.0	0.0	0.04
Part B			
HDI trimer ²⁰	38.1	38.1	38.1
ZrCAT	0.0	1.3	0.0
Water	11.1	9.8	11.1
Total	100.0	100.0	100.0

Formulation Properties

Solids, % 67
 NCO/OH ratio 1.3
 pH 7.0

2b. Cure response on aluminum panels, 1.0 mil dry film thickness

	No catalyst	ZrCAT	DBTDL
At 66 °F, 23 % Relative humidity			
Surface dry time, hours	6.0	3.7	3.5
Through dry time, hours	8.0	4.7	4.5
At 66 °F, 70 % Relative humidity			
Surface dry time, hours	8.0	4.0	3.8

Through-dry time, hours	12.0	5.0	4.8
-------------------------	------	-----	-----

2c. Film gloss vs. aging and relative humidity, 2.5 mil dry film thickness on aluminum

20 ° Gloss (%) vs. aging (t) at 66 °F, 23 % RH,	No catalyst	ZrCAT	DBTDL
t=0	70.3	94.9	94.7
t= 30 min	72.1	94.8	55.7
t=1 hour	77.2	94.6	foaming
t=2.5 hours	foaming	88.3	
t= 4 hours		77.5	
Gloss at 66 ° F, 70 % RH, 2.5 mil dry film thickness			
Gloss 60 °, %, t=0	82.8	88.6	81.7
Gloss 20 °, %, t=0	56.5	63.3	36.9

b) Catalyst comparison in an acrylic emulsion/isocyanate 2K waterborne formulation

The zirconium diketonate catalyst was also compared with DBTDL in an acrylic emulsion 2K waterborne formulation. This formulation had a short surface dry time due to fast physical drying (evaporation of water and solvents). A hydrophilic modified isocyanate prepolymer was used for better mixing. A small amount of cosolvent will help the coalescence of the acrylic emulsion. The catalysts had a less effect on the drying properties since the film requires no crosslinking for physical drying. Both the zirconium diketonate catalyst and DBTDL, however, did improve surface dry time. Again, the zirconium diketonate catalyst showed improved 20° gloss.

Table 3. Catalyst comparison of an acrylic emulsion 2K polyurethane coating

3a. Formulations

Part A	Weight, %
Acrylic emulsion ²¹	83.3
Dipropylene glycol dimethyl ether	1.9
Wetting agent ²²	0.1
Leveling agent ²²	0.3
Defoamer ²²	0.1
Thickner ²²	1.0
Part B	
Hydrophilic modified Polyisocyanate ²³	13.3
Catalysts:	
<ul style="list-style-type: none"> • DBTDL added in polyol side • ZrCAT added in isocyanate side 	0.008% metal on TRS

Total	100.0
-------	-------

3b. Film properties. Substrate: aluminum panels; Dry film thickness: 1.6 mils; Cure conditions: 70 °F, 25 % relative humidity.

	<u>No catalyst</u>	<u>ZrCAT</u>	<u>DBTDL</u>
NCO/ OH ratio	2.0	2.0	2.0
Resin solids content, %	48	48	48
Surface dry, min.	20	15	15
Through dry, min.	35	20	20
<u>Gloss vs. aged time</u>			
Aging before application	30 min	30 min	30 min
Gloss 20°, %	75	95	80
Aging before application	7 hours	7 hours	7 hours
Gloss 20°, %	65	85	68

CONCLUSIONS

The selectivity of isocyanate-hydroxy reaction over isocyanate-H₂O reaction for a number of metal carboxylates and diketonates has been investigated via an FT-IR method. Catalysis of the isocyanate reactions was found to be critical for the reaction selectivity. A zirconium diketonate catalyst with unusually high selectivity showed less gassing/foaming, longer pot life and higher gloss than dibutyltin dilaurate in two component waterborne polyurethane coatings.

ACKNOWLEDGMENT

We would like to thank David Malkin for his contributions to the FT-IR selectivity studies, John Florio for suggestions and application information, Dr. Ed Hessell for the mechanism investigations, Dr. Len J. Calbo for his assistance in proof reading the paper and King Industries Inc. for the opportunity to publish this work.

¹ P. Jacobs, K. Best, M. Dvorchak, M. Shaffer, T. Wayt, P. Yu "Two-Component, Waterborne Polyurethane Coatings: Now and Into the Next Century", Paint and Coatings Industry, October, 1998, p. 117.

² S.L. Bassner and C.R. Hegedus "A Review of Two-Component Water-Borne Polyurethane Coatings for Industrial Applications", J. Protective Coatings and Linings, Sept. 1996, p. 52.

³ Z.W. Wicks, F.N. Jones and S.P. Pappas "Organic Coatings, Science and Technology", John Wiley & Sons, NY, Vol. 1, 1992, p. 194.

⁴ L. Thiel and R. Becker "Catalytic Mechanism of Polyurethane Formation", Adv. In Urethane Science and Technology, Ed. K.C. Frisch and D. Klempner, 12, 1993, p. 59.

⁵ E.P. Spiller, J.W. Rosthauser "Catalysis in Aliphatic Isocyanate-Alcohol Reactions", Water-Borne, Higher Solids Coatings Symposium, New Orleans, Feb. 1987, p. 460.

-
- ⁶ S.D. Seneker and T.A. Portter “Solvent and Catalyst Effects in the Reaction of Aliphatic Isocyanate with Alcohols and Water”, Water-Borne, Higher Solids Coatings Symposium, New Orleans, Feb. 1989, p. 369.
- ⁷ D. Ihms and J.O. Stoffer “Effect of Catalysts on the Kinetics of the Water-Toluene Diisocyanate Reaction”, JCT, Vol. 57, No. 722, March 1985, p. 61.
- ⁸ V.J. Tramontano and W.J. Blank “Novel Water Borne Polyurethane Dispersions: Advances in Ambient Crosslinking with Polyisocyanates”, Water-Borne, Higher Solids and Powder Coatings Symposium, New Orleans, Feb. 1995, p. 246.
- ⁹ J. March “Advanced Organic Chemistry”, John Wiley & Sons, NY, 1992, p.493.
- ¹⁰ J. Florio “Non-Tin Metal Catalysts for Urethane Coatings” Paint and Coatings Industry, October, 1997, p. 110.
- ¹¹ W.J. Blank, Z.A. He and E.T. Hessel “Catalysis of the Isocyanate-Hydroxyl Reaction by Non-Tin Catalysts”, Proceedings of 24th International Conference in Organic Coatings. Athens Greece, 1998.
- ¹² S.C. Reegen and K.C. Frisch, J. Polym. Sci., A-1 Part, 1970, p.2883.
- ¹³ Unpublished King Industries’ experimental results.
- ¹⁴ R.S. Bruemmer and A.E. Oberth “On the Mechanism of Metal Chelate Catalysis in the Reaction between Alcohols and Isocyanates”, J. Org. Chem., 31, 1966, p. 887.
- ¹⁵ R.A. Ligabue, A.L. Monteiro, R.F.de Spuza and M.O. de Souza “Catalytic properties of Fe(acac)₃ and Cu(acac)₂ in the formation of Urethane from a Diisocyanate Derivative and EtOH”. J. of Molecular Catalysis A: Chemical, 130, 1998, p. 105.
- ¹⁶ K-KAT XC-6212 From King Industries, Inc.
- ¹⁷ C. J. Boudreaux, K. Arora, E. Nowicki, D. Devore, S. Shah, Y. Zhong, A. Niroomand, P.L.K. Hung and G. Roy “Waterborne 2K Acrylic Polyurethanes: Novel Low NCO/OH Systems”. Water-Borne, Higher Solids and Powder Coatings Symposium, New Orleans, Feb. 1998, p. 120.
- ¹⁸ Adura 100, 70% solids polyester dispersion from Air Products and Chemicals, Allentown, PA.
- ¹⁹ Metolat 355, wetting agent from Munzing Chemie Germany (Distributed by King Industries, Inc.).
- ²⁰ Desmodur N-3300, HDI isocyanurate trimer from Bayer Corporation, Pittsburgh, PA, Isocyanate equivalent weight 183.
- ²¹ Roshield 3275 (42%NV), acrylic emulsion from Rohm and Haas Company, PA.
- ²² Wetting agent: Agitan 288, leveling agent: Edaplan LA-402, Defoamer: Agitan 315 and thickener: Tafigel PUR 60, from Munzing Chemie, Germany (Distributed by King Industries, Inc.).
- ²³ Bayhydur XP-7063 Hydrophilic modified polyisocyanate from Bayer Corporation, Pittsburgh, PA.
- ²⁴ Tolonate HDT-LV from Rhodia Inc., NJ.

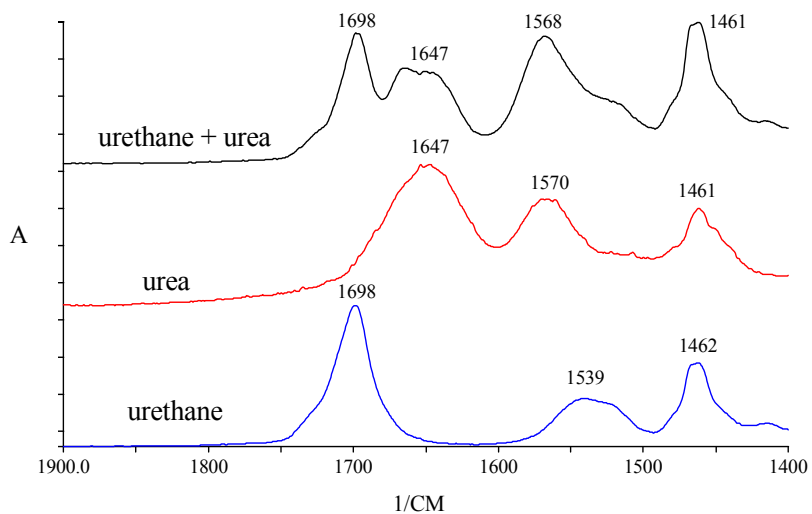


Figure 1. Peak assignments of FT-IR spectrum of urethane/urea mixture

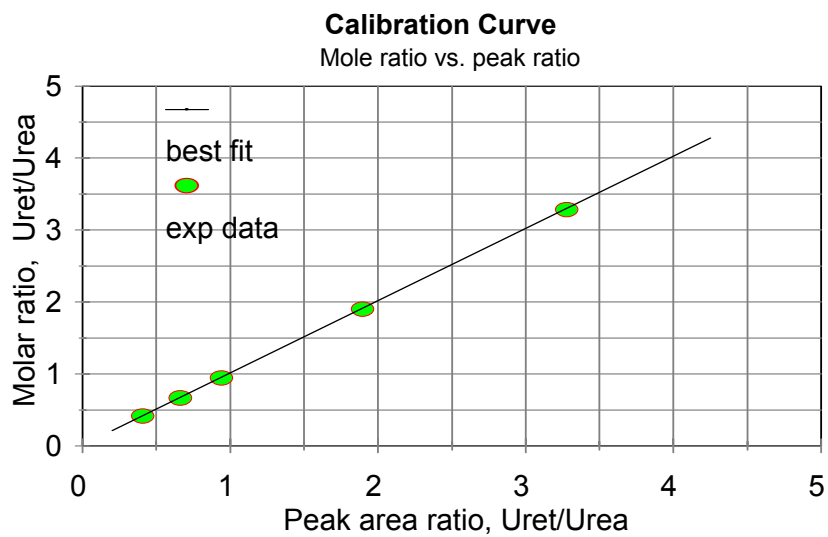


Figure 2. Calibration curve of urethane/urea molar ratio vs. peak area ratio

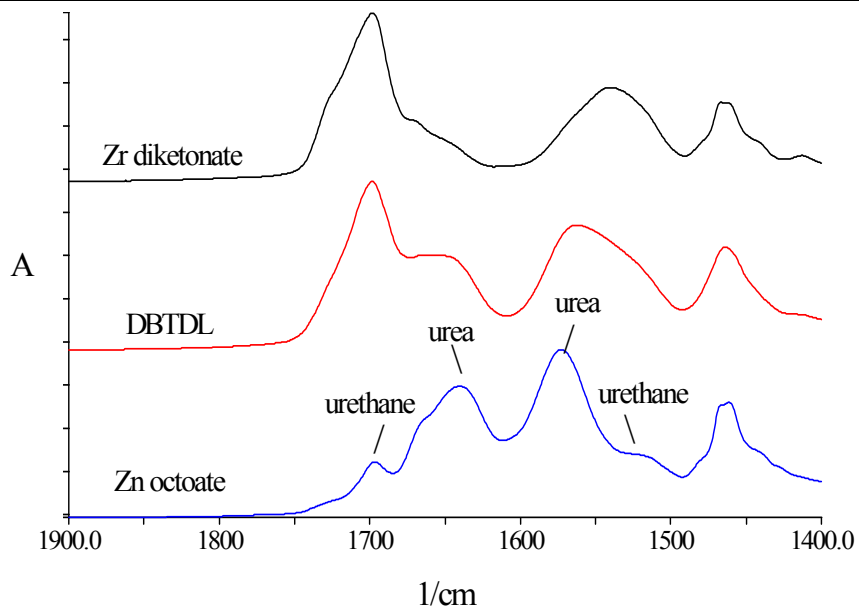


Figure 3. Typical FT-IR spectra of catalyzed urethane/urea formation, NCO/OH/H₂O = 1.0/1.0/2.0

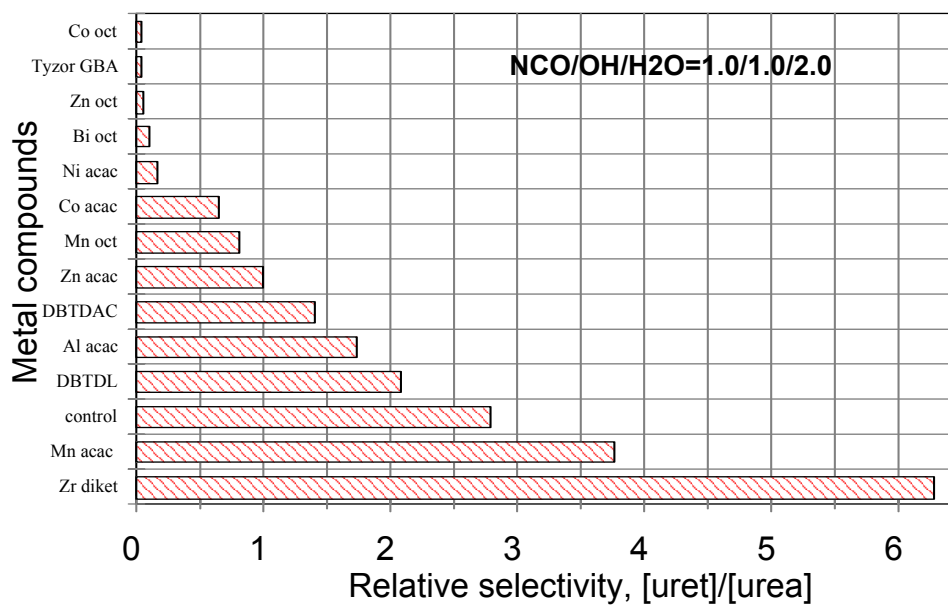


Figure 4. Selectivity comparison of metal catalysts. Acac: acetylacetonate, diket: diketonate, oct: octoate, DBTDAC: dibutyltin diacetate, Tyzor GBA: acetylacetonate titanate chelate.

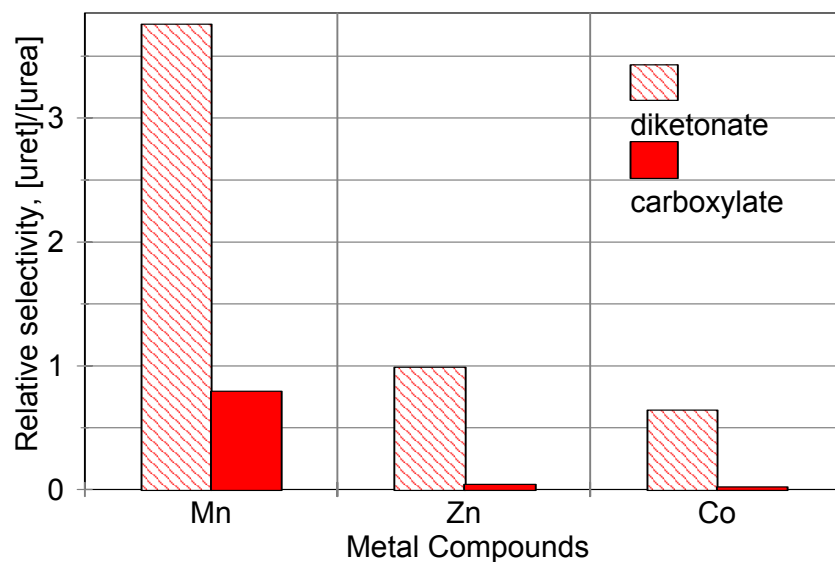


Figure 5. Selectivity comparison of metal carboxylates and metal diketonates

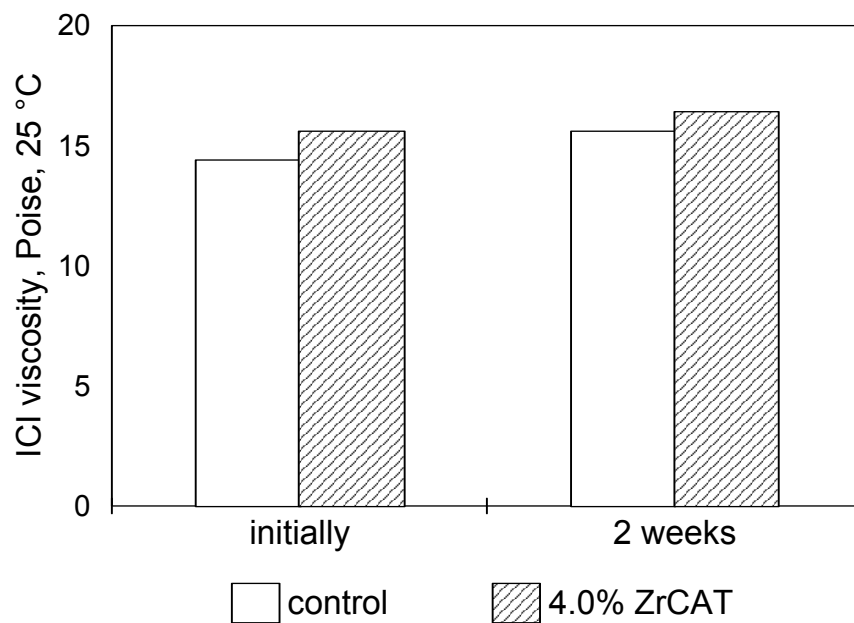


Figure 6. Stability of ZrCAT in an HDI trimer:²⁴ After aging at 50 °C for two weeks