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An expanding global supplier for the Plastics Industry

Replacing Lead in PVC Pipes in India

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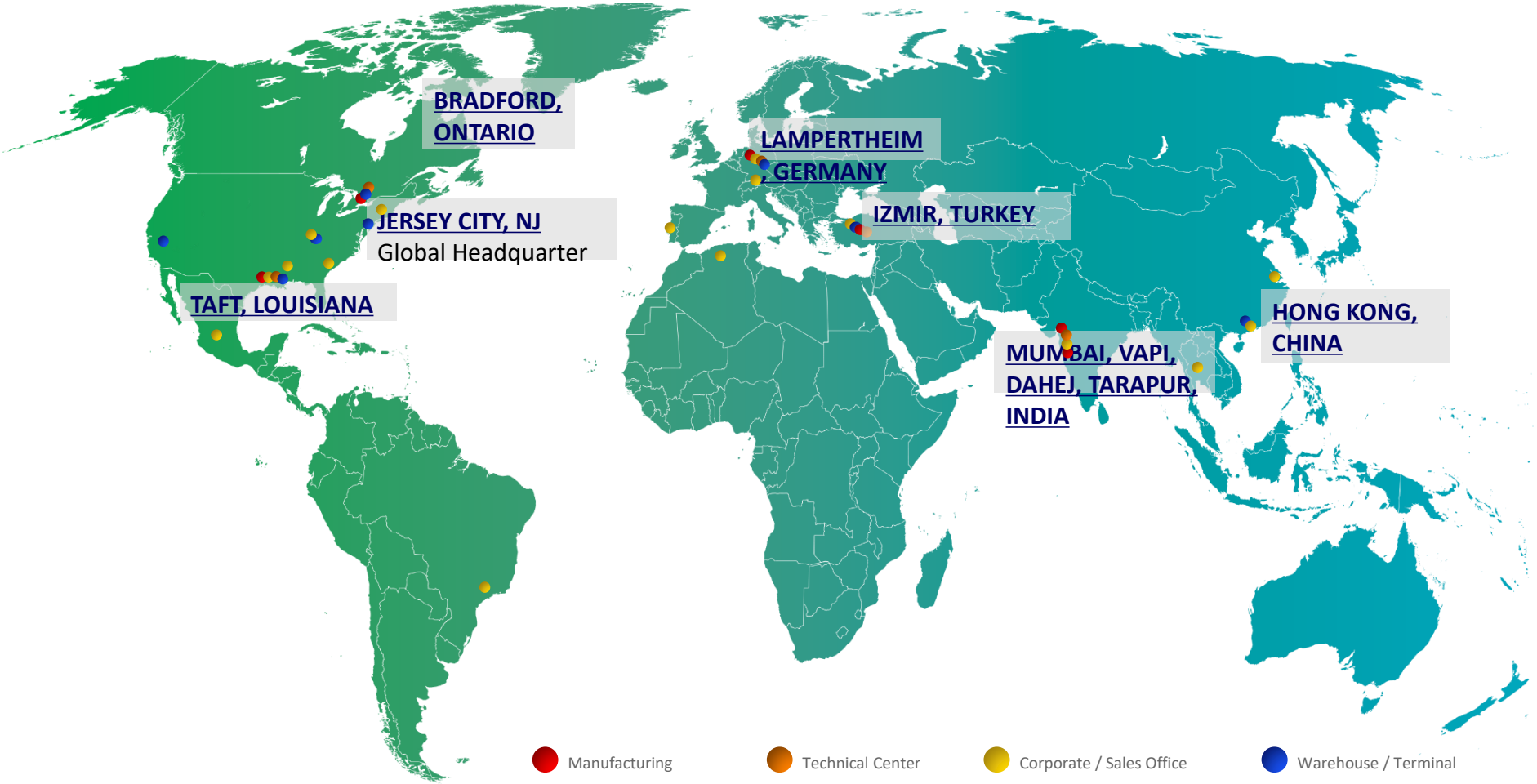
GLOBAL REACH



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Product Range

Primary Plasticizers	Drapex® Alpha® Primary Plasticizers
Secondary Plasticizers	Drapex® Epoxidized Soybean Oil Drapex® Epoxidized Tall Oil
Mixed Metal Stabilizers	Mark® Mixed Metals Heat Stabilizers
Tin Stabilizers	Mark® Organotin Heat Stabilizers
Heavy Metal Free Stabilizers	Mark OBS® Stabilizers
Polymer Modifiers	Blendex® Polymer Modifiers Blendex® Acrylic Processing Aids Blendex® Acrylic Impact Modifiers
Organotin Specialties	Fomrez® Organotin Specialties Mark® Organotin Specialties
Liquid Phosphite Esters	Markphos® Liquid Phosphites
Solid Antioxidants	Marknox® Phenolic Antioxidant Markphos® Phosphite Antioxidants
Thioesters	Marknox® Thioesters

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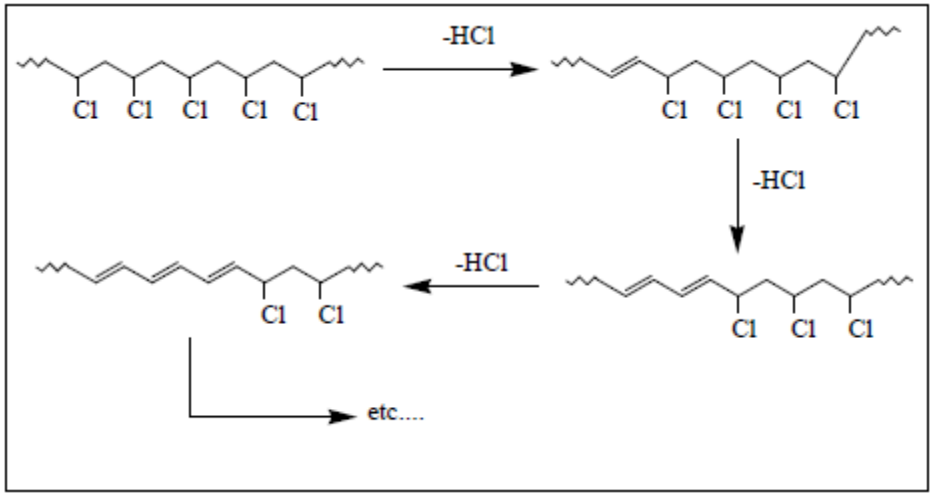
Outline

- PVC degradation and stabilization
- Comparative Analysis of heat stabilizers for rigid PVC
- Methyltin heat stabilizers for pipe applications
- Examples of replacing lead stabilizers by Methyltins
- Advantages of using organotin stabilizers
- Conclusions

PVC Degradation and Stabilization

- Degradation under the influence of heat and UV light is an intrinsic property of PVC
- PVC degradation results in loss of mechanical properties and discoloration
- Thermal stabilization of PVC can be achieved via
  - Reaction with allylic chlorides
  - Scavenging HCl that catalyzes initiation and propagation of dehydrochlorination
  - Shortening polyene sequences



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PVC Stabilizers - Industry Options

Lead Stabilizers

- Very good heat stability
- Wide process window
- Regulated out of pipe in India

Calcium – Zinc Stabilizers

- Provide good heat stability
- Good Initial Whiteness
- Higher dosages vs Lead and Tins

Tin Stabilizers

- High efficiency
- Excellent heat stability
- Cost effective & wide process window
- NSF Approvals

Organic Based Stabilizers

- Provide very good heat stability
- Long term heat stability
- Higher dosages vs Lead and Tins

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Comparative Analysis of Heat Stabilizers for Rigid PVC: Approvals and Material Form

Stabilizer Types	Food contact	Pharmacopeia	NSF Approval	Renewable content	Material Form
Tin (Sn)	Y	Yes	Yes	Yes	Solid & Liquid
Ca/Zn	Y	No	No	Yes	Solid
Lead (Pb)	N	No	No	None	Solid

- In comparison with Ca/Zn's, organotin stabilizers consist of fewer number of components, and therefore, processing characteristics imparted by the organotins are more consistent

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Comparative Analysis of Heat Stabilizers for Rigid PVC: Selected Performance Attributes

Stabilizer Types	Transparency	Efficiency	Compatibility with PVC	Crack growth rate in pipe	Recycling/ rework
Tin (Sn)	High	High	High	Lower	Yes
Ca/Zn	Good	Low	Lower	Higher	Yes
Lead (Pb)	Poor	Medium	Good	Higher	Yes

- Tins are highly efficient and dosage levels are 5 to 6 times lower than Ca/Zn

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PPI PVC Range Composition
NSF Version 30.1

Issued September 2017

Table 2 – Heat Stabilizer

Source or Vendor	Ingredient Trade Designation	Range (phr)	Limitations
Galata Chemicals, LLC	Mark 1925	0.30 - 1.00	None
Galata Chemicals, LLC	Mark 1930	0.30 - 1.00	None
Galata Chemicals, LLC	Mark 1939	0.30 - 1.00	None
Galata Chemicals, LLC	Mark 1941	0.30 - 1.00	None
Galata Chemicals, LLC	Mark 1942	0.30 - 1.00	None
Galata Chemicals, LLC	Mark 1971	0.30 - 1.00	None
Galata Chemicals, LLC	Mark 1971L	0.30 - 1.00	None
Galata Chemicals, LLC	Mark 2903	0.30 - 1.00	None

Organotin Stabilizers and Applications

Stabilizers	Tin Content, %	Attributes	Applications				
			GP Pipe	Conduit	NSF Pipe	Profile, Sheet	Fittings
Mark 1942	≥ 6.1	More lubricating, improved cost-in-use	Y	Y	Y		
Mark 1939	≥ 6.1	INDUSTRY STANDARD	Y	Y	Y		
Mark 1971L	≥ 8.0	Advanced fusion and lubrication	Y	Y	Y	Y	
Mark 2903	≥ 10.0	High efficiency			Y	Y	
Mark 1925	≥ 11.5	High efficiency and improved lubrication			Y	Y	
Mark 1930	≥ 13.5	High efficiency, long-term stability				Y	
Mark 1993	≥ 15.0	High efficiency, long-term stability	Y	Y			Y
Mark 2911	≥ 18.0	Advanced heat stability in large diameter pipe	Y	Y		Y	

- Proposed regulations mandate a phase-out of lead-based heat stabilizers in pipes and fittings in India
- Replacement of the lead-containing stabilizers has begun at several leading pipe manufacturing companies that service both local and global markets
- Due to low toxicity and ease of handing liquid organotin stabilizers are used widely throughout North and South America as well as and other global regions.

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Performance Attributes of Organotin Stabilizers

Migration, mg/m^2/day

Lead	Ca/Zn	Tin
0.1-0.9	0.007-0.110	<0.005

Lead > Ca/Zn > Tin

Processing Window

Tin ≈ Lead > Ca/Zn

Dynamic Heat Stability

Tin >/≈ Lead > Ca/Zn

Density, g/mL

Lead	Ca/Zn	Tin
1.42	1.40	1.40

Lead > Ca/Zn ≈ Tin

- E. Barth; "Das Langzeitverhalten von PVC-U-Rohren mit unterschiedlicher Stabilisierung" KRV (2005)
- M Schiller, W. Fischer: „Stabilizers for PVC Pipe Systems – Quo Vadis?" Plastics Pipes XII, Milan/Italy (04/2004)

Operational Advantages of Using Organotin Stabilizers

- Considerably Higher Efficiency: Tin > Lead ≈ Ca/Zn
- Superior product consistency and lower batch-to-batch variability in terms of product quality and mechanical properties due to wider production window
- Longer production runs without a need for shutting down to clean up
- 5-15% Higher production output
- Production cost is about the same as with the lead one-packs

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Example of Replacing Lead Stabilizer by Mark 1942 in Pipe

- Use of organotin stabilizes has been the industry standard in pipe fitting compounds

- Galata offers purge compound for removing lead from the manufacturing lines prior to incorporating organotin stabilizers in their pipe compounds

Rheology Profile (Plastograph)

Stabilizer	Fusion Time (sec)	Loading Peak (Nm)	Torque Min. (Nm)	Torque Max. (Nm)	Torque Eq. (Nm)
Pb One-pack (2.5 phr)	72	80.9	17.8	44	28.9
Mark 1942 (0.5 phr) + lubricants (0.6 phr)	72	97.6	16.7	43.6	28.8

Conditions: 180 C, 55 rpm, 58 gr

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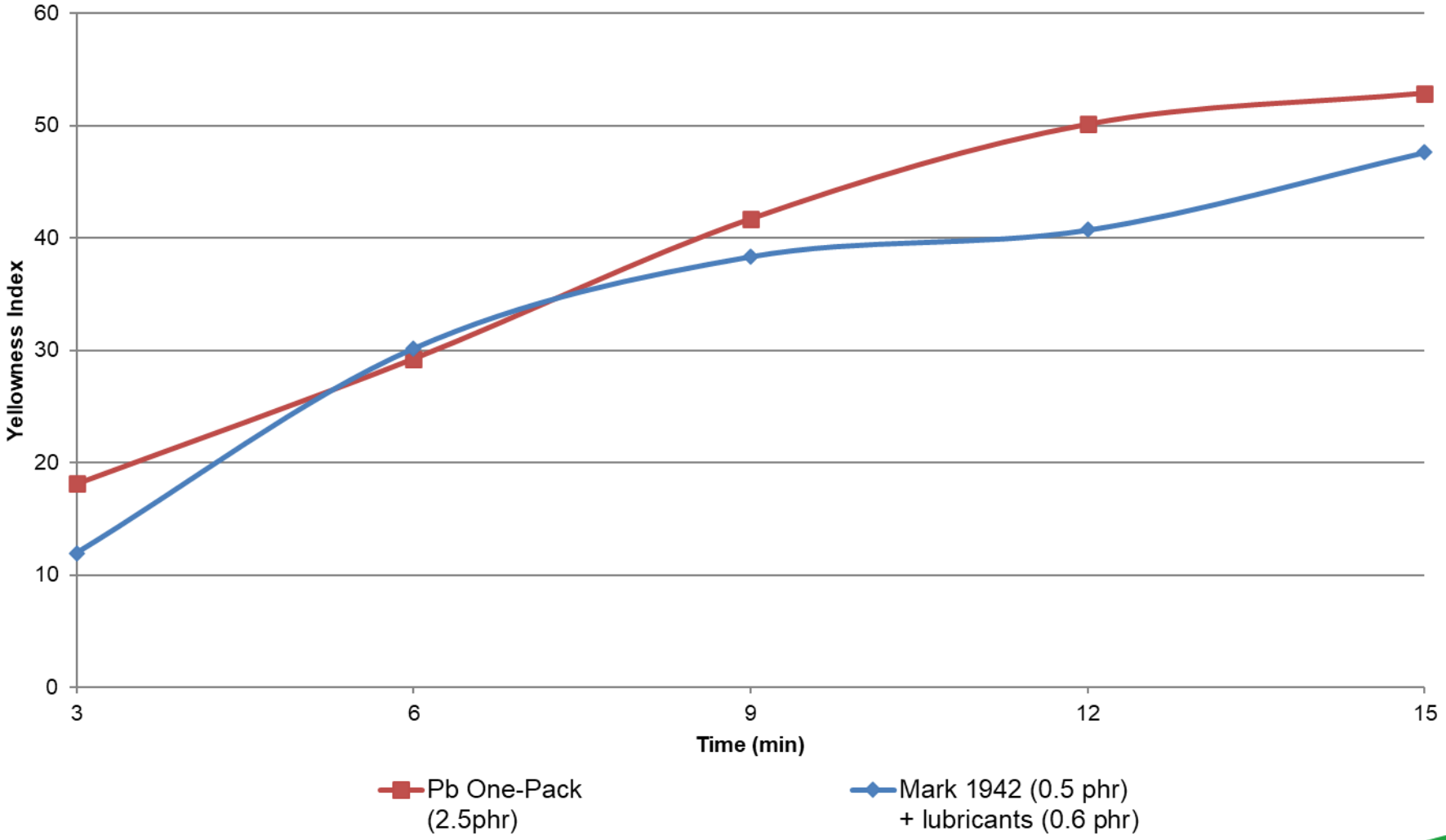

Conditions: 197 C, 3 min interval time

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Example of Replacing CZ Stabilizer by Mark 1942 in Pipe

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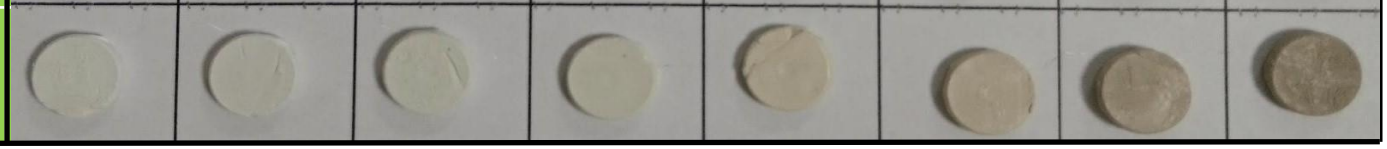
Dynamic Heat Stability

Name of Parameter	Conditions
Temperature	190ºC
Roller Speed	60 RPM
Compound Weight	60 gm

Stabilizer /Time (min)	2	4	6	8	12
CZ Control (2.6 PHR)					
Mark 1942 (0.5 PHR)					
Mark 1942 (0.6 PHR					

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CONCLUSIONS

- High efficiency methyltin stabilizers are effectively used in manufacturing rigid PVC compounds and articles including pipes and fittings.

- Certain organotin stabilizers are approved for use in potable water pipes and food contact applications

- Replacement of lead stabilizers by liquid organotin stabilizers results in enhanced processability of PVC compounds, improves mechanical properties and whiteness and extends dynamic heat stability of PVC pipes made with it.

- Formulation Changes and Outcome

- 2.5 phr Lead-containing One-pack stabilizer containing lubricants) was replaced by 0.5 phr Mark 1942, a liquid methyltin stabilizer, with 0.6 phr lubricants, matching rheology and exceeding heat stability imparted by Market Control.

- Reverse Ester Tins gives significant final compound cost saving advantage (Approx.2.0 Rs/Kg) compared to Mixed Metals (Ca-Zn) in addition to processing advantages

- Local technical support is available to facilitate the transition away from lead-containing heat stabilizers

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PARTNERING WITH GALATA CHEMICALS

- Modern design of heat stabilizers, modifiers and plasticizers addresses processing and cost-performance requirements of PVC in a sustainable manner
- Galata Chemicals is a reliable partner and a global leader in developing and providing sustainable technical solutions for all major markets and applications

Disclaimer

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