

Kat-Nips

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Additive Insights For The Coatings Professional



K-KAT[®] Catalysts

Troubleshooting Metal Catalyzed Urethane Systems

Dibutyltin dilaurate (DBTDL) and dibutyltin diacetate (DBTDA) are very versatile catalysts for the isocyanate-hydroxyl reaction and are commonly used as catalysts in coatings. Many of the reactions we believe are typical for isocyanate systems are actually the reactions of isocyanates under DBTDL catalyzed conditions.

King Industries has developed a range of K-KAT catalysts that are based on bismuth, aluminum and zirconium. These K-KAT catalysts are not only environmentally more acceptable than organotin compounds, but can offer performance advantages over these catalysts.

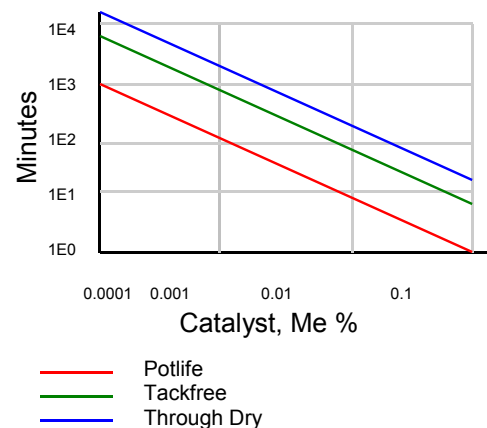
Specific K-KAT catalysts can be selected to enhance these advantages, including reduced water reaction, improved pot life, faster cure, improved catalysis in cationic electrocoating and reduced hydrolysis of polyester resins.

How to select the right catalyst ...

The reaction of isocyanates with hydroxyl groups is very slow in the absence of a catalyst. Often resins, additives and pigments contain impurities which can act as catalysts for this reaction. Some of these impurities might also interact with catalysts and deactivate them. Catalyst deactivation can also be a function of water content and acid number of the resin.

The catalytic activity of DBTDL and most other catalysts can be shown in a high solids coating to be a log time/log catalyst concentration relationship as shown in Figure 1.

Figure 1. Concentration Relationship



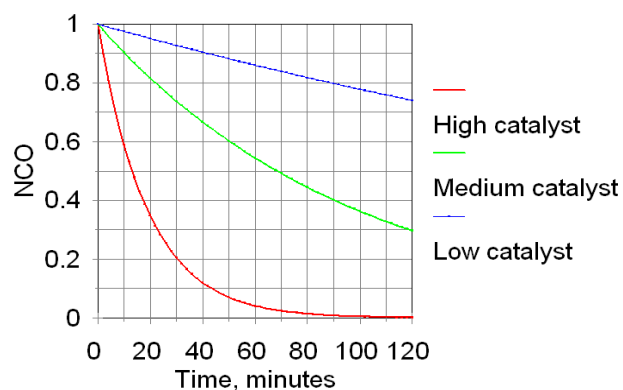
At the typical pot life for high solids formulations (pot life being defined as time to double viscosity) only about 6% of the free isocyanate is consumed. Therefore, it is difficult in such a system to balance pot life with acceptable reactivity, but an improvement in pot life is possible if the catalyst is blocked with a volatile agent such as 2,4-pentanedione. This blocking works with DBTDL, K-KAT 4205, XC-6212, XC-9213, XC-A209 and 5218. It is particularly effective with K-KAT 5218.

Route To: _____

The rate of the reaction can be measured by infrared spectroscopy. The disappearance of the isocyanate band at 2272cm wave number is a simple tool to determine the reaction rate. For a known polymer system, the pot life and tack free times are a function of isocyanate conversion. For example, double viscosity of a high solids polymer system might be attained at 6% isocyanate conversion, and the cast film might require 30% conversion of the isocyanate to become tack free.

Figure 2 illustrates the decrease in isocyanate (NCO) content over time with varying levels of DBTDL catalyst. A low catalyst level (blue line) provides a pot life of approximately 20 minutes and a tack free time of approximately 2 hours. A medium catalyst level (green line) provides a tack free coating at 35 minutes and a

Figure 2. NCO Content/Catalyst Level



pot life of only 5 minutes, where as a high catalyst level (red line) provides less than 10 minutes tack free time and a pot life of less than 2 minutes.

Description of Catalysts

ZIRCONIUM CATALYSTS

All zirconium catalysts should be incorporated with mechanical agitation.

K-KAT 4205

Zirconium chelate catalyst dissolved in 2,4-pentanedione. This catalyst offers improved reactivity and stability in 2K polyol isocyanate coatings. More importantly, there is selective catalysis of the hydroxyl versus the water reaction. To achieve the combination of pot life and reactivity it is important that the 2,4-pentanedione be able to evaporate. This catalyst is not suited for castings, moldings or elastomers. The active catalyst content in this product is too low for slower reacting systems such as isophorone diisocyanate (IPDI) - trimer and slow reacting polyols. Best suited for coatings which utilize <0.1% of DBTDL.

K-KAT XC-6212

Zirconium chelate catalyst for fast curing high solids and waterborne coatings. **This catalyst must be added to the isocyanate component.** Addition of 2,4-pentanedione permits potlife extension of solventborne formulations. Pot life of waterborne 2K systems can be increased with XC-6212 compared to use of a

non-selective catalyst in the same system. Recommended for plural component high solids coatings and waterborne spray applications.

K-KAT XC-9213

Concentrated version of K-KAT XC-6212. This product can crystallize at lower temperatures ($\leq 20^{\circ}\text{C}$). Warming to 40°C will re-dissolve crystals. Best suited for formulations which are slow curing such as IPDI crosslinked coatings.

K-KAT XC-A209

Concentrated version of K-KAT XC-6212 but dissolved in t-butylacetate to prevent crystallization. This product is also effective in slow curing formulations such as IPDI crosslinked coatings.

ALUMINUM CATALYST

K-KAT 5218

Aluminum chelate catalyst for extended potlife. This is a catalyst with lower reactivity. About 10 times the concentration of catalyst is required in comparison to DBTDL (on a metal basis). In the presence of 2,4-pentanedione, however, a very long potlife can be obtained with equal dry time compared to DBTDL.

Continued Next Page . . .

BISMUTH CATALYSTS

K-KAT 348

Bismuth carboxylate catalyst. Provides properties similar to DBTDL with less environmental concerns. Particularly effective in blocked isocyanate and elastomer systems.

K-KAT XC-8203

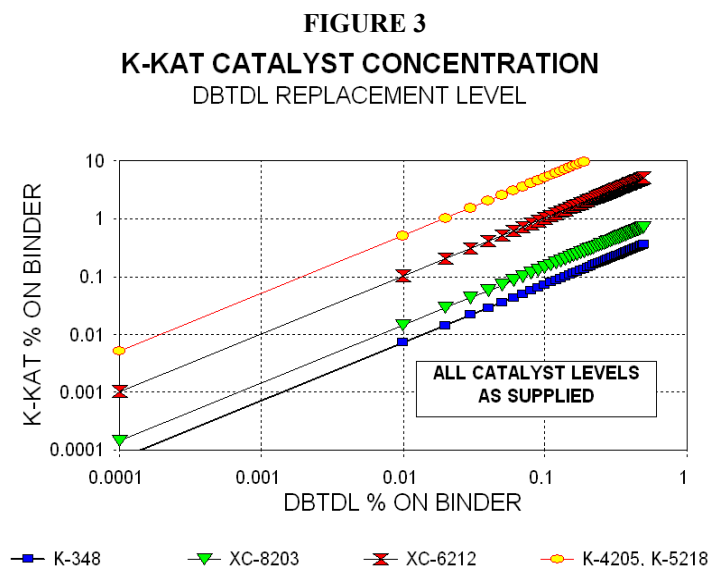
Bismuth carboxylate catalyst. Improved hydrolytic stability over 348. More effective in high temperature applications.

Table 1.—Selection of K-KAT Catalysts

PRODUCT	METAL	%	TYPICAL USE LEVEL (On Total Resin Solids)		COMMENT
			2K	BL. NCO	
K-KAT 4205	Zr	< 0.1	1-2	Not Recommended	Good potlife
K-KAT XC-6212	Zr	0.35	0.3-2	Not Recommended	Fast cure, waterborne, plural component
K-KAT XC-9213	Zr	4.0	0.05-1	Not Recommended	Fast cure, waterborne, slow reacting systems, resin synthesis
K-KAT XC-A209	Zr	3.0	0.05-1	Not Recommended	Fast cure, waterborne, slow reacting systems, resin synthesis
K-KAT 5218	Al	4.0	1-2	Not Recommended	Excellent potlife with 2,4-pentanedione
K-KAT 348	Bi	25	0.03-0.1	0.5-2	Similar to DBTDL, blocked isocyanates, elastomers
K-KAT XC-8203	Bi	12	0.05-0.2	1-3	Electrocoating, waterborne, blocked isocyanates

Catalyst Dosage

Figure 3 provides a guideline of typical use levels of K-KAT in comparison to DBTDL as supplied (18% metal). We have found variations in catalytic activity between different resins and formulations.



Catalyst Troubleshooting Guide

Many of the problems in catalysis of isocyanates are related to deactivation of the catalyst. Since K-KAT catalysts are formulated at a different metal concentration than DBTDL, replacement on an equal weight basis of DBTDL with a K-KAT catalyst is usually not sufficient. As a first approximation, the K-KAT catalysts can be used at an equal metal level to DBTDL, with the exception of K-KAT 5218 which has to be used at approximately a 10X level. Another approach is to test the K-KAT catalysts in a formulation at a level recommended in Table 1 and optimize by conducting a ladder study.

Catalyst deactivation in 2K isocyanate systems is a common problem. It is often not recognized because of the high activity of most catalysts and is overcome by over catalyzing the formulation. A part of the catalyst is used in a sacrificial fashion. Potential sources for catalyst deactivation are water, high acid number resins, anions and pigments. Problems with pigments are often not directly related to the pigment but rather to the water that the pigment carries into the coating. Typical catalyst problems and solutions are shown in Table 2 below.

Table 2: Common Catalyst Problems

FACTORS LEADING TO CATALYST PROBLEMS	RESULTS	SOLUTIONS
Water	Hydrolysis of Zr and Bi catalysts	Zr Catalyst: Add XC-6212 or XC-9213 to the isocyanate. Bi Catalyst: add moisture scavenger
High Acid Number	Slow reaction rate of Zr and Al catalysts	Neutralize with DMEA, Use K-KAT 348, With K-KAT 5218 add 2,4-pentanedione before adding the catalyst.
Anions (phosphate)	Catalyst insolubility	Treat with Ca octoate or Zr octoate
Pigments	Catalyst absorption, slow reaction rate	Often water related, not absorption of catalyst, dehydrate system.
Benzotriazole UV absorber	Yellowing with certain metals, Al, DBTDL	Use triazine UV absorber, Zr catalyst

Troubleshooting By Product

K-KAT 348 Bismuth Carboxylate Catalyst

Most of the potential problems with this catalyst are related to solubility in polar solvents and also hydrolysis with water. We suggest using only polyols low in moisture content, or to add a moisture scavenger before the addition of the catalyst. Also, acid functional resins or organic

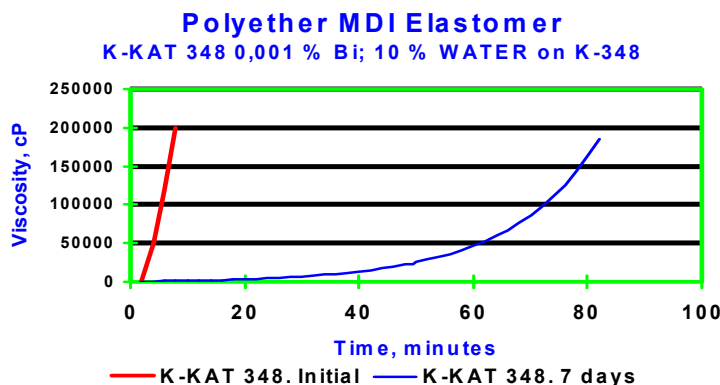
acids may improve the hydrolytic stability of the catalyst. For example, using an equal amount of neodecanoic acid can substantially improve the hydrolytic stability of K-KAT 348.

In some polymer systems the hydrolysis reaction of the K-KAT 348 catalyst is reversible and can be used to achieve a delayed reaction. In a polyester elastomer K-KAT 348

was added and the formulation was blended with methylene diphenyl diisocyanate (MDI). In the absence of hydrolysis the formulation viscosity increased immediately.

The formulation was aged for 2 and 7 days, a delayed reaction was observed as demonstrated in Figure 4, shown to the right.

Figure 4 - K-KAT 348, Polyether MDI Elastomer



K-KAT XC-8203 Bismuth Carboxylate for Cationic Electrocoating and Waterborne Coatings

In waterborne coatings the incorporation method is essential for the activity of this catalyst. The catalyst has to be added to the polymer before water addition. The water should be added slowly under high speed agitation. As water is added the bismuth carboxylate slowly hydrolyzes forming a nano particle dispersion of bismuth oxide/hydroxide. During cure the bismuth oxide/hydroxide reverts to the catalytic form.

K-KAT 4205, XC-6212, XC-9213 & XC-A209 Zirconium Chelates

These catalysts are zirconium chelates. K-KAT 4205 is a solution of a zirconium chelate in 2,4-pentanedione. This catalyst gives a good compromise in potlife and cure response. The catalyst should be added to the polyol component. Cure can be inhibited by higher carboxyl content resins. Water can also impair the catalytic activity of the catalyst. K-KAT 4205 catalyst is best suited for highly reactive high solids coatings requiring a low concentration of catalyst. The potlife/cure response of the formulation depends on the evaporation of the 2,4-pentanedione. In an enclosed system K-KAT 4205 will cure slowly.

K-KAT XC-6212 is a higher concentrated form of a zirconium chelate catalyst supplied in a reactive diluent. **K-KAT XC-6212 must be added to the isocyanate component.** It has excellent

stability in the isocyanate and does not catalyze condensation of the isocyanate. This catalyst has been designed for waterborne coatings and for fast reacting plural component formulations. Addition of 2,4-pentanedione to a formulation containing this catalyst permits an increase in the pot-life.

For very slow curing formulations that utilize low reactive isocyanates, or slow reacting polyols, the addition of higher levels of catalyst is required. Both K-KAT XC-9213 and XC-A209 can be used in such applications.

K-KAT 5218 Aluminum Chelate

It is important that the recommended incorporation method be followed with this catalyst. The catalyst requires some 2,4-pentanedione for viscosity stability, which should be added to the polyol before the K-KAT 5218 is added. Preblending of the K-KAT 5218 with the 2,4-pentanedione results in the formation of a poorly soluble precipitate. Yellowing with K-KAT 5218 is often caused by the chelation of the aluminum compound with benzotriazole light stabilizers. If a UV stabilizer is required, it is important to use a triazine type such as TINUVIN 400. TINUVIN 400 is a product of Ciba Specialty Chemicals.

COMMON PROBLEMS - CHART

The following page has a chart of potential catalyst problems and solutions.

Catalyst/Coating Problems Troubleshooting Chart

PROBLEM	POSSIBLE CAUSE	SUGGESTED SOLUTION
Low Gloss	Isocyanate reacting with water to form insoluble ureas	Use more selective zirconium catalysts
Loss Of Cure On Aging	Poor catalyst solubility	K-348: Reduce ketone content, particularly MEK
	Catalyst deactivated by acid groups	K-5218/K-4205: Neutralize carboxylic acid groups with 3° amines
	Catalyst deactivation by anions (phosphate)	Treat system with Ca or Zr octoate K-4205: Add Ca octoate
	Pigment/catalyst interaction	K-4205: Reduce silica content
	Hydrolysis of catalyst	Use zirconium catalysts that are added to isocyanate component Use moisture scavenger (p-TSI, orthoformates) K-KAT 348: Add neodecanoic acid
Poor potlife/dry time	Catalyst too active in the pot	Solvent-borne: Add 2,4-pentanedione K-5218: Add 2,4-PD to polyol component prior to K-5218 addition Waterborne: Add XC-6212 to isocyanate component
Yellowing	2,4-pentanedione reacting with iron	Use lined containers
	2,4-pentanedione reacting with amine	Reduce amine or switch to 3° amine
	2,4-pentanedione reacting with silica	Use pigments treated with higher levels of alumina
	Reaction of Al or Sn with benzotriazole UV absorber	Use triazine UV absorber
Poor leveling in waterborne 2K	Surface tension of reactive diluent in XC-6212 is too high	Use XC-6212A version of XC-6212 (supplied with different reactive diluent)
Poor cure in waterborne 2K	Metal catalyst content too low	XC-9213 allows incorporation of higher levels of zirconium



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