Metal Catalysts for Polyurethanes

PATCHAM

A Sustainable Approach to Technology

Patcham FZC is a global manufacturer of specialty additives headquartered in the United Arab Emirates. Since its inception, Patcham has steadily grown to become a leading supplier of metal carboxylates and specialty additives for Paint & Coatings, Inks, PVC, Composites and Polyurethane. We also manufacture a range of tin based and tin free catalysts for various end use industries.

The company's Pat-Add range of coating additives includes driers, wetting & dispersing agents, defoamers, slip & leveling agents, rheology modifiers. All our products are APEO free and many are produced from green raw materials. Several are designed to enable our customers to make products that are low VOC or VOC free.

Patcham has a strong manufacturing and R&D infrastructure that enables rapid transition from concept to products. The company has strategically located technical service laboratories, offices and representatives around the world to provide efficient customer service. In addition, a well-developed robust supply chain network enables us to deliver our products and services to customers around the globe with minimal lead-time.

General Information

Polyurethanes (PU) are one of the most versatile plastic materials.

There are several chemical reactions that occur in the formation of Polyurethane PU and Polyisocyanurate PIR products that require the assistance of catalysts.

Blow reaction is important for many foams but produces unwanted gassing in other systems.
Gel reaction is the defining reaction for all urethanes.
Trimerization is required for the production of rigid foams.

These reactions occur readily at temperatures above 110°C. However, at room temperature without a catalyst, they are slow, taking days.

	Isocyanate reaction with	
FAST	water	blow reaction
MEDIUM	polyols	gel reaction
SLOW	isocyanate	polymerization of which Trimerization is the most important

Catalysts exert a considerable influence on PU structures and its end properties by changing the relative rate of these primary chemical reactions.

Catalysts have a tendency to catalyze several of these reactions at once, although to differing degrees, and their individual action can be highly temperature and time dependent.

A mix of catalysts is often required to achieve a critical balance between these reactions in order to achieve the desired end product properties and workability.

Additions of metal-containing catalysts, in concentrations that can be measured in ppm, have a profound effect on the rate of reactions and can produce synergy with tertiary amine catalysts.

Catalyst deactivation can be a function of water content in the PU system and thus hydrolytic stability of the catalyst is also an important formulating consideration.

PU/PIR Catalysts are mainly tertiary amines and metal-containing compounds

Principal Reactions		Product	Amines	Metal-Based Catalysts
Trimerization	NCO/NCO Isocyanate/isocyanate	Polyisocyanurate	Weak	Very Strong
Gel reaction	NCO/OH Isocyanate/polyol	Polyurethane	Strong	Very Strong
Blow reaction	NCO/H2O Isocyanate/water	Urea + CO_2	Strong	Weak

Metal based catalysts are far more desirable than amines

Amines	Metal-Based Catalysts
Bad smell	Low odor
Corrosive	Non-corrosive
High pH	Neutral
Toxicity issues	Many have very low toxicity
Instability with acid treated pigents	Non-reactive towards acid treated pigments
Deactivation of HFO blowing agents	Stable with HFO blowing agents
Low Flash Point	Many have high flash point
End product discoloration	Several have very low color

Section 1: Trimerization Catalysts / Catalysts for PIR Applications

Trimerization reaction in the PIR industry is essential for the formation of rigid closed cell structures that impart dimensional strength and improved insulation properties to the end products.

PATcat 5000 series catalysts can be used as the sole catalyst in PIR systems.

They provide catalysis for the Blow, Gel and Timeization reactions.

Variations in system formulations and production equipment place different demands on the catalyst such as viscosity, OH and water content.

Trimerization is normally the slowest of the isocyanate reactions and requires catalysts to increase the rate of production and yield of trimerized material:

Patcham produces a wide range of amine free trimerization catalysts to meet those needs:

Metal	Anion	Carrier Diluent	Catalyst strength Metal content %wt/wt	Water content	Typical OH value	Typical viscosity (Cp) at 25°C	PATcat
Potassium	Octoate	DEG	15.0	5.0% max	525	3500	**5001**
			15.0	3.5% max	460	7000	**5003**
			10.0	2.0% - 4.0%	700	1200	**5011**
		MEG	15.3	3.0% - 4.0%	660	3500	**5016**
			15.0	9.5% - 10.5%	965	550	**5012**
	Acetate	DEG	15.0	5.5% max	910	350	**5005**
			13.2	2.0% max	815	350	**5008**
			10.0	5.5% max	1060	150	**5004**
		MEG	18.0	3.0% - 4.0%	1130	200	**5018**
			15.3	1.0% max	1100	150	**5019**
			15.0	3.0% - 5.0%	1290	75	**5007**
			13.0	2.7% - 3.5%	1340	100	**5013**
			10.0	3.0% - 5.0%	1530	50	**5006**
	Neodecanoate	DEG	10.0	3.0% - 5.0%	700	3500	**5010**

DEG gives lower OH values (less unwanted consumption of isocyanate). MEG gives lower viscosity for ease of handling.

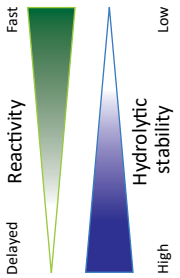
Higher metal content affords lower dosage and better economy.

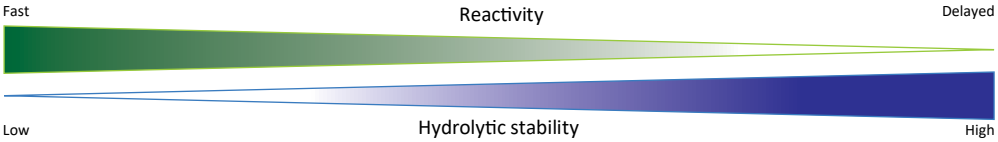
Higher water content gives lower viscosity for ease of handling but increases the OH value.

Lower Viscosity improves ease of handling.

Tin based gel catalysts cover a rage of activity from Fast Acting to Delayed Action and varying degrees of hydrolytic stability.

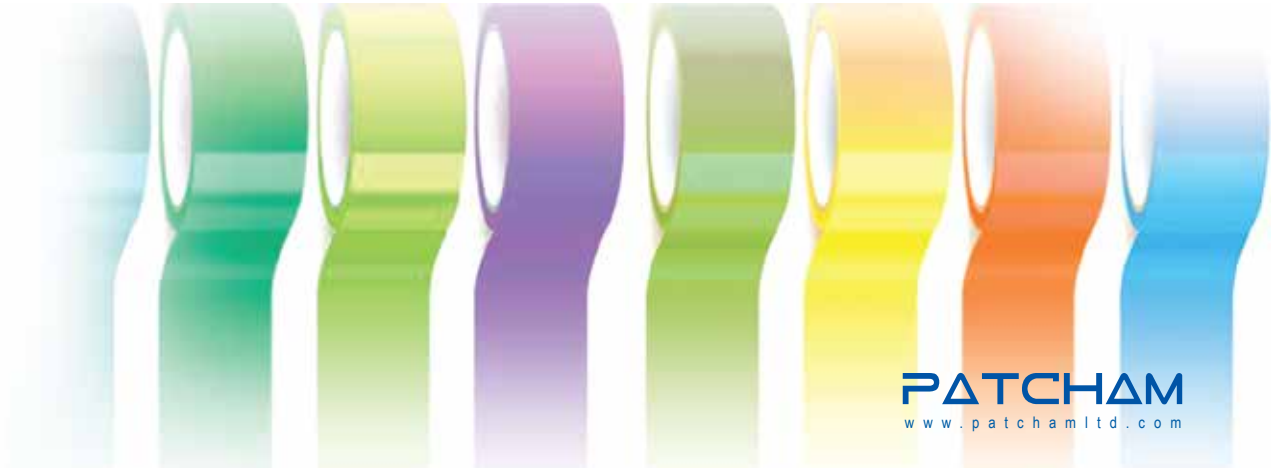
Type of Tin Catalysts		Di-acetate	Octoate	Mixed Carboxylate	Di-neodecanoate	Di -(2-ethylhexyl malate)	Di-laurate	Acetyl acetonate	Di-(lauryl mercaptide)	Di-(2 ethylhexyl thioglycolate)
Tin +2	Stannous		3012							
Tin +4	Mono butyl		3017							
	Dimethyl				3028				3027	3030
	Dibutyl	3003		3015	3004	3025	3001/3020	3006	3014	3026/3046
	Dioctyl	3023		3009	3024		3005	3016	3029	3022





Generally tin catalysts that demonstrate delayed action tend to have better hydrolytic stability.

PATcat Tin Catalyst		
PATcat 3017	Monobutyltin trioctoate	19.0%
PATcat 3028	Dimethyltin dineodecanoate	23.5%
PATcat 3027	Dimethyltin dilauryl mercaptide	21.0%
PATcat 3030	Dimethyltin di (2 ethylhexyl thioglycolate)	19.0%
PATcat 3003	Dibutyltin diacetate	33.0%
PATcat 3004	Dibutyltin dineodecanoate	20.0%
PATcat 3001	Dibutyltin dilaurate	18.0%
PATcat 3014	Dibutyltin lauryl mercaptide	18.0%
PATcat 3026	Dibutyltin di (2 ethylhexyl thioglycolate)	18.0%
PATcat 3046	Dibutyltin di (2 ethylhexyl thioglycolate)	2.0%
PATcat 3020	Dibutyltin dilaurate (lower crystallization temperature)	18.0%
PATcat 3025	Dibutyltin di (2 ethylhexyl maleate)	17.0%
PATcat 3015	Dibutyltin carboxylate laurate	18.0%
PATcat 3006	Dibutyltin acetyl acetonate	27.0%
PATcat 3024	Dioctyltin dineodecanoate	17.0%
PATcat 3005	Dioctyltin dilaurate	16.0%
PATcat 3022	Dioctyltin di (2 ethylhexyl thioglycolate)	15.0%
PATcat 3023	Dioctyltin diacetate	26.0%
PATcat 3009	Dioctyltin carboxylate laurate	16.0%
PATcat 3016	Dioctyltin acetyl acetonate	21.0%
PATcat 3029	Dioctyltin di (lauryl mercaptide)	15.5%



Fast-Acting Gel Catalysts for Spray Foam Applications

Tin-Free metal Based

- Apart from being more environmentally accepted, these catalysts may offer performance advantages over tin catalysts.
- Bismuth catalysts' activity is comparable to fast-acting tin catalysts. They provide low toxicity, and have better hydrolytic stability than fast-acting tin catalysts.

Sprayfoam

PATcat	Bismuth			
PRODUCT	General	HFO systems	low/no Amine	
4012	✓		✓	
4013			✓	
4016	✓	✓		Improved Shelf life
	Other metals			
13001			✓	Improved Blow

Delayed Action Gel Catalysts

Also referred as Mercury Replacement Catalysts

- These catalysts show low initial activity at ambient temperature.
- Their activity increases as the exotherm rises over time and/or when external heat is applied.

Delayed Action Catalysts

PATcat	
PRODUCT	
3022	Tin based
3029	Tin based
3026	Tin based
7001	Nickel based
18026	Tin-Free / Nickel-Free
19007	Improved Snap-Cure. Colorless

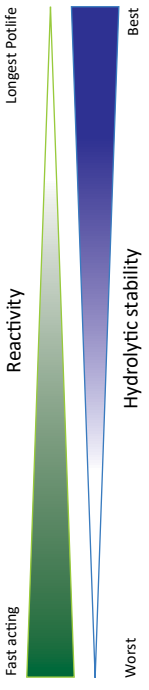
Patcham produces a range of metal based catalysts for CASE urethane systems.

Unlike amine catalysts most metal based catalysts do not strongly promote the reaction between isocyanate and water (blow reaction, generating CO_2) and thus are less likely to create microfoam, pinholes and other surface defects.

Polyurethane CASE systems can be two component (2k) or one component (1k), both of which can be solvent-based or waterborne and may or may not require heat for curing.

Selection of catalysts depends primarily on the curing chemistry and secondly on processing requirements:

Solvent based & 100% solids 2k and 1k Urethanes	Waterborne 2k and 1k Urethanes curing:
2k Urethane curing: Solvent evaporation followed by urethane cross-linking (gel reaction) requiring catalysts. **1k Urethane curing:** Oil modified Urethanes cure by auto-oxidation – see **Patcham Paint Driers** for more information about catalysts (driers) for these alkyd containing coatings. **Moisture-cured** (Urethane reactions initiated by water followed by gelling) or **blocked isocyanates** (require heat to unblock them so they can react with polyols) these systems require catalyst to accelerate curing.	Water soaking into the substrate or evaporating followed by cross-linking (gel reaction) requiring catalysts. May also require the application of heat. **Oil modified PUDs** cure by auto-oxidation – see **Patcham Paint Driers** for more information about catalysts (water dispersible driers) for these alkyd containing systems.
2k systems often require catalysts that can provide longer pot life (delayed action).	**Require catalysts that demonstrate a degree of hydrolytic stability**



TIN CATALYSTS
Solvent based and water based

Tin Catalysts	
PATcat 3022	Dioctyltin thioglycolate
PATcat 3029	Dioctyltin di (lauryl mercaptide)
PATcat 3026	Dibutyltin thioglycolate
PATcat 3030	Dimethyltin thioglycolate
PATcat 3014	Dibutyltin lauryl mercaptide
PATcat 3027	Dimethyltin lauryl mercaptide
PATcat 3005	Dioctyltin dilaurate
PATcat 3016	Dioctyltin acetyl acetonate
PATcat 3006	Dibutyltin acetyl acetonate
PATcat 3001	Dibutyltin dilaurate
PATcat 3020	Dibutyltin dilaurate (low crystallization temp)
PATcat 3025	Dibutyltin di (2 ethylhexyl maleate)
PATcat 3024	Dioctyltin dineodecanoate
PATcat 3004	Dibutyltin dineodecanoate
PATcat 3028	Dimethyltin dineodecanoate
PATcat 3009	Dioctyltin carboxylate
PATcat 3015	Dibutyltin carboxylate
PATcat 3017	Monobutyltin trioctoate
PATcat 3023	Dioctyltin diacetate
PATcat 3003	Dibutyltin diacetate

TIN-FREE CATALYSTS

Solvent based		Water based	
Bismuth		**Bismuth**	
PATcat 4005	All purpose	**PATcat 4012**	Hydrolytically stable
PATcat 4006	Most economical	**PATcat 4013**	Hydrolytically stable
PATcat 4007	2EHA-free	**PATcat 4007**	All purpose
Bi/Zn		**Bi/Zn**	
PATcat 4009	Balanced	**PATcat 4009**	Balanced
Zinc		**Zinc**	
PATcat 9001	Most economical	**PATcat 9001**	Most economical
PATcat 9002	All purpose	**PATcat 9003**	2EHA-free
PATcat 9003	2EHA-free	**PATcat 9008**	Hydrolytically stable
PATcat 9009	Longer pot life	**PATcat 9009**	Longer pot life
Aluminum			
PATcat 17002			
Other	**Delayed action catalysts**	**Other**	**Delayed action catalysts**
PATcat 7001	Standard Nickel based	**PATcat 7001**	Standard
PATcat 18026	Tin-Free /Nickel-Free	**PATcat 18026**	Tin-Free /Nickel-Free
PATcat 19007	Better snap cure	**PATcat 19007**	Better snap cure

1K Polyurethane Blocking agent

PATox 1	MEKO Methyl Ethyl Ketoxime

PATCHAM

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