PVC Stabilizer Update:
Stabilizer Options in an Unstable World

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The Plastics Industry “Landscape”

- PVC contributes about 35 million tonnes to this production total (78.4 b)
- Non-plasticizer additives: approx. 2.1 MM tonnes in 2007
- Heat Stabilizers: 0.91 MM tonnes, or 43% of the total additives market
PVC Additives
Where do they go…

Provide process and performance characteristics to over 35 Million Tons of PVC resin Worldwide

- PVC in North America:
  - 55 - 60% Rigid PVC
    - Major applications exist in rigid PVC for building and construction, bottles, molded parts and extruded sheet
  - 40 - 45% Flexible PVC
    - Use is widespread. Include film, wallcoverings, wire & cable, flooring and tubing, medical, toys….
    - Dosage rates of 6-8 phr
  - Long term growth rates above GDP, but less than consumption rates in polyolefins
    - Predicted Growth, 2007 to 2012: 2% / Year!

Source:
Townsend Polymer Services
ANTEC 2007, Cincinnati, OH
PVC Additives Can Be Classified into 3 Categories:

- **Modifiers**
  - Plasticizers
  - Chemical blowing agents
  - Coupling agents
  - Impact modifiers
  - Organic peroxides

- **Property extenders**
  - **Heat stabilizers**
  - Antioxidants
  - Flame retardants
  - Light stabilizers
  - Antistatic agents
  - Biocides

- **Processing aids**
  - Lubricants
  - Mold releases
  - Slip agents
  - Antiblocking agents

Source: Townsend Polymer Services Plastic Additives 7 Report, 2008
Stabilizer Choices for Various PVC Applications

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FLEXIBLE

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• Mixed Metal Systems have quickly become the system of choice in Flexible PVC
### Heat Stabilizer Consumption by Region and Type, 2007 (in Tonnes)

<table>
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<tr>
<th>Type</th>
<th>North America</th>
<th>Europe</th>
<th>China</th>
<th>Global Total</th>
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<tr>
<td><strong>Mixed Metals</strong></td>
<td>36,150 (46%)</td>
<td>97,300 (44%)</td>
<td>72,300 (22%)</td>
<td>309,820 (34%)</td>
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<tr>
<td><strong>Tin</strong></td>
<td>41,200 (52%)</td>
<td>18,000 (8%)</td>
<td>17,900 (6%)</td>
<td>110,900 (12%)</td>
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<td><strong>Lead</strong></td>
<td>1,900 (2%)</td>
<td>101,900 (46%)</td>
<td><strong>159,800</strong> (50%)</td>
<td>414,900 (46%)</td>
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<td><strong>Others</strong></td>
<td>50 (&lt;1%)</td>
<td>3,700 (2%)</td>
<td>71,400 (22%)</td>
<td>75,380 (8%)</td>
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<tr>
<td><strong>Total</strong></td>
<td>79,300 (9%)</td>
<td>220,900 (24%)</td>
<td>321,400 (35%)</td>
<td>911,000</td>
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</table>

**Source:**
Townsend Polymer Services
Plastic Additives 7 Report, 2008
Heat Stabilizer
Performance Criteria, Constraints & Challenges

Primary Purpose of Heat Stabilizers: To prevent degradation of the PVC polymer during:
  • PVC Compound Processing
  • Throughout the product’s life cycle

Heat Stabilizers do the following:
  • Efficiently scavenge HCL and replace labile chlorine, Remove metal chlorides
  • Scavenge free-radicals
  • Remove single unsaturation in PVC chain
  • Provide lubrication

The type and amount of heat stabilizer employed are dictated by:
  • Formulation Variables,
  • Processing Conditions,
  • End Use Characteristics

This leads numerous custom-designed stabilizers to address individual client CTQ’s
Mixed Metal Stabilizer Composition
5 major components

- **Primary Stabilizer**
  1. Ba, Ca, K, Mg Salt
     - Improves LTHS at expense of ICH
  2. Zinc salt
     - Improves ICH at expense of LTHS

- **Secondary (co-)Stabilizer**
  3. Organophosphite Liquid
     - Improves ICH of most Ba / Zn
  4. ESO stabilizer
     - Improves LTHS
  5. Hydrotalcites, Diketones, Antioxidants, Acid Scavengers, Carriers Diluents, etc…

- Blends of various primary and secondary stabilizers increase processing and performance windows.

- Typically one raises both the level and ratio of Ba (Ca) to Zn in moving from:
  
  Plastisols → Flexible PVC → Semi-Rigid PVC → Rigid PVC

- Stabilization efficiency generally increases with higher metal content

- Good initial color and color hold are achieved by low Ca (Ba)/Zn ratios.

- Good long term heat stability requires higher Ca(Ba)/Zn ratios
Stabilizer Design
Formulation Variables

Stabilizers must be compatible, interact & perform efficiently in the presence of many formulation variables:

- Plasticizer
- Resin
- Fillers
- Flame Retardants
- Lubricants
- Antioxidants
- Pigments
- Costs

Typical Flexible-PVC formulation

- PVC resin: 100 phr
- Plasticizer: 18 – 70 phr
- Secondary plasticizer: 3 – 5 phr
- Fillers (CaCO₃): 10 – 50 phr
- Flame retardants: 2 – 15 phr
- Heat stabilizer: 1 – 10 phr
- Small adds: as needed
- UV-stabilizer
- Lubricants
- Pigments
- Biocides
- Antistatic agents
- & more….
Stabilizer Design
Processing Conditions

- **Processing equipment**
  - Processing type
- **Storage Stability**
- **Machine set-up, efficiency**
  - Temperature
  - Rates
  - Process stability
- **Processing characteristics**
  - Plasitcizer
  - Rheology
  - Dispersion
  - Compatibility
  - No Plate-out
- **Optimal heat stabilization**

- **Material Safety & Handling**
  - VOC's
  - Storage / Handling equipment
- **Solids:**
  - Ease of handling
  - Poorly dispersed
  - Limitations in clear applications
- **Liquids:**
  - Sometimes difficult to handle
  - Adds lubricity
  - May use lower levels
  - Contribute to taste/odor
  - May interact with other raw materials in rigid/semi-rigid formulations
Stabilizer Design
End-Use Characteristics

Good useability of finished articles during whole lifetime
- Cost-benefit to customer
- Industry Standards
- Heat Stability
  - Moderate Temp Heat Stability
  - Long-term Heat stability
- Volatility and Odor
  - VOC’s
  - Automotive Fogging
- Compatibility
  - Migration
  - Plate-out

- Light Stability (UV)
  - Weatherability
  - Regional / climatic variation
- Appearance
  - Color, Clarity, Gloss, Haze
- Regulatory
  - Positive ecobalance
  - Regional trends
  - Legal Requirements
- Specific technical performance
  - Electrical properties
  - Printability
Environmental and Regulatory Challenges

Use of PVC and its additives as a “material of choice” face numerous concerns:

- Demand for more knowledge about the impact of chemicals
  - REACh - Registration, Evaluation, Authorization and Restriction of Chemicals
  - RoHS – Restriction on Hazardous Substances
- Risk Assessment (EPA, TSCA, etc…):
  - Phthalates
  - Nonylphenol (TNPP)
  - Bisphenol-A
  - Animal-based Fatty Acids
  - Airborne particles (‘Dust-free’ Additives)
  - Volatile Organic Compounds (VOC’s)
- Global Harmonization of Data
- Waste Reduction / Recycling of Plastics
**REACH – Registration, Evaluation, Authorization and Restriction of Chemicals**

A single system for non-phase-in (new) and phase-in (existing) substances

- **Main Steps in REACH:**
  - Pre-Registration (completed)
  - Data sharing to avoid unnecessary testing (Consortia established)
  - Registration of substances of >1 TPA per Manufacturer or Importer
  - Information throughout the supply chain
  - Evaluation of dossiers by Member States
  - Authorization for substances of concern
  - Restrictions – the safety net
- **ECHA (European Chemicals Agency) will manage the system**

**No Registration = No Marketing in EU!**

- Global Harmonization of Data…
Eliminating Substances of Concern: Another Driving Force for Reformulation

CMR: Carcinogens, Mutagens & Reprotoxins

CMR Category 1:
- Lead

CMR Category 2:
- Dibutyltin Stabilizers
  - 2010 registration deadline
  - Phase out by marketing and use directive (2012 or 2015)
  - Threatened by authorization
- p-t-butyl benzoic acid (ptbba)

CMR Category 3:
- Octyltins, Methyltins
- 2-ethylhexanoic acid
- Bisphenol-A

PBT – Persistent, Bioaccumulative & Toxic
- vPvB - very Persistent & very Bioaccumulative

Materials of Equivalent concern
- e.g. Endocrine Disruptors
  - Nonylphenol
    - criteria for Annex XIV candidates (authorisation)
  - Phenol
- Impacts both liquid MM’s and phosphites usage
PBT assessment of Octyltins: final results
Source: Brigitte Dero, ETINSA Update February, 2010

• Testing was required on Dioctyltin (CAS 15571-58-1), with delivery of the results by November 2009.

• **Mono- and di-octyl tin tested far below the test threshold limit of 2000 qualifying a molecule as Bioaccumulative**
  • The concentration of tin in the fish tissues was checked by two analytical methods, which agreed with each other.

• **Mono- and di-octyl tin are not PBT**

• The final data pkg on PBT assessment delivered to UK Environment Agency in Feb. 2010.
• Data allowing the PBT assessment of substances are required for each REACH registration dossier (by 2010):
  • the data obtained will be used for all the octyltin substances registration dossiers
  • the submission of the required information will ensure the future of these substances in downstream users applications
Commercial Challenges
Flexible PVC Process / Application Roadmap

Multiple Processes & Applications to account for in Flexible PVC
Heat Stabilizer Global Trends

Lead Stabilizers

• Losing Share Due to Health/Regulatory Pressure
  • Vinyl 2010 Initiative: EU production of lead decreased by 26,000 tons from 2005
  • Full Phase-out by 2015
  • REACh: Pb-stabilizers will likely be submitted for authorization

Tin Stabilizers

• Accepted in NA, but not so in EU
  • Pricier than MM’s but has better thermal properties
    • Improved products with phr 1-2% becoming available
  • Reflects widespread use in the NA rigid PVC market
  • Need to defend against “Collateral Damage” of Butyltins
Heat Stabilizer Global Trends

Mixed Metal Stabilizers

• Benefitting from Pb reformulation
  • Some Ba/Zn’s rival Pb’s performance without the toxicity issues
  • Ca/Zn systems growing rapidly replacing lead, but with reformulating
  • Ca/Zn has great utility in FDA, medical and non-toxic applications
  • Custom stabilizer formulations dominate, but may also inhibit further growth

• Keep pace with the chances in material use
  • Resin: Increased use of rework and recycled PVC demands better LTHS
  • Plasticizer: New plasticizers require proper stabilizer package selection

Others (OBS, Rare Earths)

• Limited growth to date
  • Looking for a Market Driver (price, regulatory, etc…)
Additional Commercial Challenges
Inter-material Competition

“Why PVC?”

The Cost/Performance Dynamic works in favor of PVC

• PVC properties and its versatility in transformation /processing / application (rigid - flexible)
• High chlorine content of about 56 % - important role in the alkali/chlorine-balance
• High chlorine content - certain independence of Naphtha and crude oil prices

BUT…

Polyolefin processing technology advances represent an increasing threat

• Pipe market is seeing some erosion due to a switch to PO’s (up to 5%/yr volume)
• Medical device manufacturers seeking to phase out PVC due to leachate concerns in blood bag, tubing applications
• TPO’s looking to gain share in automotive interior market (fogging, VOC’s)
• PET gaining momentum in packaging applications (bottles, jars, pharmaceuticals)
Additional Commercial Challenges

Cost Pressure

• Raw Material Feedstocks
  • Tin Volatility
  • Demand for new & improved acid scavengers (hydrotalcites)
• Reformulation
  • Removing component costs while maintaining technical performance

Supply Chain Management

• Strong desire to reduce shop inventory
• Consolidate purchasing via ‘bundling’

Differentiation from the Competition

• New / Better intermediates
• Better %Metals incorporation
• Improved Acid Scavengers
Who We Are

Mark® PVC Stabilizers
• Mark® Tin Stabilizers
• Mark® Mixed Metal Stabilizers
• Mark OBS® Organic-Based Stabilizers
• Mark® EZ Stabilizers

Drapex® Epoxidized Oils

Markstat® Antistatic Agents
• Marklube® Lubricants
• Blendex® Impact Modifiers
• Weston® Phosphite Esters
• Celogen® and Actafoam® Chemical Foaming Agents

Formerly the PVC Additives business of Chemtura Corporation
• Formed on May 1, 2010

Historical descendent of Argus and Witco Chemicals, Uniroyal Chemical, GE Specialty Chemicals, Crompton Corp.

Global Capabilities, with Manufacturing in the US and Germany

Product lines / Trade Names Include: