Macromol. Symp. ***187**, 261–270 (2002)*

New Developments in Catalysis

Werner J. Blank

King Industries, Inc. Norwalk Ct, 06897 Science Road USA

wblank@kingindustries.com, www.wernerblank.com

Summary: Environmental, safety and health concerns are major driving forces for the development of new coating systems, which in turn require catalysts with a different performance profile. One critical area for the development of new catalysts is the replacement of organotin compounds in polyurethanes with environmentally friendly catalysts, such as bismuth, aluminum and zirconium chelates. For applications in epoxies new catalysts for the epoxy-carboxyl reaction are also being developed. To gain the needed improved performance multiple cure mechanisms are being employed in coatings requiring dual action catalysts.

Introduction

New developments in the industrial coating market are driven by environmental regulations, worker safety, energy concerns and the need for improved performance. These problems are being addressed by the development of low volatile organic content (VOC) coating systems. Differences in regulations between countries have created a highly fragmented line of attack to these problems.

In isocyanate and blocked isocyanate crosslinked coatings organotin compounds are the primary catalysts used. New regulations require the replacement of these versatile catalysts with organotin-free candidates. High solids, solvent-free coatings, powder coatings and waterborne coatings have distinctly different application and cure characteristics, which are dissimilar from low solids coatings. Often existing chemistry cannot meet these application and performance requirements. A combination of different crosslinking chemistries is used to upgrade coating properties.

Coating Technologies under Development

System	Challenge
High solids, solvent-free	Viscosity/non-volatile, cure response, stability
Waterborne	Stability, co-solvents, reactivity, amine
Electrocoating	Co-solvents, cure temperature
Powder	Film thickness, reaction temperature, flow-leveling
UV/Electron beam	Pigments, complex shapes

CCC 1022-1360/00/$ 17.50+.50/0

Catalysts for Isocyanate Crosslinking

Dibutyltin dilaurate (DBTDL) is the typical catalyst used for aliphatic isocyanates in both 2K isocyanate and blocked isocyanate crosslinked coatings. Because of environmental concerns, however there is a need for alternate catalysts.

Table 1 shows the periodic table and the elements, which according to the literature and our own screening studies[1,2], are active catalysts for the isocyanate reaction.

Table 1.Periodic Table

1	**1A**	**2A**											**3A**	**4A**	**5A**	**6A**	**7A**	**8A**
2	3 Li	4 Be											5 B	6 C	7 N	8 O		
3	11 Na	12 Mg	**3B**	**4B**	**5B**	**6B**	**7B**	|------	**8B**	------|	**1B**	**2B**	13 Al	14 Si	15 P	16 S		
4	19 K	20 Ca		22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga					
5		38 Sr		40 Zr				44 Ru	45 Rh					50 Sn	51 Sb	52 Te		
6		56 Ba	57 La	72 Hf		74 W	75 Re	76 Os				80 Hg		82 Pb	83 Bi	84 Po		

The metals were tested as the carboxylate salts, sulphonate salts or as dionate complexes.

We selected zirconium, bismuth and zinc compound for a detailed reaction study and compared their catalytic activity to DBTDL. The results are shown in Figure 1.

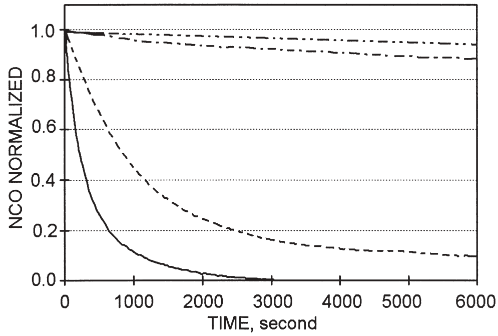

Figure 1. Reaction of 1,6-hexamethylene diisocyanate trimer with n-butanol (1.12 mol/l NCO) in xylene. Molar ratio NCO/OH 1/1. Catalyst 0.014 % metal on total reactant. Catalyst conc.: ----- DBTDL; —— Zr Chelate; – · – Bi carboxylate; —··—· Zn octoate.

The disappearance of the IR isocyanate band at 2272 cm^{-1} wave number is a simple tool to determine the reaction rate. Under the reaction conditions shown a zirconium dionate complex shows substantially higher catalytic activity on a metal basis in comparison to DBTDL, bismuth carboxylate and zinc octoate catalyst.

In the next experiments because of the low reaction rate with bismuth and zinc catalysts the level of catalyst was increased.

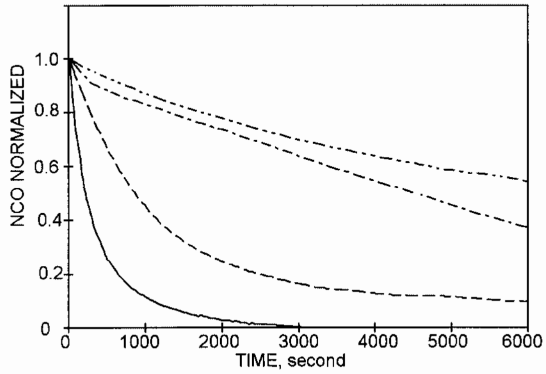

Figure 2. Reaction of 1,6-hexamethylene diisocyanate trimerwith n-butanol. (1.12 mol/l NCO) in xylene. Molar ratio NCO/OH 1/1. Catalyst conc.: ----DBTDL 0.014 % Sn; ——Zr Chelate 0.014 % Zr; –·– Bi carboxylate 0.13 % Bi; —··– Zn octoate 0.27 % Zn on total reactants.

The results in Figure 2 illustrate, that under the reaction conditions shown both Zr chelate and DBTDL are faster catalysts than bismuth or zinc carboxylates. A faster catalyst is not necessarily superior in a coating formulation. Potlife, pigment absorption, application properties, selectivity of hydroxyl over water reaction and durability have to be considered.

We were also interested how reaction rates of catalysts vary with different functional groups. We used the catalyst concentration shown in Figure 2 for the additional experiments. As functional compounds, we selected the hydroxyl compounds shown in Table 2.

Table 2. Hydroxyl Compounds used in Reaction Rate Study

Compound	Characteristics
n-Butanol	Primary hydroxyl group, no steric hindrance
Isobutanol	Primary hydroxyl group, some steric hindrance
2-Butanol	Secondary hydroxyl group
2-Butoxyethanol	Primary β-hydroxylethyl ether group
2-Hydroxyethyl ester (HEE)	Primary hydroxyl, model for polyester
2-Hydroxyethyl carbamate (HEC)	Primary hydroxyl, polyurethane diol
Methoxtripropylene glycol (TPM)	Sec. hydroxyl, model for polypropylene glycol

Figure 3 shows the half-life of DBTDL, Zr Chelate, Bi carboxylate and Zn octoate as measured by the catalyzed reaction of 1,6-hexamethylenediisocyanate trimer with the alcohols shown in Table 2.

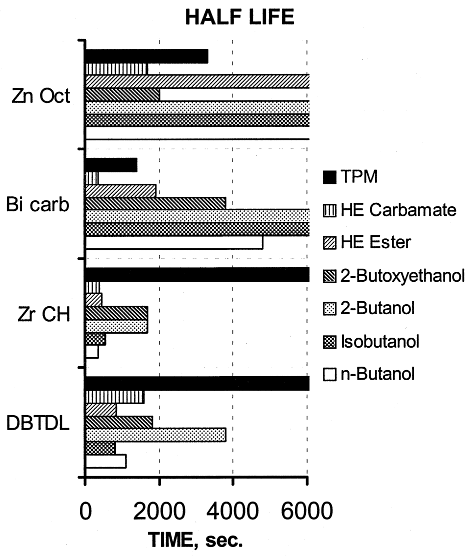

Figure 3. Half-life isocyanate concentration of 1,6-hexamethylene diisocyanate trimer with alcohols. (1.12 mol/l NCO) in xylene. Molar ratio NCO/OH 1/1. Catalyst concentration: DBTDL 0.014 % Sn; Zr Chelate 0.014 % Zr; Bi carboxylate 0.13 % Bi; Zn octoate 0.27 % Zn on total reactants.

Half-life of the isocyanate concentration was calculated from the rate equation of isocyanate/time as determined by FT-IR. DBTDL catalyzes as expected, giving high reaction rates with primary alcohols. Even within the group of primary alcohols there are significantly different reaction rates. Secondary OH, as in 2-butanol, reacts substantially slower. TPM, a model for polypropylene glycol gives a very slow reaction rate. The Zr chelate gives substantially faster reaction with primary OH. 2-Butoxyethanol and 2-butanol are slower and TPM essentially deactivates the catalyst. The relative rates with bismuth are rather surprising. Neighboring groups have a substantial effect on reaction rate. Steric effects and secondary hydroxyl groups do not influence the reaction rate as much.

Conclusions for Isocyanate Catalysts

Many metal compounds can catalyze the reaction of isocyanates with hydroxyl groups. DBTDL is a very effective catalyst for the reaction of isocyanate with hydroxyl compounds. The notion of primary hydroxyls reacting faster with isocyanates is confirmed using DBTDL as a catalyst. But not all primary hydroxyl groups are equal in reaction rate. As shown in Figure 3, neighboring groups such as ether, ester or carbamate groups have a substantial effect on reaction rate.

Reaction rates with Zr chelate catalyst are substantially higher with all primary hydroxyl functional compounds with the exception of 2-butoxyethanol. Secondary hydroxyls are substantially slower. With TPM we see an almost complete inhibition of reaction.

With bismuth carboxylate catalyst the results are rather surprising, since neighboring groups have a substantial effect on reaction rate. The general rule of higher reaction rate with primary hydroxyl groups does not apply. Carbamate, ester and ether groups in the β position give superior reaction rates. Even secondary hydroxyl functional polyethers are faster reacting than primary hydroxyl compounds. This raises some interesting questions about the mechanism for the bismuth-catalyzed formulations. Generally it is been thought that bismuth functions as a Lewis acid catalyst and activates the isocyanate groups. Although zinc is a weak catalyst for the isocyanate reaction, we again see that neighboring groups affect catalysis. Ether and carbamate groups assist in increasing reaction rate, but ester groups have no effect.

Catalysis of Blocked Isocyanates

For many blocked isocyanates an elimination-addition mechanism is indicated[3] as shown in EQ. 1. The overall reaction rate depends on k_1, k_{-1} and k_2, k_{-2} and the volatility of the blocking agent, (Bl-H). Prior art suggests that catalysts only affect k_2 but not the deblocking reaction (k_1, k_{-1}). For a number of blocked isocyanates a displacement reaction[4,5,6] appears to be the predominate mechanism (Eq. 3). DBTDL is an excellent catalyst for both the isocyanate-hydroxyl and also for the displacement (transesterification) reaction. If indeed catalysis of the isocyanate-hydroxyl reaction determines the rate, there should be little difference in their catalytic activity between catalysts for 2K and blocked isocyanate coatings.

$$\text{R-NHCOO-Bl} \xleftrightarrow[k_{-1}]{k_1} \text{R-NCO} + \text{Bl-H} \qquad \text{EQ (1)}$$

$$\text{R-NCO} + \text{R'-OH} \xleftrightarrow[k_{-2}]{k_2} \text{R-NHCOOR'} \qquad \text{EQ (2)}$$

$$\text{RNHCOOR'} + \text{R''OH} \xleftrightarrow[k_{-3}]{k_3} \text{RNHCOOR''} + \text{R'OH} \uparrow \qquad \text{EQ (3)}$$

Comparative cure studies[7] of the catalysts used in Figure 3 and also Table 1 show that many catalysts that are effective in 2K formulations do not perform in blocked isocyanates. Deactivation of the catalyst[8] due to hydrolysis during cure and the loss of the ligands (carboxylate or dionate) are just some of the problems encountered during cure of blocked isocyanates. (Eq. 4), Table 4.

$$\text{R-COOMe}^{(a)} + H_2O \longleftrightarrow \text{MeO (OH)} + \text{R-COOH} \qquad \text{EQ (4)}$$

(a) Metal moiety

Table 3 shows the active catalysts for blocked isocyanates[9]. For the blocking agents ketoxime, 3,5-dimethyl-1H-pyrazole, e-caprolactam, phenol and malonate, a 1,6-hexamethylenediisocyanate trimer was used as isocyanate. For the alcohol[10] blocked isocyanate a polymethylene polyisocyanate was used. For these tests either the 2-ethylhexanoate, laurate or naphthenate salts of metals were used. 1,5-Diazobicyclo [4.3.0] non-5-ene (DBN) and 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) were used as the amine catalysts. For malonate blocked isocyanates, which crosslinks via a transesterification reaction[11] no effective catalyst was found.

Table 3. Catalysis of Blocked Isocyanates

Blocking Agent	Temperature, °C	Catalyst
Ketoxime	130-150	Bi, Co, Cr (III), DBTDL, Zn, Ca,
3,5-Dimethylpyrazol	120-140	DBTDL, Bi, Co, Cr, Zn
Caprolactam	150-170	Zn, DBTDL, Co, Bi
Phenol	120-140	Zn, Mn, Bi, DBTDL, Ca, Cr (III)
Alcohol	150-170	Bi, Co, Zn, DBTDL,
Uretdione	170-200	Zn, Bi, DBTDL, Sn (II), DBN, DBU
Malonate	100-120	No effective catalyst

Table 4 shows the effect of ligands on the methylethylketone (MEK) resistance of a cationic electrocoating resin and a polymethylphenyl polyisocyanate blocked with 2-butoxy(2-ethoxyethyanol) and cured at different temperatures for 20 minutes. Metal concentration in the formulation was 0.25 % based on total binder. The incorporation method for certain metal catalysts was found important for catalyst effectiveness. Bismuth carboxylate catalysts are known to hydrolyze in water. We added the bismuth carboxylate catalyst to the solvent-free cationic resin/blocked isocyanate crosslinker and emulsified this system in water. We propose that the bismuth carboxylate catalyst hydrolyses in this formulation and forms nano particles of bismuth oxide. During heating to >120°C the bismuth carboxylate catalyst reforms.

Table 4. Bismuth Catalyst Effects of Ligands on Reaction Temperature (MEK double rubs)

Catalysts/ temperature of cure	180° C	170 ° C	165° C
No catalyst	10	10	10
Dibutyltin dilaurate	63	30	10
Bismuth tris(2-ethylhexanoate)	150	70	20
Bismuth tris(isostearate)	200	150	20
Bismuth dimeric fatty acid	200	70	13
Bismuth tris(oleoyl sarcosine)	200	150	70

Epoxy Catalysts

Epoxy chemistry is important in low VOC coatings because of the absence of volatile reaction products and the excellent resistance properties that can be obtained. There is an interest in epoxy/carboxyl systems used in powder coatings and high solids coatings to improve the formulation stability, cure response and resistance properties. Traditional amine and phosphonium catalysts have deficiencies in yellowing, storage stability and resistance properties. We screened[12] a range of known amine catalysts, metal dionate complexes, carboxylate, phosphate and sulfonate salts in glycidylether and glycidylester/carboxyl formulations for cure response, stability and film properties. The metal catalysts evaluated were from the group of Al, Bi, Ca, Ce, Co, Cr(III), Fe, Mg, Mn, Ni, Sn(II), organotin, Ti, Zn and Zr compounds. Only Zn, Co, Mg, Sn(II) and Zr compounds showed activity. Generally the ligands had an effect on catalytic activity and the weaker acidic ligands such as dionate or carboxylate were superior to sulfonate. Zinc chelates and salts showed superior catalytic behavior and also room temperature stability. A new zinc chelate catalyst[13] was developed which gives improved stability, cure response and superior film properties. This catalyst is applicable for liquid and also powder coatings.

Epoxy resins can be homopolymerized as evidenced by UV cured coatings using cationic catalyst being in wide commercial use. The absence of functional groups which do not hydrogen bond produces reactants which are very low in viscosity[14]. This makes epoxy resins very attractive candidates for solvent-free and high solids coatings. We were interested in blocked superacid catalysts for thermal cure of epoxy resins[15] as an alternative to melamine crosslinked coatings. Thermally catalyzed cycloaliphatic epoxies are effective crosslinker for hydroxyl functional acrylic polymers and can be used to replace melamine crosslinkers in applications which cannot tolerate any formaldehyde emission.[16] The low viscosity of the system permits the formulation of 100 % reactive solvent free coatings.

Hybrid or Dual Function Catalysts

Crosslinking agents of different chemistries are being combined in coating formulations in order to improve performance and retain the low cost of existing formulations. Therefore, increasing emphasis is being placed on the development of catalyst for multiple curing mechanisms. As shown in Table 5 melamine formaldehyde crosslinked coatings can modified with isocyanates[17] and blocked isocyanates[18] to improve mechanical properties, acid resistance[19] and cure behavior. Isocyanate crosslinking can also be combined with the catalysis of siloxane reactions. DBTDL is an excellent catalyst for the siloxane and isocyanate reaction, but the level of catalyst required for siloxane reaction is several orders of magnitude larger than for the isocyanate reaction, leading to a heterogeneous network.

Table 5. Catalysis of Hybrid Crosslinked Coatings Polymer Hydroxyl Functional

Melamine Resin/Blocked Isocyanate a)		Catalyst	Improvement
HMMM b)		R-SO_3-Ester[20]	Acid etch resistance
		Zn Chelate/ Lewis acid[21]	Impact/stone chip
IMINO, Part Alkylated		R-SO_3-Ester	Acid etch resistance
		R-PO_4-Amine	Impact/stone chip
		Zn Chelate[22]	
HMMM	Siloxane c)	R-SO_3-Ester	Acid etch resistance
Isocyanate	Siloxane	Al Chelate[23]	Scratch resistance
Isocyanate blocked a)	Siloxane	Zn Chelate	Chemical resistance

a) Blocked isocyanate; malonate, ketoxime, 3,5-dimethylpyrazol blocked aliphatic isocyanates; b) Hexakis(methoxymethyl)melamine; c) Alkoxysilanes

Conclusion

Catalysis plays a critical role in the development of new coating systems. To meet the requirements for solvent-free, high solids, waterborne and powder coatings, a variety of metal chelates are being developed which are environmentally acceptable and meet the cure requirements of the industry.

Any new catalyst is not a direct replacement for an existing product. The present know-how and experience does not necessarily apply to a new catalyst.

DBTDL as a catalyst shows increased reaction rates with primary hydroxyl groups over secondary hydroxyls. This information has been used in the design of polyols for polyurethane applications. With Zr catalysts this relationship still holds, although we find with some polyethers an extremely slow reaction.

With Bi based catalysts our conventional thinking of reaction rates requires a revision. ß-hydroxyalkyl ester, carbamate and ether groups show significantly higher reaction rates than sterically unhindered hydroxyls.

Thermally cationic catalyzed epoxy resins offers performance properties not attainable with other crosslinking systems. Low viscosity and high application solids make these systems candidates for zero VOC coatings.

Hybrid or dual crosslinked systems have achieved an important position in the automotive clearcoat market. Combinations of melamine resins with siloxanes or with blocked isocyanates are used to upgrade the acid resistance of melamine crosslinked coatings and still retain scratch resistance and lower cost.

Acknowledgement

I would like to thank King Industries Inc. for the permission to publish this work and for supporting the lifestyle I have been accustomed to. I also thank my coworkers in the R&D and TS department for their contributions. I also like to acknowledge the efforts of Dr. Leonard J. Calbo and Dr. Carl Seefried in proofreading this paper.

References

[1] Z. A. He, W. J. Blank, M. E. Picci " A Selective Catalyst for two component waterborne polyurethane coatings" Proceedings of the Twenty-Sixth Annual International Waterborne, High-Solids, and Powder Coatings Symposium, New Orleans, LA, 1999

[2] Communication with J. J. Florio, unpublished King Industries, Inc. Information

[3] S.P. Pappas, E.H.Urruti, Proceedings of the 13th International Waterborne, High-Solids, and Powder Coatings Symposium, New Orleans, LA, 1986

[4] Z.W.Wicks Jr., Prog. Org. Coat., 3 (1975); 73

[5] Z.W.Wicks Jr., Prog. Org. Coat., 9 (1981); 3

[6] Z.W. Wicks Jr. and B.W. Kosty, J. Coat. Technol.,49 (634) (1977); 77

[7] Private communication with Z. A. He and M. Piccie King Industries, Inc.

[8] US. 6,353,057 (2002), King Industries, Inc.,"Catalyzing cationic resin and blocked polyisocyanate with bismuth carboxylate". Invs.: Z. He; Zhiqiang

W.J.Blank, M.E. Picci;

[9] W.J. Blank, Z.A. He, M. E. Picci, (King Ind. Inc., Norwalk, CT 06852, USA). "Catalysis of blocked isocyanates with non-tin catalysts" Polym. Mater. Sci. Eng., 79, 399-400, 1998 ACS

[10] W. J. Blank, "Crosslinking with Polyurethanes", Polym. Mater. Sci. Eng., 63, 1990 ACS

[11] Z. W. Wicks, B. W. Kostyk, J. Coat. Tech. 49 No.634, (1977) 77.

[12] W. J. Blank, Z. A. He, M. E. Piccie, J. Coat. Tech. 74 No.926, (2002) 33-41

[13] US 6,335,304 (2002), King Industries, Inc., "Metal Salts of Phosphoric Acid Ester as Crosslinking Catalyst", invs.: Z. He; Zhiqiang W.J.Blank, M.E. Picci;

[14] Z. W. Wicks, G. F. Jacobs, I. C. Lin, E. H. Urruti, L. G. Fitzgerald, "Viscosity of Oligomer Solitions" J. Coat. Tech.., Vol. 57, No. 725 (1985), pp. 51-66.

[15] R. P. Subrayan, D. J. Miller, M. M. Emmet and W. J. Blank, "Catalysis of Thermally Curable High Solids Cycloaliphatic Epoxy Formulations", ACS PMSE Preprints Chicago Meeting (2001).

[16] King Industries, Inc. Technical literature "NACURE® Epoxy Catalysts"

[17] G..Teng, R.P. Subrayan, F.N. Jones, "Sag-Resistant High Solids Baked Coatings with Mixed Polyisocyanate and Melamine-Formaldehyde Crosslinkers," *Polym. Mater. Sci. Eng.*, 1997, *76*, 117-118.

[18] Ger. Offen. DE 4204518 A1 19 Aug 1993, (BASF Lacke und Farben A.-G., Germany). Invs: U. Roeckrath, G. Wigger, U. Poth.

[19] W.J. Blank, Z.A. He, E.T. Hessell, R.A Abramshe, (King Industries Inc, Norwalk, CT 06852, USA). "Melamine formaldehyde networks with improved chemical resistance.". Polym. Mater. Sci. Eng., 77, 391-392, 1997, ACS

[20] NACURE® 5414 catalyst, a product of King Industries, Inc. Norwalk, CT 06852 USA

[21] NACURE® XC-8212 catalyst, a product of King Industries, Inc. Norwalk, CT 06852 USA

[22] NACURE® XC-9206, XC-B219 catalyst, products of King Industries, Inc. Norwalk, CT 06852 USA

[23] NACURE® 5218 catalyst, a product of King Industries, Inc. Norwalk, CT 06852 USA