A Selective Catalyst for Two-Component Waterborne Polyurethane Coatings
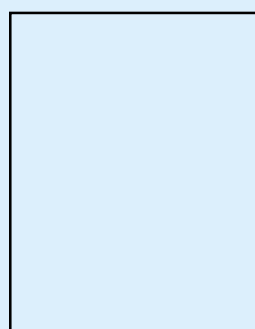
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INTRODUCTION

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 waterborne 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 CO_2 also lowers the pH of the emulsion or dispersion which can reduce the stability of the waterborne 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.
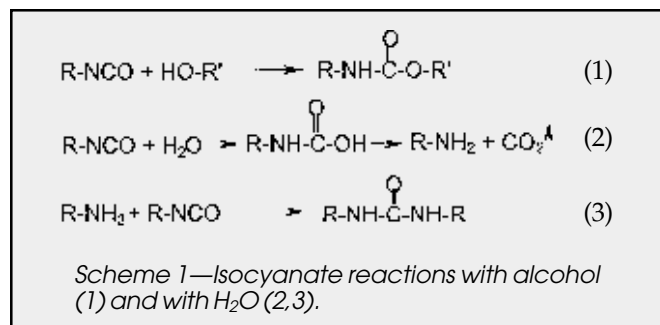
The reactions of isocyanate, especially aliphatic isocyanate, with hydroxyl or water are relatively slow at ambient temperature in the absence of a catalyst. Organo metallic compounds or tertiary amines are normally needed to catalyze the crosslinking of isocyanate with hydroxyl groups for ambient cure applications.[3-5] It is possible to control the 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

The potential for formulating low VOC, high performance, two-component waterborne isocyanate crosslinked coatings has generated a great deal of 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 FTIR method. A zirconium complex has shown unusually high selectivity for the isocyanate-polyol reaction in comparison to the standard dibutyltin dilaurate catalyst. This zirconium complex catalyst has been evaluated in several waterborne 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.

$$R\text{-NCO} + \text{HO-R'} \longrightarrow R\text{-NH-}\overset{O}{\underset{||}{C}}\text{-O-R'} \qquad (1)$$

$$R\text{-NCO} + H_2O \longrightarrow R\text{-NH-}\overset{O}{\underset{||}{C}}\text{-OH} \longrightarrow R\text{-NH}_2 + CO_2\uparrow \qquad (2)$$

$$R\text{-NH}_2 + R\text{-NCO} \longrightarrow R\text{-NH-}\overset{O}{\underset{||}{C}}\text{-NH-R} \qquad (3)$$

Scheme 1—Isocyanate reactions with alcohol (1) and with H_2O (2,3).

isocycanate-H_2O 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 bis(2-methoxyethyl)ether 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 exceptionally high rate of isocyanate-H_2O reaction. It was also reported that the pKa value of an amine catalyst had a big effect on the isocyanate-water reaction. The amine catalyst with a higher pKa value showed more catalytic activity for the isocyanate-H_2O reaction.[8]

We were interested in a catalyst with high selectivity for the isocyanate-hydroxyl reaction and its applications
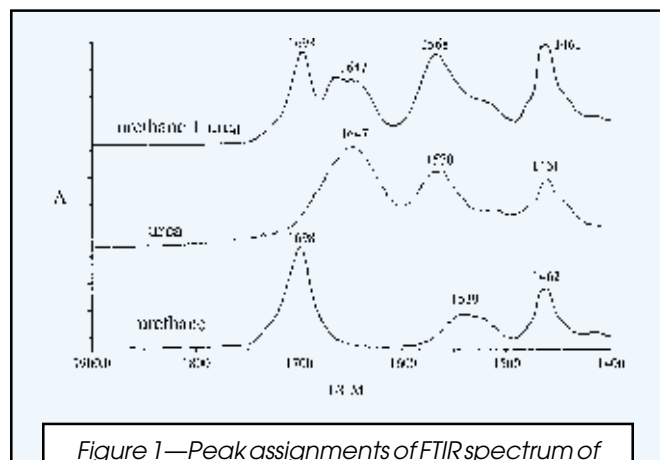

Figure 1—Peak assignments of FTIR spectrum of urethane/urea mixture.
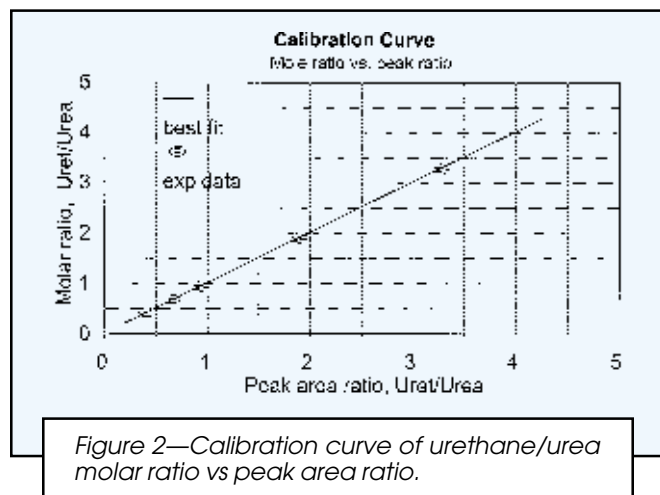

Figure 2—Calibration curve of urethane/urea molar ratio vs peak area ratio.

in two-component waterborne polyurethane formulations. The relative selectivity of a variety of metal polyurethane catalysts was determined utilizing an FTIR method. A zirconium diketonate catalyst with unusually high selectivity for the isocyanate-polyol reaction was tested with several waterborne 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 ß-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 ß-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.

FTIR Selectivity Studies

A homogeneous stock solution of H_2O 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/H_2O 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 five hours under ambient temperature (ranging from 0.005 to 0.05 metal %). The uncatalyzed reaction took over 20 hr to complete under the same conditions. After the reaction was completed (disappearance of isocyanate checked by FTIR 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 min under ambient temperature for each sample before recording the FTIR spectrum. A Perkin Elmer Spectrum 2000 spectrometer was used for recording FTIR 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

FTIR 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.).

$$S = [urethane]/[urea] \qquad (4)$$

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 FTIR spectra. *Figure* 1 shows the FTIR 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 ß-diketonates (*Scheme* 2). *Figure* 3 shows some typical FTIR spectra of reaction products of some catalyzed homogenous solutions of butyl isocyanate, 2-ethyl hexanol and H$_2$O. 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 FTIR 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/H$_2$O=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 H$_2$O 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.

Scheme 2—Metal diketonates (a) and metal carboxylates (b)
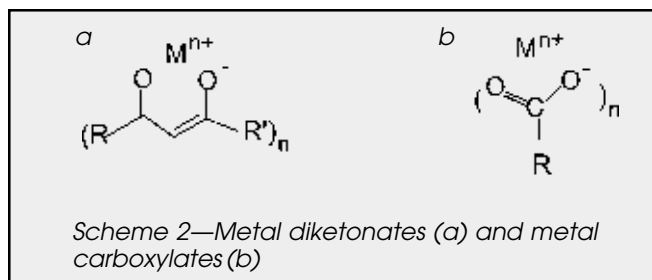
For example, zirconium diketonates are highly active while zirconium carboxylates are virtually inactive.[10,11]

The mechanism involving isocyanate-hydroxyl catalysis is not yet fully understood. A Lewis acid mechanism (activating isocyanate) was proposed for commonly used organotin 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
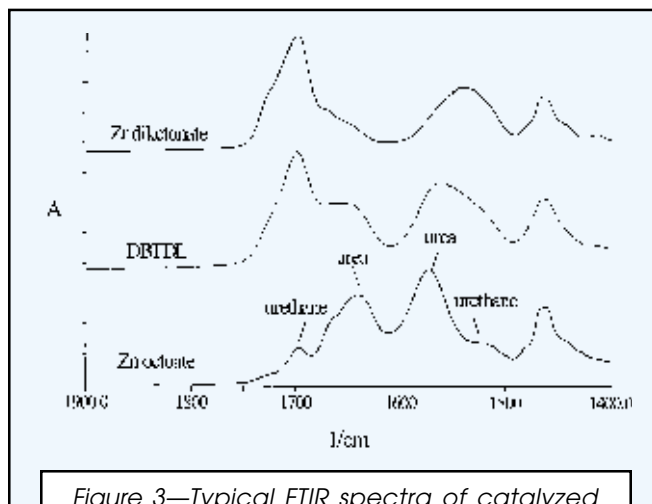
Figure 3—Typical FTIR spectra of catalyzed urethane/urea formation, NCO/OH/H$_2$O = 1.0/1.0/2.0.
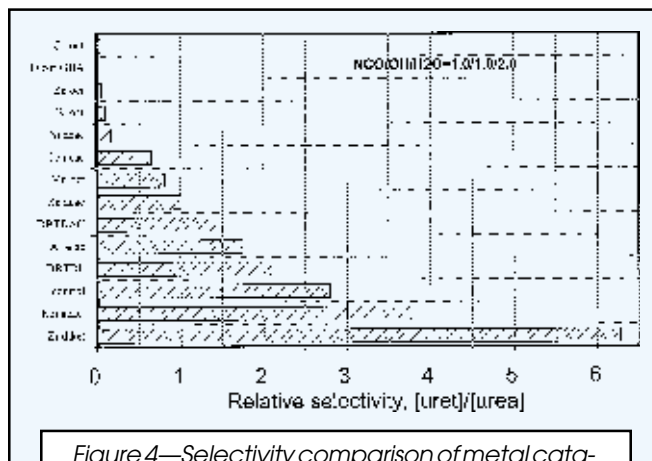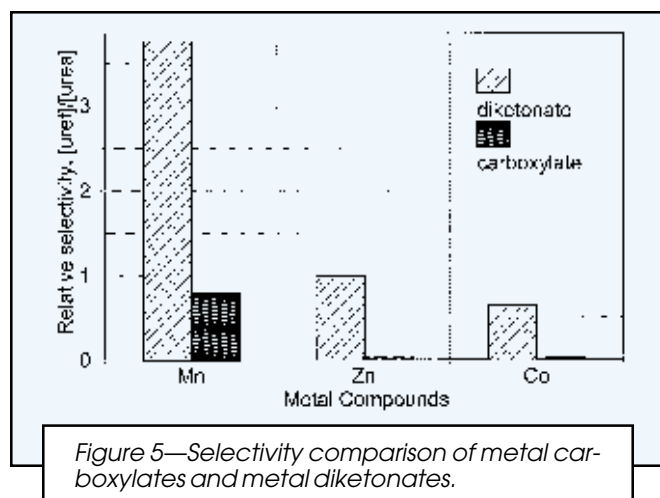
Figure 4—Selectivity comparison of metal catalysts. Acac: acetylacetonate, diket: diketonate, oct: octoate, DBTDAC: dibutyltin diacetate, Tyzor GBA: acetylacetonate titanate chelate.

Figure 5—Selectivity comparison of metal carboxylates and metal diketonates.

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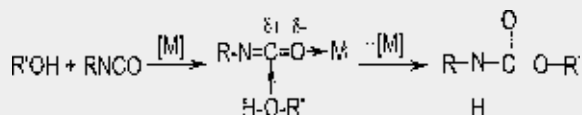
Scheme 3—Proposed mechanism of Lewis acid catalyzed isocyanate-OH reaction.

Scheme 4—Proposed insertion mechanism of Zr diketonate catalyst. AcAc = acetylacetone
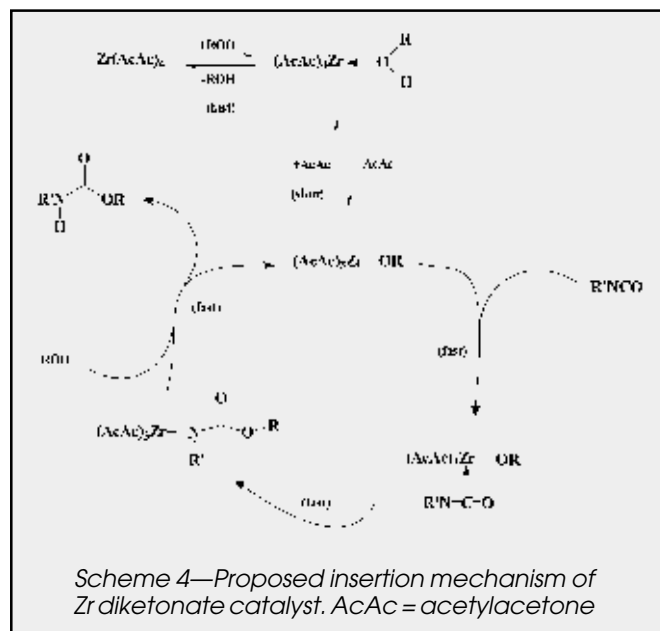
showed some interaction at room temperature, but at a much lower degree than with butanol. An insertion mechanism which involves activation of hydroxyl by zirconium diketonate followed by insertion of isocyanate was proposed (*Scheme* 4).[11] Other metal diketonates may follow a similar mechanism to 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-H_2O complex may also contribute to the high selectivity.

Comparison of Zirconium Diketonate and DBTDL in Waterborne 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.

One of the difficulties in catalyzing 2K waterborne 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 two 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.

Figure 6—Stability of ZrCAT in an HDI trimer[24] after aging at 50°C for two weeks.
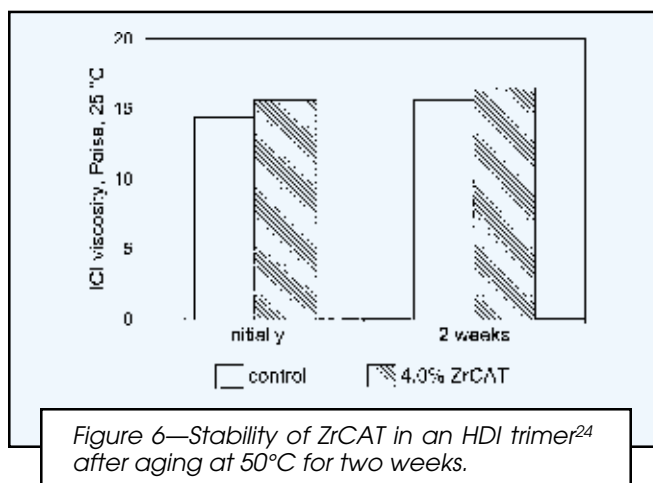
Table 1—Typical Properties of a Commercial Zirconium Catalyst (ZrCAT)

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

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 allow 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 waterborne 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 one-half hour while Zr diketonate catalyzed formulation had a pot life of over three 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.

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 (*Table* 3). 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 did improve surface dry time. Again, the zirconium diketonate catalyst showed improved 20° gloss.

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
<u>Formulation Properties</u>			
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, hr	6.0	3.7	3.5
Through dry time, hr	8.0	4.7	4.5
At 66°F, 70% relative humidity			
Surface-dry time, hr	8.0	4.0	3.8
Through-dry time, hr	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 hr	77.2	94.6	foaming
t=2.5 hr..	foaming	88.3	
t= 4 hr		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

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
Thickener[22]	1.0

Part B	
Hydrophilic modified polyisocyanate[23]	13.3
Catalysts:	
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.

	No catalyst	ZrCAT	DBTDL
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
Gloss vs aged time			
Aging before application	30 min	30 min	30 min
Gloss 20°, %	75	95	80
Aging before application	7 hr	7 hr	7 hr
Gloss 20°, %	65	85	68

CONCLUSIONS

The selectivity of isocyanate-hydroxyl reaction over isocyanate-H_2O reaction for a number of metal carboxylates and diketonates has been investigated via an FTIR 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

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(18) Adura 100, 70% solids polyester dispersion from Air Products and Chemicals, Allentown, PA.

(19) Metolat 355, wetting agent from Munzing Chemie, Germany.

(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.

(23) Bayhydur XP-7063 Hydrophilic modified polyisocyanate from Bayer Corporation, Pittsburgh, PA.

(24) Tolonate HDT-LV from Rhodia Inc., NJ.