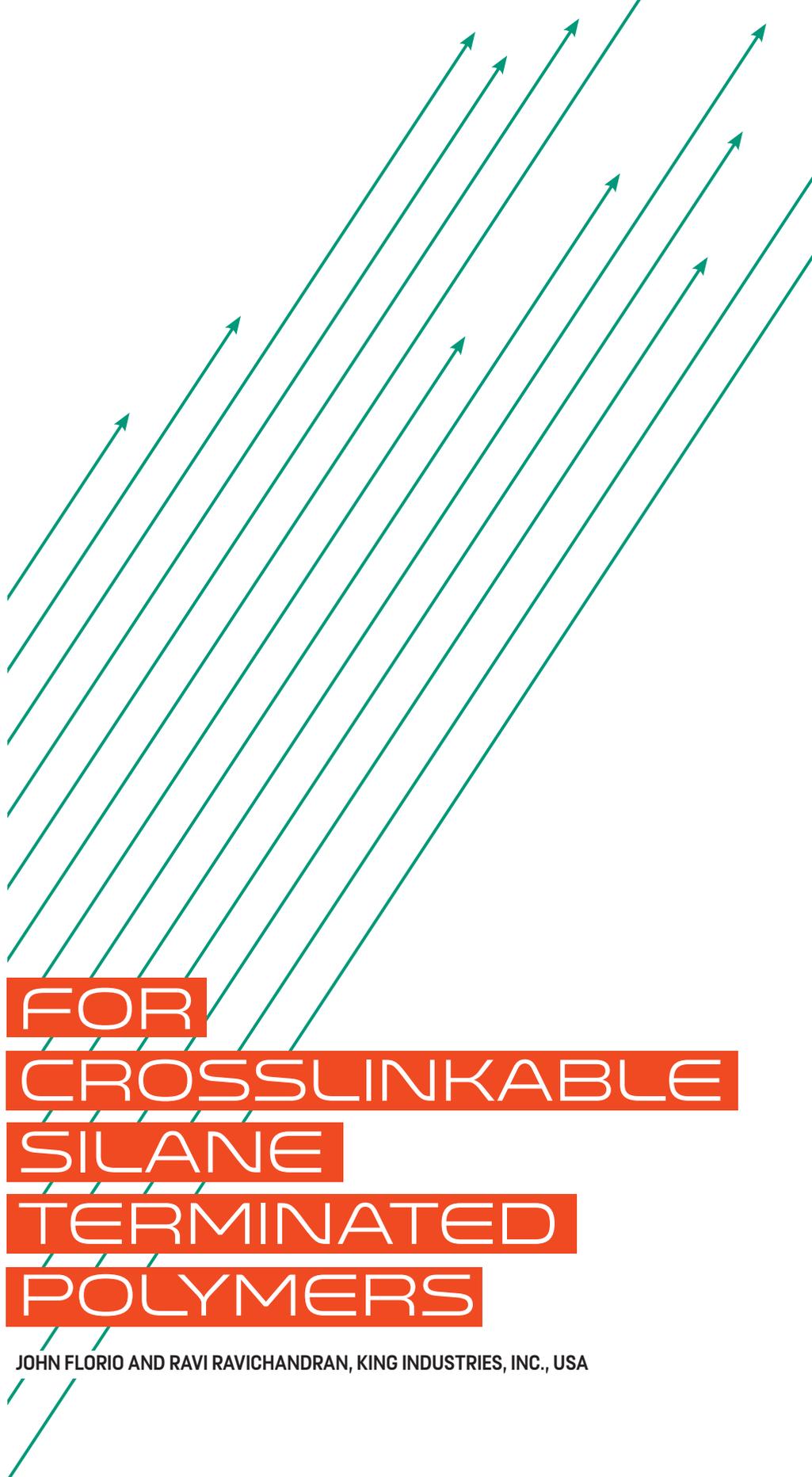


NON-TIN CATALYSTS



FOR
CROSSLINKABLE
SILANE
TERMINATED
POLYMERS

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Crosslinkable organosilane systems can be based on a variety of chemistries and can be utilized for a variety of applications. Selecting a proper catalyst is a critical step in the formulating process of organosilane systems. Along with the increasing need to replace tin catalysts for regulatory reasons, some tin catalyzed organosilane systems lack activity and performance properties. A new series of tin-free compounds has been developed for the catalysis of crosslinkable silane-terminated polymer systems. Each of the developed catalysts demonstrates superior activity with different organosilane chemistries used for a variety of applications.

Introduction

Organosilane polymers are utilized in adhesives, sealants, and coatings as either coupling agents or crosslinkers. As coupling agents, their role would be to promote adhesion between organic and inorganic substrates. As crosslinkers, organosilane polymers react with other functional groups to form covalent bonds that can generate products with structural properties.

Catalysis of organosilane crosslinking reactions is a system-specific process, particularly if the objective is to use a tin-free catalyst. Organosilane crosslinking chemistries include one-component moisture-cured systems that can be based

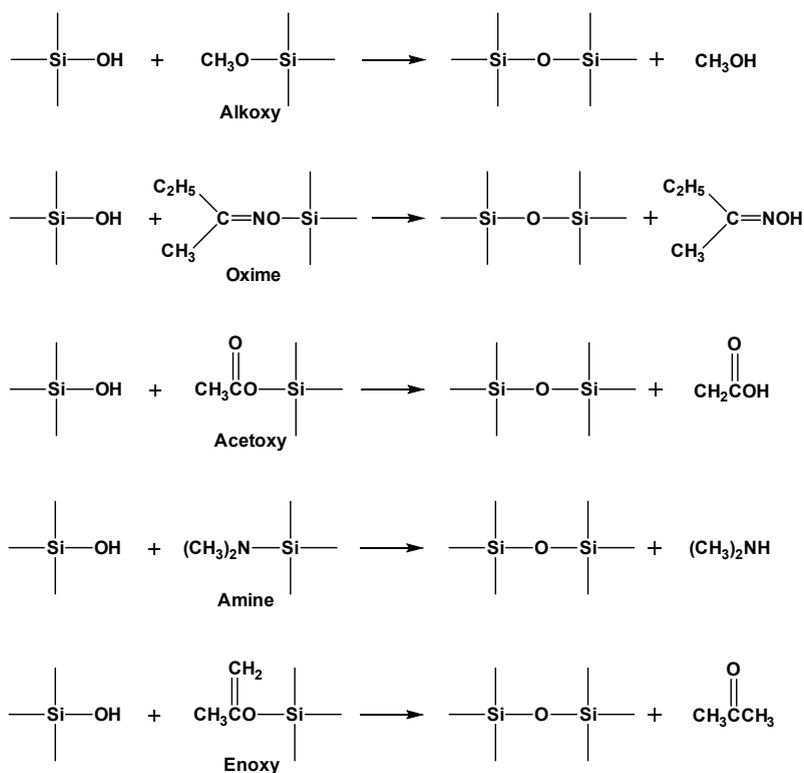


FIGURE 1—Common silanol condensation reactions.

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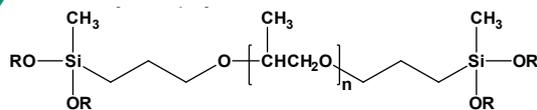


FIGURE 2—Structure of alkoxy terminated polymer.

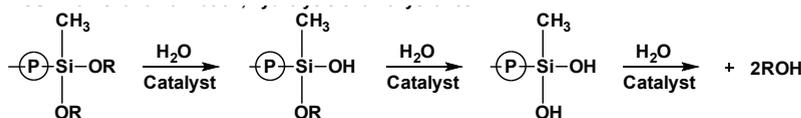


FIGURE 3—Silanol formation, hydrolysis of alkoxy terminated.

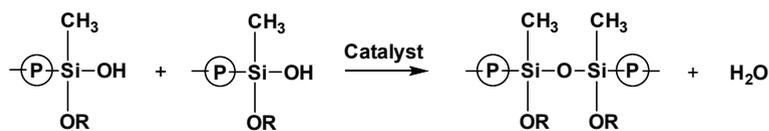


FIGURE 4—Formation of siloxane crosslinks by condensation of silanols.

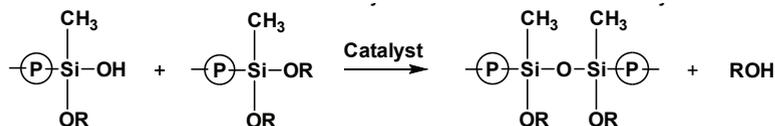


FIGURE 5—Formation of siloxane crosslinks by condensation of silanol and alkoxy terminated.

on different functionalized backbone polymers that have alkoxy terminated groups. The backbone chemistries of these systems could be polyether, polysiloxane, or polyurethane. Cured properties (e.g., T_g , hardness, flexibility, etc.) can be dependent on the chemistry of the backbone. Other cure chemistries involve one- and two-component systems crosslinking silanol-terminated polydimethylsiloxane (PDMS) with alkoxy terminated, oximino terminated, or acetoxy terminated crosslinkers.

In addition to the condensation reactions which are the focus of this article, vinyl functional silanes are commonly cured by an addition reaction which involves the addition of a silicon hydride to a terminal vinyl double bond. Platinum based homogeneous strong acids like chloroplatinic acid (Karstedt acid) are typically used here and the cures can either be at ambient or higher temperatures. A

second, less utilized approach involves the use of an organic peroxide in a radical induced polymerization.

Hydroxy-terminated polydimethylsiloxanes are curable to elastomers by a wide variety of crosslinkers. Equations listing the most common cure pathways are presented in Figure 1. All of these systems undergo condensation cure resulting in elimination of a volatile byproduct such as acetic acid, an oxime, or alcohol. Metallic corrosion can result from elimination of acetic acid or possibly alcohols. Oxime or enoxy cure systems are preferred for applications that involve metal contact. The previously mentioned homogeneous platinum catalyzed systems are utilized in many applications that involve electronics and fiber optics because of issues with volatile byproducts or corrosion associated with silanol based systems.

This article first reviews the crosslinking process of one-component alkoxy terminated systems, one- and two-component PDMS systems crosslinked with oximino terminated, and two-component PDMS systems crosslinked with acetoxy terminated. This review is followed by an in-depth summary of different catalyst processes for organosilane chemistries. Finally, a catalyst evaluation for each of the chemistries is presented to demonstrate the effect different catalyst chemistries have on each system.

Organosilane Crosslinking Processes

A basic structure for an alkoxy terminated polymer is shown in Figure 2. Complete crosslinking of a one-component moisture cure alkoxy terminated system requires acceleration of two chemical processes. In this case, the catalyst must accelerate both the hydrolysis of the alkoxy terminated (Figure 3) and condensation of the formed silanol groups (Figure 4), or condensation of other alkoxy terminated groups with formed silanol groups (Figure 5) to produce crosslinked siloxane structures. As demonstrated in Figures 3 and 5, hydrolysis and condensation of alkoxy terminated groups will generate an alcohol byproduct. For the purpose of this discussion, it is convenient to assume that the hydrolysis reaction initially occurs, followed by the condensation reactions. However, in practice, hydrolysis and condensation occur concurrently unless special efforts are made to separate the steps.¹

Products based on this chemistry can be supplied as a single component in sealed tubes and applied with dispensers for caulk, sealant, and adhesive applications. They are widely used for DIY projects and commercial construction projects for a variety of indoor and outdoor applications on a variety of substrates. Organosilane polymers can promote adhesion, weatherability, and reinforcement of coatings, adhesives, sealants and fillers.



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Efficiency of non-tin catalysts for accelerating the crosslinking of one- and two-component silanol-terminated PDMS systems can vary significantly. Examples of crosslinkers for one- and two-component silanol-terminated PDMS are acetoxy-silanes and oximinosilanes. Crosslinking mechanisms are shown in *Figures 6 and 7*. The crosslinking processes for these chemistries differ from the one-component moisture-cured systems with alkoxy silane terminal groups in that they do not require moisture to initiate the reaction.

With the silanol groups already formed, the oximinosilane and acetoxy silane crosslinked systems are less stable than the alkoxy silane systems that require atmospheric moisture to generate reactive silanol groups. However, even with the presence of silanol functional groups, the systems containing the oximinosilane crosslinker are more stable than those containing alkoxy silane and acetoxy silane crosslinkers. The carbonyl group in the acetoxy group has a higher activation effect on the Si-OC hydrolysis, compared to the C=N double bond in the oxime group.² Formulated oximinosilane systems can sometimes be supplied as a one-component system because the oximinosilane is more resistant to hydrolysis.

Catalysis of Organosilane Crosslinking

The hydrolysis and condensation reaction rates of organosilane systems are dependent on pH of the system and on the substituents on the silicon. The rate minimum for the hydrolysis and condensation reactions occurs at approximately pH 7 and pH 4, respectively. Each pH change of one unit in either direction produces a 10-fold rate acceleration, assuming an excess of water is available. At pH > 10, hydrolysis of the first intermediate, $\text{RSi}(\text{OR})_2\text{OH}$, is inhibited due to the ionization of the silanol group.³ The effect of pH on the organosilane hydrolysis and condensation reaction rates is illustrated in *Figure 8*. Both hydrolysis and condensation reactions are reversible. Alcohols will reverse the silane hydrolysis.

The hydrolysis and condensation reactions can be accelerated by acids, bases, and organometallics. Osterholtz and Pohl described specific mechanisms for each of the acid- and base-catalyzed reactions. Torry, Campbell, Cunliffe and Tod extensively studied activity of organometallic compounds in organosilane systems and they propose tin compounds as the

most active. However, the tin catalysts must initially hydrolyze to form the active species.⁴ Tin compounds are commonly used to catalyze the crosslinking of organosilane systems including alkoxy, acetoxy, and oximinosilane systems. Dioctyltin and dibutyltin compounds that efficiently catalyze many of these crosslinking reactions include dioctyltin diacetylacetonate and dibutyltin dilaurate. However, concerns about toxicity of tin compounds have driven formulators to explore other catalyst options. Although the options can include acids, bases, and other organometallics, finding a single non-tin catalyst that could provide sufficient reaction acceleration for all of the mentioned silane crosslinking chemistries is difficult. Along with reaction acceleration, physical properties of the cured product can be dependent on the catalyst. For example, some acids might provide good acceleration of the crosslinking reaction, but the acid might also accelerate rearrangement of the formed polysiloxane backbone causing product degradation. Some tertiary amines could accelerate the crosslinking reaction, but they might also contribute color and odor.

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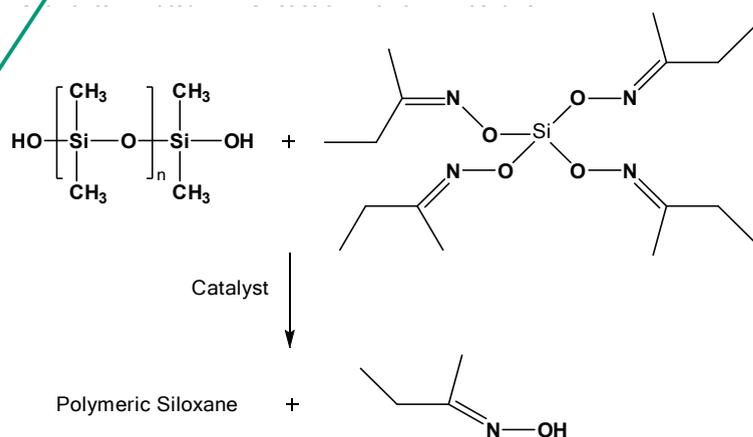


FIGURE 6—Silanol-terminated PDMS reaction with oximosilane.

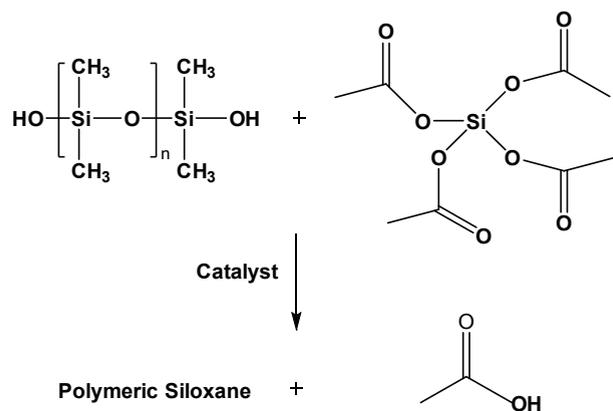


FIGURE 7—Silanol-terminated PDMS reaction with acetoxysilane

Base-Catalyzed Hydrolysis of Alkoxysilanes

Osterholtz and Pohl proposed a bimolecular nucleophilic displacement reaction consistent with their kinetic data, as depicted in *Figure 9* for base catalysis of alkoxysilane hydrolysis, involving a pentacoordinate intermediate, and two different transition states, T.S.1 and T.S.2. In the presence of a base and water, the transition state T.S.1 is formed with a partial negative charge on the alkoxysilane silicon during the first step of the hydrolysis reaction. T.S.1 then dissociates to generate the pentacoordinate intermediate which subsequently breaks down to the desired silanol through a second transition state, T.S.2. In the proposed mechanism, negative

charge development on the silicon in the transition state (T.S.1 or T.S.2) is considerable. This is supported by experimental observations where electron-withdrawing substitution on the alkyl groups attached to the Si accelerates the rates of hydrolysis. This is due to the stabilization of the developing negative charge which lowers the energy of the transition states.

In General Base Catalysis of the hydrolysis of alkoxysilanes, any basic species accelerates the reaction by assisting the removal of a proton from water in the transition state. In Specific Base Catalysis of the hydrolysis of alkoxysilanes, the hydroxide anion accelerates the reaction rate by directly attacking the substrate.

Base-Catalyzed Condensation of Silanols

Chojnowski and Chrzczonowicz found that secondary and tertiary amines (piperidine, triethylamine, tri-*n*-butylamine) catalyzed the condensation of a series of dialkyl- or diarylsilanedols in aqueous dioxane.⁵ They proposed that primary and secondary amines catalyzed the reactions by nucleophilic attack on silicon which was followed by the rapid attack of dialkylsilanediol on the silamine formed, as shown in *Figure 10*. Tertiary amine catalyzed reactions were proceeded by a general base-catalyzed mechanism.

Acid-Catalyzed Hydrolysis of Alkoxysilanes

The mechanism for the acid-catalyzed alkoxysilane hydrolysis reaction proposed by Osterholtz and Pohl is shown in *Figure 11*. According to Osterholtz and Pohl, the mechanism for acid-catalyzed hydrolysis is a rapid equilibrium protonation of the substrate, followed by a bimolecular $\text{S}_{\text{N}}2$ -type displacement of the leaving group by water.

Acid-Catalyzed Condensation of Silanols

The acid-catalyzed condensation reaction proceeds by an initial protonation of the silanol followed by an $\text{S}_{\text{N}}2$ displacement reaction at the Si leading to formation of water and regeneration of the acid catalyst as depicted in *Figure 12*.

Tin Catalysis Mechanism

As previously mentioned, tin catalysts are utilized in alkoxy, acetoxy, and oximosilane systems. The tin catalyst can be in the form of dioctyltin and dibutyltin diacetylacetonate and dibutyltin dilaurate (DBTDL).

Catalysis of organosilanes with tin compounds begins with hydrolysis of the tin compound. As shown in *Figure 13*, the tin compound undergoes hydrolysis and forms an organotin hydroxide, which is the true catalytic species.⁶ The organotin hydroxide reacts with

an alkoxy silane group to form an organotin silanolate (Figure 14). The tin silanolate will react readily with alcohols and water to form the silanol (Figure 15). The organosilanolate will also react with formed silanol groups to produce siloxane linkages, and the organotin hydroxide catalyst is regenerated (Figure 16).

Tin EU Regulations

European Commission Decision 2009/425/EC, which includes restrictions on the use of dibutyltin, dioctyltin, and tri-substituted organotin compounds, was incorporated into ANNEX XVII of REACH through regulation (EU) 276/2010.⁷ A summary of these restrictions is presented in Table 1.⁸ With the stigma of being environmentally regulated, tin compounds are more often avoided regardless of the dosage required to sufficiently accelerate the reaction. For example, sufficient acceleration of the reaction of polyols with polyisocyanates for many two-component coating applications usually requires levels of tin metal that are well below the $\leq 0.1\%$ limitation. Regardless, coatings formulators still often strive to formulate completely tin-free systems.

The dosage of tin metal that is often required to achieve sufficient cure of moisture-cured organosilane polymer systems is typically very close to the $\leq 0.1\%$ limit established in REACH Annex XVII, Entry 20. Therefore, while tin replacement is an issue for the polyurethane coatings industry, it is a greater issue for industries that use moisture-cured organosilane polymer coatings, adhesives, sealants.

Methanol Emission

If the R groups in Figures 2 and 4 are methyl, then the byproduct generated in the hydrolysis and condensation reactions would be methanol. The European Agency for Safety and Health at Work (EU-OSHA) directive 67/548/EEC, and the 25th updating of this directive (98/98/EC), has defined methanol as harmful with danger of very serious

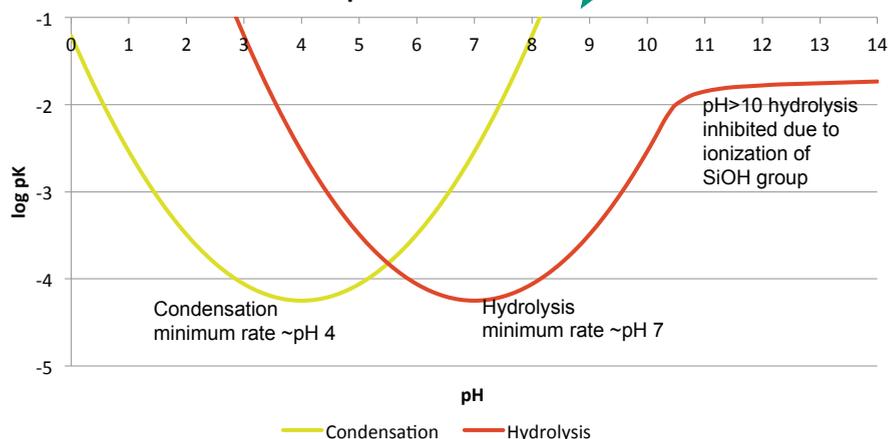


FIGURE 8—Organosilane hydrolysis and condensation effect of pH on reaction rates.

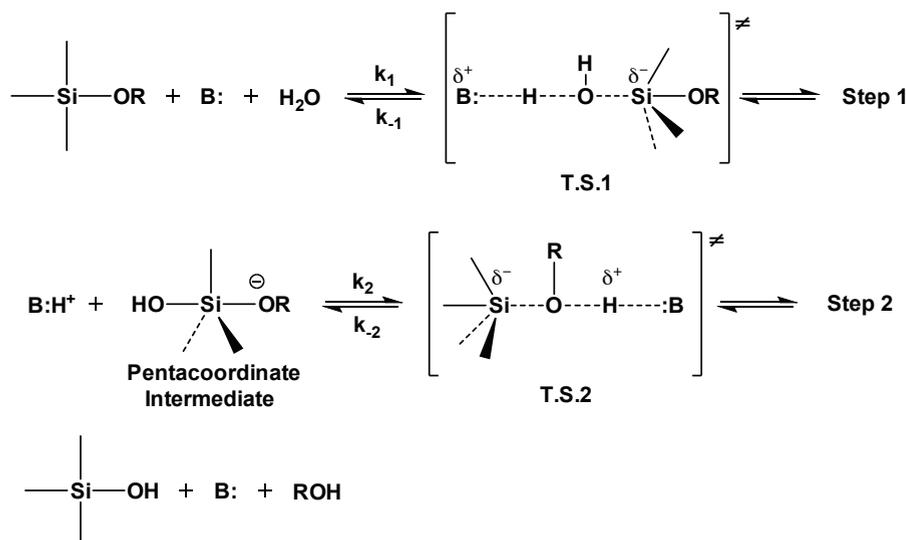


FIGURE 9—Base-catalyzed hydrolysis of alkoxy silanes.

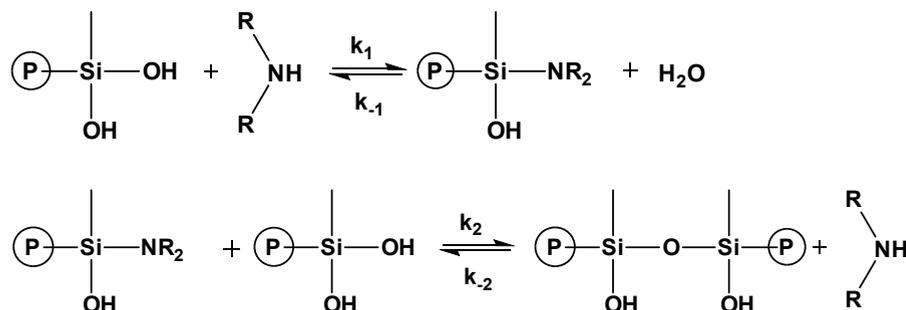


FIGURE 10—Base-catalyzed condensation of silanols.

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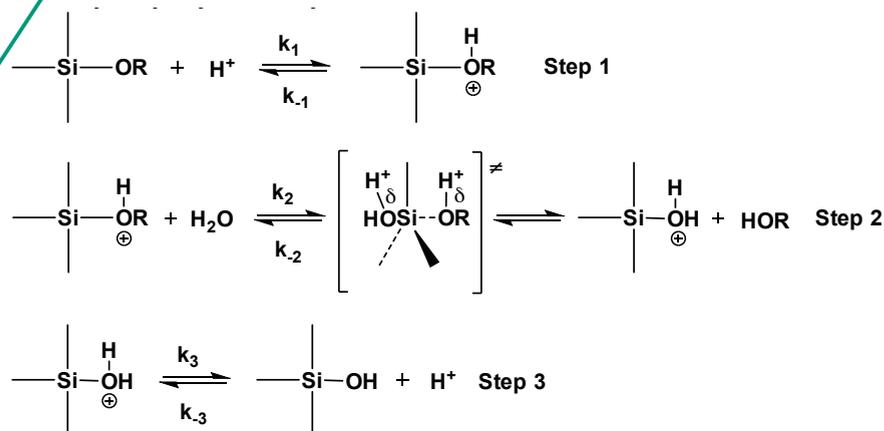


FIGURE 11—Acid-catalyzed hydrolysis of alkoxysilanes.

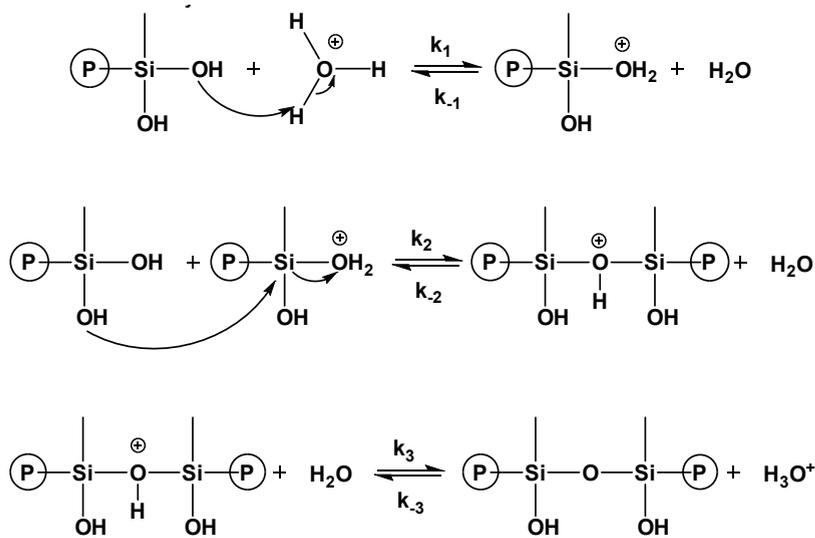


FIGURE 12—Acid-catalyzed condensation of silanols.

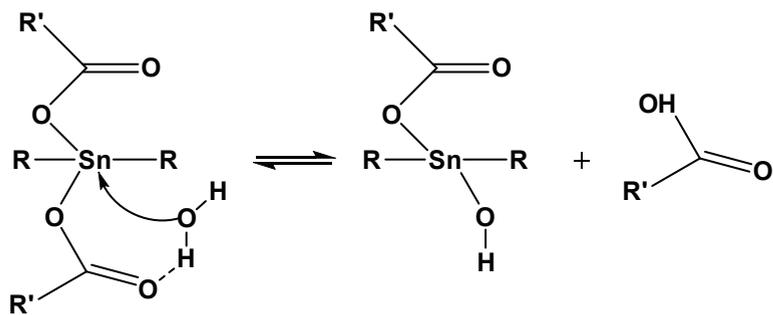


FIGURE 13—Hydrolysis of tin catalysts.

irreversible effects by inhalation, skin contact, and ingestion. According to Commission Directive 2006/15/EC of February 7, 2006, the maximum allowable methanol exposure for an eight-hour workday is 260 mg/m³. Methanol exposure studies of a methoxysilane floor adhesive based on an NIOSH method⁹ have been conducted that report 5400 mg/m³ emission of methanol during an eight-hour period.¹⁰

An approach to completely eliminating methanol from the alkoxysilane curing process is to use ethoxylated silane polymers. However, catalysis of the ethoxysilane crosslinking reaction is challenging. Tin compounds have proven inefficient for these reactions.

Catalyst Options

Tin compounds are very effective catalysts and they are commonly used for crosslinking many of the organosilane systems. The motivation for replacing tin catalysts in these systems can be for performance issues, but often the motivation is due to regulatory issues. Extensive studies were conducted to identify compounds that could be considered alternatives to tin catalysts in organosilane systems crosslinked with alkoxy, acetoxy, and oximinosilanes. The compounds evaluated in the following experiments were a range of metal compounds, acids, amines, and combinations of each. In each of the systems tested, a different compound emerged as the most efficient.

In addition to the catalyst evaluation in the following experiments, the issue of methanol emission is addressed.

The control systems in each of the following experiments were catalyzed with a tin catalyst. Non-tin catalysts included in each of the experiments were K-KAT 670 (zinc complex), a proprietary catalyst (Proprietary Compound), and K-KAT XK-651 (bismuth carboxylate). Compared to tin compounds, bismuth and zinc compounds are more innocuous. They do not carry the environmental and biological restrictions of tin compounds. Extensive utilization of bismuth

and zinc compounds in the field of medicine exemplifies their non-toxic nature. However, in general, Bi(III) is known to have a high affinity for oxygen.¹¹ Hydrolysis of bismuth carboxylate catalysts is usually a negative consequential effect of this affinity for oxygen. K-KAT XK-651 is a bismuth carboxylate that addresses the hydrolysis issue.

These catalysts were compared to tin catalysts in several different formulated

organosilane systems. Experiment I is based on a dimethoxymethylsilyl (DMS) polyether polymer and Experiment II addresses the issue of methanol generation by using an organosilane based on a diethoxysilyl (DES) polyether polymer. Experiment III is another one-component study, but the chemistry of the reactive polymers is based on a hydroxyl-terminated siloxane and an oximinasilane crosslinker. Finally, a

two-component system based on a silanol-terminated PDMS crosslinked with an alkoxy silane is described in Experiment IV.

Experimental

Fully formulated single component moisture-cure alkoxy silane systems were used in the following experiments. The uncatalyzed one-component formulations were stored in dispense cartridges. Approximately 30 grams of uncatalyzed material was dispensed into a speed mixer container with a caulk gun before addition of the catalyst. The material was mixed on a speed mixer for 30 sec at 1500 rpm then 2 min at 2200 rpm. Experiment IV followed the same mixing process, but since it was a two-component system, the components were added to the mixing container separately. An adjustable doctor blade was used to apply approximately 3 mm of the blends onto a paper substrate. The degree of dryness was determined by using a Model 415 Drying Time Tester¹² in accordance with DIN 53 150. The dryness test involved applying a force onto a paper disk that covered a test site on the casting for 60 sec. The results are based on the amount of tack and on visual impressions that develop from the applied force. The dryness testing was done at 25°C and 50% relative humidity. Degree 1 of the DIN 53 150 method was substituted with a glove test to determine touch dry. *Table 2* defines the rating system used.

Where tested, hardness of the castings was determined with a Shore A¹³ hardness tester after the castings were allowed to cure under ambient conditions for two weeks. Other mechanical properties were measured on an Instron¹⁴ tester using dogbone-shaped samples cut from the fully cured 3 mm thick castings.

Experiment I: Moisture-cure system based on dimethoxymethylsilane (DMS) polymer

The control system in this experiment was catalyzed with dioctyltin diacetylacetonate (DOTDAA) in a fully

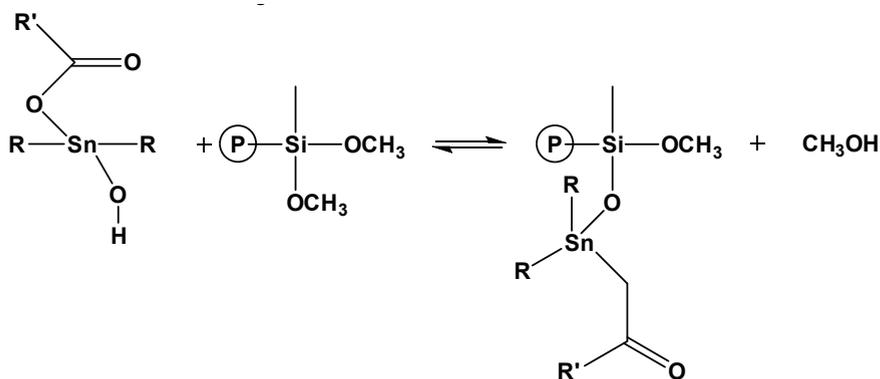


FIGURE 14—Formation of organotin silanolates.

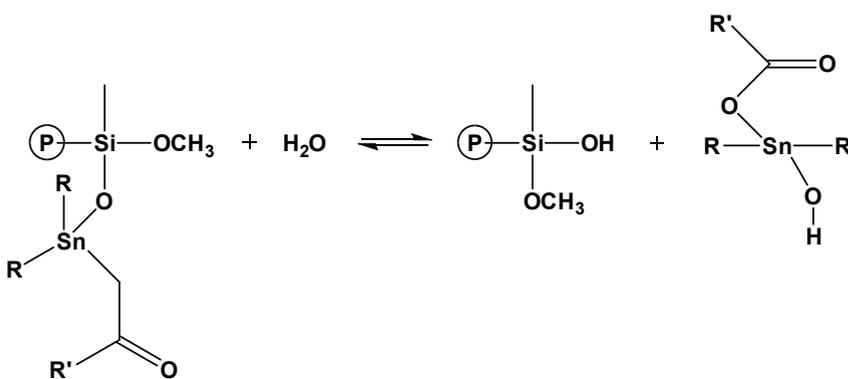


FIGURE 15—Formation of silanol groups.

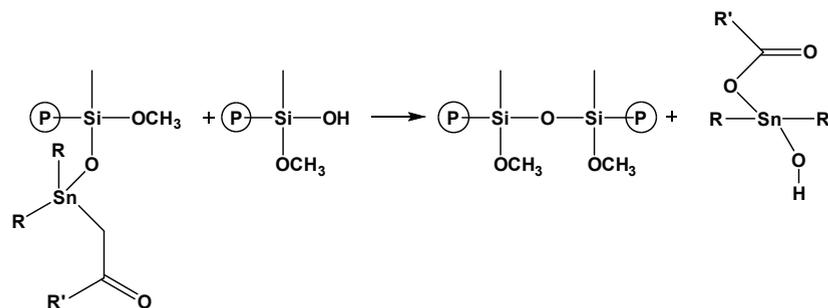


FIGURE 16—Formation of siloxane groups.

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SUBSTANCE	SCOPE	REQUIREMENT	EFFECTIVE
Tri-substituted organostannic compounds such as Tributyltin (TBT) compounds and Triphenyltin (TPT) compounds and Dibutyltin (DBT) compounds	Article or part of an article	≤ 0.1%	1 July 2010
	1. Mixture 2. Article or Part of an article (Except Food contact materials)	≤ 0.1 %	1 January 2012
Diocetyl tin (DOT) compounds	1. One-component and two-component room temperature vulcanisation sealants (RTV-1 and RTV-2 sealants) and adhesives, 2. Paints and coatings containing DBT compounds as catalysts when applied on articles, 3. Soft polyvinyl chloride (PVC) profiles whether by themselves or coextruded with hard PVC, 4. Fabrics coated with PVC containing DBT compounds as stabilisers when intended for outdoor applications, 5. Outdoor rainwater pipes, gutters and fittings, as well as covering material for roofing and façades.	≤ 0.1 %	1 January 2015
Diocetyl tin (DOT) compounds	1. Textile articles intended to come into contact with the skin, 2. Gloves, 3. Footwear or part of footwear intended to come into contact with the skin, 4. Wall and floor coverings, 5. Childcare articles, 6. Female hygiene products, 7. Nappies, 8. Two-component room temperature vulcanisation moulding kits (RTV-2 moulding kits).	≤ 0.1 %	1 January 2012

TABLE 1—Summary of Organotin Requirements under European Regulation (EU) 276/2010 Amending Annex XVII of REACH. REACH Annex XVII, Entry No 20

	%
DMS POLYMER ¹⁵	32.8
PLASTICIZER	16.4
FILLER	39.3
TITANIUM DIOXIDE	6.6
THIXOTROPE	1.6
HALS	0.3
UVA	0.3
MOISTURE SCAVENGER	0.7
ADHESION PROMOTER	2.0
	100.0

TABLE 3—Experiment I, DMS System Formulation

formulated system based on a polyether backbone DMS polymer. Catalyst levels were derived from ladder studies. The dosage of tin catalyst in the control system was 0.6% DOTDAA. The tin content of DOTDAA is approximately 21%. At 0.6%, the tin content in the formulated control system is approximately 0.12% which would not comply with EU regulations. The general formulation is in Table 3.

Dryness ratings of 3 mm thick castings according to DIN 53 150 are in Table 4. The DOTDAA and K-KAT 670 catalyzed systems dried similarly with each achieving the highest degree of dryness (paper does not adhere to 20Kg load, no visible change to coated surface) in 6 h. The Proprietary Compound and KKAT XK-651 catalyzed systems cured significantly slower. Differences in the performance of the DOTDAA and K-KAT 670 catalyzed systems were not significant based on the mechanical property results (Table 5). The DOTDAA and K-KAT 670 castings developed similar tensile stress (which can be associated with toughness), modulus (elastic modulus) and strain (elongation).

Experiment II: Moisture-Cure System Based on Diethoxysilane (DES) Polymer

Results of the DES polymer study were very different compared to the

1	TOUCH DRY, NO VISIBLE RESIDUE REMAINING ON RUBBER GLOVE
2	PAPER DOES NOT ADHERE, BUT VISIBLE CHANGE WITH 20 G LOAD
3	PAPER DOES NOT ADHERE, BUT VISIBLE CHANGE WITH 200 G LOAD
4	PAPER DOES NOT ADHERE, BUT VISIBLE CHANGE TO COATED SURFACE WITH 2 KG LOAD
5	PAPER DOES NOT ADHERE, NO VISIBLE CHANGE TO COATED SURFACE WITH 2 KG LOAD
6	PAPER DOES NOT ADHERE, BUT VISIBLE CHANGE TO COATED SURFACE WITH 20 KG LOAD
7	PAPER DOES NOT ADHERE, NO VISIBLE CHANGE TO COATED SURFACE WITH 20 KG LOAD

TABLE 2—Degree of Dryness (DIN 53 150)

	1	2	3	4	5	6	7
0.6% DOTDAA	0.8	2.3	3.5	4.0	4.5	5.0	5.5
2.0% K-KAT 670	1.5	2.3	3.0	3.5	4.5	5.5	6.0
2.0% PROPRIETARY COMPOUND	24+	24+	24+	24+	24+	24+	24+
2.0% K-KAT XK-651	6+	6+	6+	6+	6+	6+	<23

TABLE 4—Experiment I, Degree of Dryness (h)

	SHORE A	STRESS AT MAX, PSI	STRAIN AT MAX, %	MODULUS, PSI
0.6% DOTDAA	52	378	234	265
2.0% K-KAT 670	52	324	256	243

TABLE 5—Experiment I, Mechanical Properties. Cure: Two weeks ambient

DMS results. The basic uncatalyzed DES formulation is given in *Table 6*. DOTDAA was essentially not active in this system. At 0.5% and 1.0% on total formulation weight DOTDAA was not effective. Higher dosages were not evaluated since the tin level incorporated with the 1.0% dosage was more than double the maximum allowed by EU regulations. The 3 mm thick castings required more than 120 h to achieve a dryness rating of 7. Dryness ratings are presented in *Table 7*.

To investigate a tin compound with a different ligand, dibutyltin dilaurate

(DBTDL) was added to the study. However, as with DOTDAA, activity of the DBTDL system was poor. The Proprietary Compound and K-KAT XK-651 catalyzed systems also cured poorly. Dry times of the DES system catalyzed with K-KAT 670 were significantly faster than the tin catalyzed systems. The K-KAT 670 system developed dry times that were comparable to the DMS system.

The DOTDAA system required a month of ambient cure before it was suitable for testing on the Instron. Even so, the casting had very weak properties (*Table 8*).

	1	2	3	4	5	6	7
0.5% DOTDAA	120	120	120	120	120	120	120
2.0% K-KAT 670	1.3	3.0	4.5	5.0	6.0	6.5	7.0
2.0% PROPRIETARY COMPOUND	7+	7+	7+	7+	7+	7+	7+
2.0% K-KAT XK-651	7+	7+	7+	7+	7+	7+	7+

TABLE 7—Experiment II, Degree of Dryness (h)

	SHORE A	STRESS AT MAX, PSI	STRAIN AT MAX, %	MODULUS, PSI
0.5% DOTDAA ^a	22	93	267	85
2.0% K-KAT 670	48	291	608	103

(a) one-month ambient cure

TABLE 8—Experiment II, Mechanical Properties. Cure: Two weeks ambient.

	%
DES POLYMER ¹⁶	20.2
PLASTICIZER	23.1
FILLER	49.2
TITANIUM DIOXIDE	3.3
ANTIOXIDANT	0.3
HALS	0.3
MOISTURE SCAVENGER	0.8
THIXOTROPE	1.4
ADHESION PROMOTER	1.5
	100.0

TABLE 6—Experiment II, DES System Formulation

Experiment III: One-Component Moisture-Cure System Based on Oximosilane Polymer

The chemistry of another organosilane crosslinking reaction that is effectively accelerated with tin catalysts is based on the reaction of hydroxyl terminated polydimethylsiloxane polymers and oximosilane crosslinker resins. These systems can be supplied in a one-component package.

The degree of dryness data in *Table 9* exhibits efficient reaction acceleration with DBTDL. With a dosage of only 0.1% catalyst on total formula weight, the DBTDL system achieved the highest degree of dryness (dryness degree = 7, casting not effected by 20 Kg load) in 1.5 h. However, the system catalyzed with 2.0% K-KAT 670, which demonstrated good activity in the one-component moisture cure alkoxy silane studies, required nearly 4.5 h to achieve the same level of dryness. The uncatalyzed control system required 6 h to reach a dryness degree of 7. The system catalyzed with 2.0% K-KAT XK-651 performed similarly to the K-KAT 670. Effective non-tin catalysis of the crosslinking reaction was accomplished with the Proprietary Compound. The degree of dryness of the system catalyzed with 0.5% of the Proprietary Compound was essentially equal to the system catalyzed with 0.1% of DBTDL.

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	1	2	3	4	5	6	7
NO CATALYST	2.0	2.5	3.0	4.0	4.5	6.0	6.0
0.1% DBTDL	0.5	0.8	0.8	0.8	1.3	1.3	1.5
2.0% K-KAT 670	2.5	3.0	3.0	3.5	4.3	4.3	4.3
2.0% K-KAT XK-651	1.5	2.0	2.0	2.0	2.5	3.0	4.5
0.5% PROPRIETARY COMPOUND	0.3	1.0	1.0	1.0	1.3	1.5	1.5

TABLE 9—Experiment III, Degree of Dryness (h)

	1	2	3	4	5	6	7
NO CATALYST	24+	24+	24+	24+	24+	24+	24+
1.0% DBTDL	1.0	2.0	2.3	2.5	2.8	2.8	3.5
2.0% K-KAT 670	9+	9+	9+	9+	9+	9+	9+
2.0% PROPRIETARY COMPOUND	6+	6+	6+	6+	6+	6+	6+
2.0% COSCAT 83	6+	6+	6+	6+	6+	6+	6+
2.0% K-KAT XK-651	0.8	1.8	2.3	2.5	3.0	3.0	4.0
3.0% K-KAT XK-651	0.8	1.5	2.0	2.3	2.5	2.5	3.0

TABLE 10—Experiment IV, Degree of Dryness (h)

Experiment IV: Two-Component Silanol-Terminated PDMS with Alkoxysilane Crosslinker

The following study of a two-component organosilane formulation was based on a silanol-terminated PDMS cross-linked with an alkoxysilane polymer. The control catalyst in this study was DBTDL. K-KAT 670 and the Proprietary Compound, which were the most effective non-tin catalysts in the one-component alkoxysilane and oximinosilane studies, were included in this study. Also included were two bismuth carboxylate catalysts, Coscat 83¹⁷ and K-KAT XK-651.

As with the alkoxysilane studies, the cure rate of the uncatalyzed system was significantly slower than the optimized systems with catalyst. In this case, the K-KAT XK-651, which performed poorly in the previous studies, provided the best catalysis compared to the other non-tin catalysts.

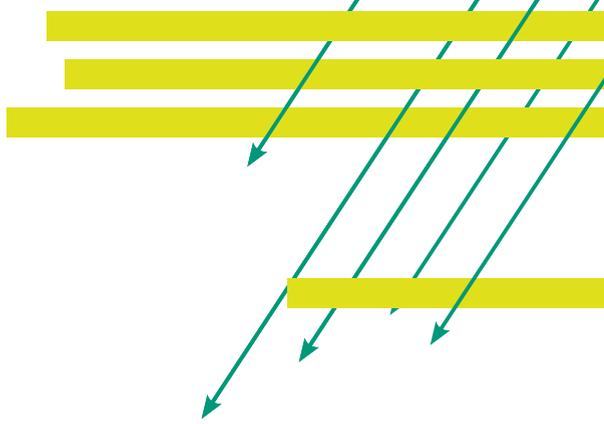
As previously mentioned, a potential drawback of bismuth catalysts is limited hydrolytic stability. K-KAT XK-651 was designed to provide improved hydrolytic stability compared to typical bismuth carboxylate catalysts. The results in *Table 10* demonstrate a significant improvement in the drying of the K-KAT XK-651 catalyzed system compared to the Coscat 83 catalyzed system, which could be a manifestation of the improved hydrolytic stability of K-KAT XK-651.

Experiment V: Two-component silanol terminated PDMS with acetoxysilane crosslinker

The following experiment was conducted with a simple clear system based on a silanol terminated polydimethylsiloxane¹⁸ with an acetoxysilane crosslinker.¹⁹ The weight ratio of the resins was 10:1. Films were cast with a dry thickness of about 1.5 mils. Because

the films were relatively thin, dry times were determined with circular drying time recorders.²⁰ This method is based on the circular scribe pattern on the coating made by a teflon sphere stylus that makes a complete 360° revolution in 6 h. The three reported dry time stages are Set to Touch—the time when material stops flowing back into the channel created by the stylus; Surface Dry—when the stylus no longer leaves a clear channel and begins to rupture the dry upper layer of the film (also considered dust-free); and Through Dry—when the stylus no longer ruptures or dents the film. All films were aged at 25°C and 50% RH.

The system without catalyst was still wet after 6 h. The system catalyzed with 0.05% DBTDL reached the Set to Touch stage in about 0.1 h, a Surface Dry in about 0.25 h, and a Through Dry in about 0.5 h. Each of the non-tin



	SET TO TOUCH	SURFACE DRY	THROUGH DRY	FILM APPEARANCE
NO CATALYST	6+	6+	6+	CLEAR
0.05% DBTDL	0.1	0.25	0.5	CLEAR
2% K-KAT 670	0.3	0.9	2.0	CLOUDY
2% PROPRIETARY COMPOUND	0.25	2.5	3.0	CLOUDY
2% K-KAT XK-651	0.1	0.25	4.0	CLOUDY
2% K-KAT XK-648	0.2	0.6	1.4	CLEAR

TABLE 11—Experiment V, Circular Recorder Dry Times (h)

catalysts included in the previous studies demonstrated some activity in this study. However, some of the catalysts developed compatibility issues that were evident in the formulated blends in the pot and in the films. Table 11 includes results of systems catalyzed with the catalysts tested in Experiments I through IV. An addition to the catalyst list was K-KAT XK-648, another zinc complex catalyst. The catalyst dosages were 2% based on formula weight.

The K-KAT 670 catalyzed system developed relatively slow dry times and appeared to have a compatibility issue. The system catalyzed with the proprietary catalyst was slower than the DBTDL control, particularly in Surface Dry. It also appeared to be incompatible. K-KAT XK-651 provided the best Set to Touch and Surface Dry of the non-tin catalysts, but Through Dry tailed off, possibly because of poor compatibility that was evident in the film appearance. The K-KAT XK-648 catalyzed system developed good dry times and it appeared to be compatible.

Conclusion

A variety of chemistries fall under the organosilane umbrella. Acceleration of the curing process for many of the chemistries is efficiently achieved with tin catalysts. However, increasing

regulatory restrictions have formulators searching for alternatives to tin catalysts. This work has demonstrated system specific catalysis in several organosilane systems. K-KAT 670 was the most efficient non-tin catalyst in a one-component dimethoxymethylsilane system which required acceleration of both the hydrolysis and condensation reactions. K-KAT XK-651 provided good cure response in a system based on a two-component alkoxy silane crosslinked with a silanol-terminated polydimethoxysilane (PDMS). A proprietary compound was the most effective non-tin catalyst in a one-component oximinasilane crosslinked system, and K-KAT XK-648 was the best tin alternative catalyst in a silanol-terminated PDMS crosslinked with an acetoxysilane.

Also addressed in this work was the catalysis of a non-methanol emitting moisture cure organosilane system based on a diethoxysilane polymer. In this case, K-KAT 670 catalyzed the crosslinking reaction while tin catalysts were essentially not active even at levels that doubled the maximum tin concentrations allowable in current EU regulations.

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