Selecting Heat Stabilizers for PVC

Poly(vinyl chloride) (PVC) is one of the most important commercial plastic but, it is thermally unstable at processing temperatures. Therefore, **heat stabilizers** are widel products at all stages by **improving resistance of PVC products at high temperature**.

Due to the upsurge in the quantity of stabilizers that are marketed to the PVC industry, selecting and evaluating a stabilizer can be a cumbersome process. Review the consider when selecting heat stabilizers for PVC with detail understanding of:

- **Role of Heat Stabilizers in PVC**
- **Types of Heat Stabilizers for Vinyl Compounds**
- **Impact of PVC Ingredients on Heat Stabilizers Selection**

(Continue reading or click to go on specific section of the page)

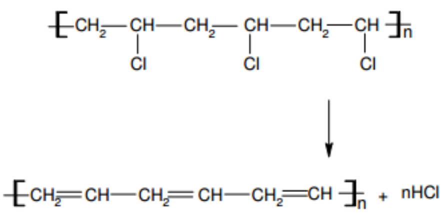
PVC Heat Stabilizers: Role, Types and Ingredient Selection

Role of PVC Heat Stabilizers

Poly(vinyl chloride) (PVC) is one of the most important commercial plastic and its compounds have a great diversity of applications and methods of processing. But, PVC is thermally unstable at processing temperatures.

The amount and type of energy input varies considerably among the many different production methods and end-use applications of PVC. In fact, resin degradation starts in the polymerization reactor. It can continue under storage conditions through oxidation, carbonyl formation, etc. even before use.

Once PVC gets heated up to 170°, hydrogen and chlorine are eliminated. Decomposition starts and leads to the release of HCl (autocatalytic dehydrochlorination). Unstable molecules (allylic chlorine structure) appear, which in turn, stimulate the next HCl loss. And so on, this is a chain reaction.



Thermal Degradation of PVC

The factors which promote PVC degradation include:

- Mixing cycles (dry blend, banbury, high speed plastisol dispersators)
- Processing (calender, extruder, molder)
- Fabricating (embossing, thermoforming, laminating)
- Scrap re-work
- Heat and light energy of outdoor exposure
- Heat of a product's use environment (auto interior, hot air duct)
- Gamma ray sterilization

Thus, heat stabilizers play a crucial role to **improve the resistance of PVC compounds to heat or high temperatures**. The goal of heat stabilizers is to safeguard the vinyl product at all stages. To prevent degradation of PVC compounds, heat stabilizers work by:

- Neutralizing hydrogen chloride
- Replacing weakened carbon-chlorine bonds
- Preventing oxidation

Nowadays, compounding industry also expects PVC heat stabilizers to fill many specific requirements on top of heat stabilization.

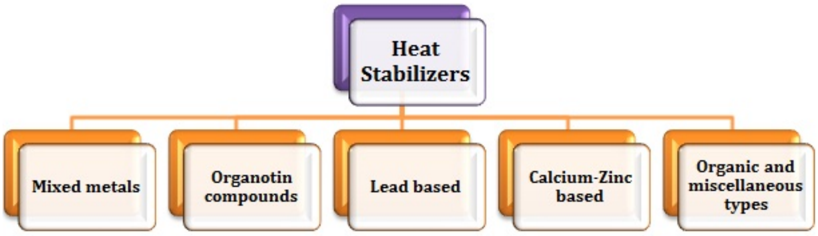
» **View All the Commercially Available PVC Heat Stabilizers Here!**

This polymer additives database is available to all, free of charge. You can filter down your options by suitable polymer, system or application, recommended application, conversion more, supplier, regional *availability and many more.*

Let's discover the types of heat stabilizers and criteria for selecting the suitable stabilizer for PVC applications.

Types of Heat Stabilizers for Vinyl Compounds

There are several basic groups of heat and light stabilizers currently offered to the vinyl industry which include:



Mixed Metals

Organic acid salts (liquid and solid), consisting of any one or a combination of barium, calcium, cadmium (disappearing), and zinc. Typically, C8 to C18 straight chain or branched chain aliphatic carboxylic acids are used. Aromatic (alkyl benzoic) acids once used are no longer in favor due to toxicity concerns.

» View All Mixed Metal PVC Heat Stabilizers Here!

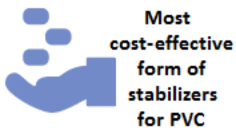
Organotin Compounds

The physical and chemical properties of this organotin heat stabilizers solely depend on the nature of the chemical groups linked to the tin atom. Organotin mercaptides offer excellent thermal performance and therefore, are employed as the most efficient thermal stabilizers.

Organotin stabilizers are well compatible with the other additives used in PVC therefore minimizing processing challenges. Organotin mercaptides also offer outstanding color retention in plasticized and rigid PVC processing.

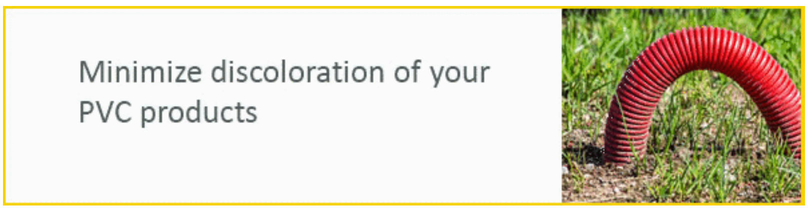
Lead Salts and Soaps (Liquid and Solid)

Heat Stabilizers based on lead salts and soaps offer exceptional long-term heat stability. These heat stabilizers are considered as one of the most cost-effective form of stabilizers for PVC. PVC compounds when stabilized with lead heat stabilizers show:



- Excellent heat and light stability
- Exceptional mechanical and electrical properties
- Display a wider processing range

Apart from these benefits, lead heat stabilizers have some limitations associated with them as well. Lead stabilizers when used in PVC windows lead to their discoloration.
Leads offer the best electrical properties mainly due to the insolubility of lead chlorides formed during stabilization. Currently, lead is under pressure for possible replacement by special mixed metal systems, in secondary and decorative wire insulation. However, primary insulation is still best stabilized by lead.



Calcium or Zinc-based Compounds

Calcium or Zinc-based stabilizers usually contain calcium stearate and small quantities of zinc soaps like zinc octoate.

Calcium/zinc-based stabilizers that are used for **rigid PVC applications** are generally available in liquid/powder forms. Such heat stabilizers improve color stability during processing of PVC and maintain it during the lifetime of the PVC article.

Ca/Zn systems are mostly employed in applications requiring USFDA approval for direct or indirect food contact

Organic and Miscellaneous Types

Organic heat stabilizers include alkyl/aryl phosphites, epoxy compounds, beta-diketones, amino crotonates, nitrogen heterocyclic compounds, organosulfur compounds (i.e. ester thiols), hindered phenolics, and polyols (pentaerythritols). These types currently are being heavily researched, and their use at the expense of metal-containing stabilizers is expected to grow significantly.

A minor group consisting of carboxylic or mercaptoester salts of antimony, strontium, potassium.

Calendered, extruded, or molded and plastisol flexible vinyl compounds are often stabilized with mixed metal **Ba/Zn**, **Ca/Zn** heat stabilizers. Ca/Zn systems are mostly employed in applications requiring USFDA approval for direct or indirect food contact.

In North and South America, and parts of the Far East, rigid vinyl compounds for extrusion and molding are frequently stabilized with organotin mercaptides and lead or mixed metal systems are used for this purpose in Europe.

	Building & Construction	Healthcare/ Medical	Automotive/ Transportation	Packaging	Electronics
Mixed Metal Stabilizer	✓			✓	
Organotin Compounds					
Lead Salts and Soaps					
Calcium/Zinc Based	✓	✓		✓	✓
Organic/Miscellaneous					

Impact of PVC Ingredients on Heat Stabilizers Selection

The best approach in most cases is to **check heat stability and color retention of the formulation** with and without these additives. It helps to pre-determine the extent of any potential problem.

Vinyl ingredients which can have a potential impact on PVC heat stability are discussed below:

- Vinyl Resins
- Modifying Resins
- Plasticizers
- Fillers
- Pigments
- Lubricants
- Other Additives

Vinyl Resins

The wide variety of PVC resins is probably the single greatest factor which explains the large stabilizers offering confronting compounders.

PVC homopolymer is made by suspension, bulk (or mass), and emulsion polymerization methods. The amount and type of residual components on the resin shipped to users (catalyst residues, suspension agents, emulsifying agents, etc.) can differ a lot. Two vinyl resins made via the same method by two different producers can have a different response to the same stabilizer system.

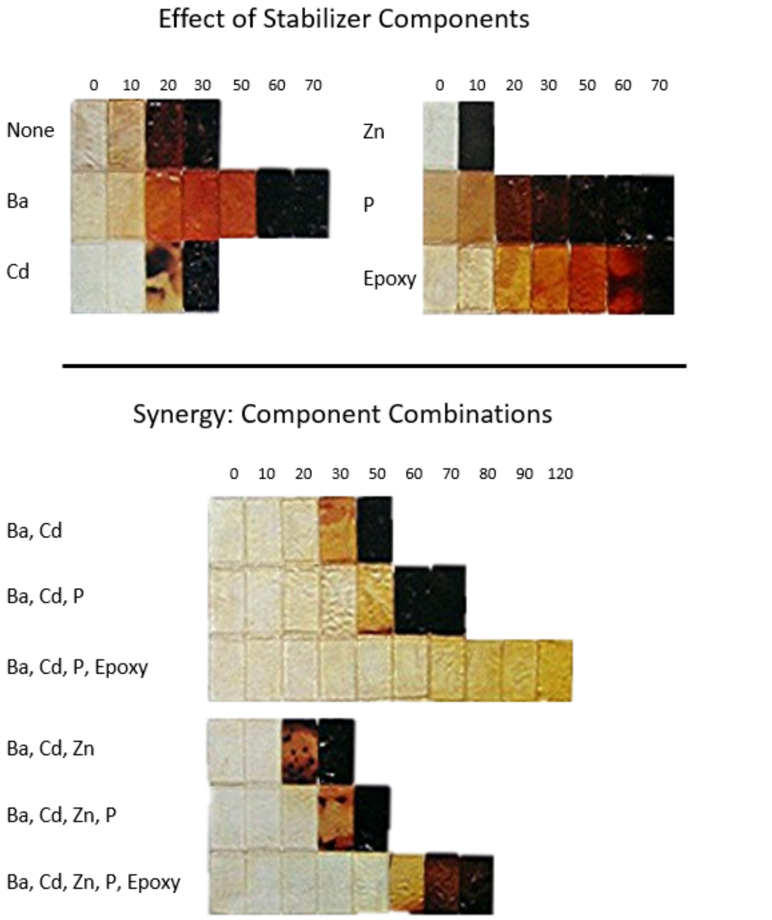
PVC copolymers and PVC with other co-monomers (propylene, cetyl vinyl ether, vinylidene chloride) also have a different response to a given stabilizer system.

Zinc Sensitivity

Drastic discoloration- even burning- in PVC compounds subjected to progressive exposure to heat

One of the most striking differences in stabilizer response occurs with mixed metal Ba/Zn and Ca/Zn. We call this phenomenon **"Zinc Sensitivity"**. It is a drastic discoloration- even burning- in PVC compounds subjected to progressive exposure to heat.

The degradation which occurs with zinc (sudden blackening & burning) is typical. Indeed, zinc chloride forms when the zinc salt's carboxylic acid displaces labile chlorine on the polymer chain. It is a strong Lewis Acid and a degradation catalyst for PVC. The phosphite component provides a measure of long-term stability by itself.



In the figure above, **Ba/Cd** and **Ba/Cd/Zn systems** benefit upon addition of the phosphite. It is believed to chelate or "**tie up**" zinc and cadmium chlorides formed during the process of stabilization. For this reason, phosphites are known to retard the "**zinc burning**" effects described above. The further addition of the epoxy component to a mixed metal system results in dramatic improvement in heat stability. This is truly synergistic (recall epoxy performance alone).

A study also shows that a zinc sensitive resin can become more "zinc tolerant" by washing it from residual catalysts, suspending agents, or emulsifying agents.

Vinyl acetate - vinyl chloride copolymers are quite zinc sensitive (depending on acetate content). The use of zinc in the stabilizer system should be avoided. The one exception to this recommendation will be discussed under the subject of 'Fillers'.

Other types of copolymers generally respond to stabilizers like PVC suspension homopolymers. They exhibit varying degrees of zinc sensitivity. Most of these copolymers (propylene, cetyl vinyl ether modified PVC) have greater inherent heat stability than the acetate copolymers.

Bulk or mass polymerized PVC shows heat stability like corresponding K-value suspension PVC resins. They both respond well to a wide variety of mixed metal, organotin, and lead stabilizer systems.

Emulsion polymerized PVC resins of today are mainly plastisol dispersion resins. They have very small, smooth surfaced particles. Most dispersion resins respond well to mixed metal and organotin stabilizer systems.

Modifying Resins

Many thermoplastic resins are used with PVC to:

- Enhance strength and/or processing and fusion of rigid PVC
- Change properties of flexible PVC such as the retention of embossing during post-forming operations

These modifying resins include:

- Chlorinated polyethylenes (CPE's)
- Ethylene vinyl acetate/carbon monoxide terpolymers (Modified EVA's)
- Acrylonitrile butadiene styrene (ABS)
- Methacrylate butadiene styrene (MBS), and
- Acrylic polymers

When incorporated with PVC, some of these modifiers can detract from heat and light stability to varying degrees. In general, the stabilizer system can be the same. Although, a slightly higher level of stabilization may be needed, depending on severity of the process.

The EVA terpolymers and chlorinated polyethylenes have the less impact on heat and light stability. They perform very well in rigid applications requiring good outdoor weathering.

Acrylic polymer modifiers also are recommended for outdoor exposure applications. Some acrylic and ABS modifiers are good for clear vinyl applications (minimal stress-whitening), but impact heat stability. The nitrile portion of ABS especially is thought to detract from PVC's heat and light stability.

Impact modifiers can be classed as:

- "**Matrix**" types (chain entanglement with PVC molecules) like EVA terpolymers and chlorinated polyethylene
- "**Discreet particle**" types (resin-rubber interfaces, or shock-absorbers) like **acrylic**, **MBS** and **ABS**.

The use of certain **acrylic polymers as processing aids** is widespread. They contribute towards smooth melt flow and good surface finish. They also tend to promote earlier, faster fusion of PVC at a given temperature. They can even lower the fusion (or gelation) temperature of the compound.

Plasticizers

Plasticizers impart flexibility, elongation, and elasticity to the compound. These materials are generally low volatile organic compounds.

The most common plasticizers include:

- Esters of aromatic and aliphatic dibasic acids
- Glycol diesters of monobasic acids
- Linear polyesters
- Epoxidized glycerides and mono-esters
- Phosphate esters
- Aromatic hydrocarbons, and
- Aliphatic chlorinated hydrocarbons

The choice of stabilizer is not affected by the type or amount of plasticizer present in a formulation.

The two exceptions are as follows:

1. With **phosphates** and **chlorinated paraffins**, you will need more epoxy co-stabilizer, and extra phosphite chelator in a mixed metal barium/zinc or calcium/zinc system.

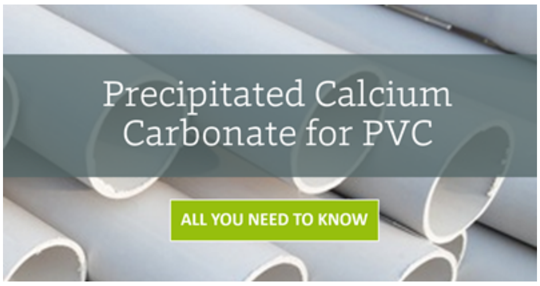
2. **Epoxy plasticizers** (epoxidized soybean, linseed oils and tallate esters) are often used in PVC compounds as an auxillary co-stabilizer with mixed metal stabilizer systems. Functioning as HCl acceptors primarily, epoxy Plasticizers enhance the heat and light stability of most mixed metal/phosphite stabilized compounds.

Fillers

Inert, solid inorganic mineral compounds are used in vinyl formulations as extenders. The purposes are to:

- Reduce overall costs
- Provide opacity
- Achieve certain desirable end-use properties (abrasion resistance, tear strength, dry "**hand**", or feel to the touch, hardness and stiffness, and even with alumina trihydrate ATH-fire retardancy).

Calcium carbonate is the most commonly used filler in PVC formulations. Although calcium carbonate itself does not impact heat stability, you still need to alter the metal ratio of mixed metal stabilizer systems with increasing levels of calcium carbonate.



The class of **silicate fillers offers no great stability problem**. Usually an increase in the amount of epoxy plus inclusion of an additional 0.5 part of a phosphite will be sufficient to overcome any stability problem that might occur.

ATH (alumina trihydrate) behaves very much like calcium carbonate in terms of stabilizer considerations.

Pigments

Organic and inorganic dyes and pigments used in the PVC industry have been studied in-depth. There are lots of data about their impact on:

- Heat stability
- Light stability
- Chemical resistance
- Oxidative resistance, etc.

If you select a PVC stabilizer system that is best suited for your resin, plasticizer, filler content, process and end use properties, it will generally suffice in protecting the pigment as well.

Yet, a couple of special cases need to be mentioned.

- **Metallic pigments** generally keep best color stability in the presence of alkaline stabilizers. Look for barium alkyl phenate or alkaline stabilizers which contain little or no zinc. Lower epoxy use levels, and the use of inert lubricants (mineral oil or low molecular weight polyethylene) are also recommended.

- **Fluorescent pigments** are best stabilized for both heat and light exposure with alkyltin mercaptoester stabilizers. Good results are also obtained with high zinc mixed metal/phosphite systems.

» Explore the Commercially Available Pigments for PVC Here!

Lubricants

One of the least understood for years, and yet most important aspects of PVC technology is the **phenomenon of lubricity**. It's especially important to understand in when developing rigid PVC. Indeed, lubricity and stability considerations can't be separated during a rigid PVC process.

Lubricants can be classified to some extent by relating chemistry and behavior. The terms “**internal**” and “**external**” have been used to describe the nature of lubricants with respect to their use in PVC compounds. However, more realistically, there is a spectrum of lubricating behavior from:

- The “internal” lubricity of polar molecules (stearic acid, **metal stearates**, fatty acid esters, and glycerides).
- To the materials containing both polar groups and long carbon chains (balanced internal-external characteristics).
- The “external” lubricity of long chain hydrocarbon derivatives of paraffin oils, **paraffin waxes** and **low molecular weight polyethylenes** (oxidized and non-oxidized PE’s).

1. Internal lubricant have a plasticizing effect.
    - They lower melt viscosities and reduces internal friction between polymer molecules.
    - Faster fusion is also seen with internal lubricity behavior.

2. External lubricants function essentially by their insolubility in PVC.
    - They migrate to the surface where they can reduce frictional drag between PVC melt and hot metal surfaces of the extruder, calender, etc.
    - This type of lubricant behavior is very dependent on its molecular weight and melting point.
    - It determines where in the process (i.e. barrel, adapter, die) it will deliver the desired lubricity.

Current lubrication technology offers specially designed lubricant "**one-packs**". It makes use of these internal and external characteristics. These packs are designed for specific processing and product applications.

Stabilizer selection in light of lubricity requirements is especially critical in rigid PVC processing. Most lubricants, internal or external, have no adverse effects upon PVC heat stability, and respond well to normal stabilizer use levels.

One exception: when using N,N' ethylene bis-stearamide wax, you will need higher stabilizer levels. This is due to the degrading effects of amides on PVC resin.

Tin mercaptoester stabilizers contribute to lower melt viscosities than tin carboxylates, barium/zinc, calcium/zinc, and lead stabilizers. Most tin mercaptide stabilizers are essentially non-lubricating. Yet, based on their compatibility and viscosity effects, they might have some internal lubricity behavior. Therefore, tin mercaptides generally need more external lubricant in rigid PVC processing than the mixed metal or lead types.

Lubrication requirements for plasticized, flexible PVC are not nearly so critical.

Stearic acid and stearyl alcohol are by far the most common lubricants in the industry. They work well with a wide variety of stabilizers including most mixed metal (Ca/Zn, Ba/Zn) systems. Stearic acid is especially recommended with alkaline stabilizers based upon barium phenates. Stearic acid should be avoided, however, with tin mercaptide stabilizers. Highly incompatible alkyl tin stearates may be formed. It can result in exudation or "**spew**" in plasticized formulations.

Other Additives

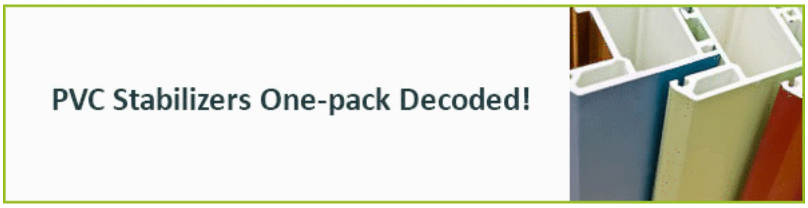
Other additives used in many vinyl formulations include:

- **Blowing (foaming) agents**
- **Wetting agents for plastisol viscosity control**
- **Biocides**
- **Anti-static agents**
- **Anti-fog agents for food wrap film**
- **UV absorbers**

Be careful when selecting a stabilizer for PVC compounds containing any of these additives. They may react with certain stabilizers. It would lower heat stability or create colored reaction products.

For example, some anti-static agents - quaternary ammonium compounds- can reduce heat stability significantly.

Certain UV absorbers may form a yellow reaction product with alkaline stabilizers. In such cases, you need a higher stearic acid level to counteract this problem. Some UV absorbers (triazoles) may exhibit a "**pinking**" tendency with tin mercaptide stabilizers.



Commercially Available PVC Heat Stabilizers

Check the Latest News About Heat Stabilizers