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PVC Stabilizers

Polyvinyl chloride (PVC) is probably one of the most fascinating, most versatile, and oldest thermoplastic polymers. It is the polymer with which a person comes into contact within minutes of their birth: the bracelet bearing a newborn's name and birth date is commonly made of PVC. Products made of PVC accompany us through life—from toys to drinking water pipes. One of the most outstanding characteristics of PVC is its enormous longevity with an almost unchanged functionality. The French chemist Henri V. Regnault was the first to synthesize vinyl chloride monomer (VCM) in 1835. He noticed the formation of a white powder—polyvinyl chloride (PVC)—when it was exposed to sunlight. However, Regnault was not aware of the significance of his discovery. Thirty-seven years later, in 1872, the German chemist Eugen Baumann made PVC in a laboratory after extended experiments and investigation. It took about 40 years more until the German chemist Fritz Klatte together with Emil Zacharias and Adolf Rollet developed the production process of VCM and PVC. However, it did not attain an industrial use until 1928. The production of PVC in Germany started in 1930 at BASF, and in 1935 at I. G. Farben. Fritz Klatte died in 1934 in Klagenfurt/Austria, about 65 km away from the place where the author lives.

1.1 The Production of Polyvinyl Chloride (PVC)

For the production of PVC, a distinction can be made between an older process based on calcium carbide, which is converted into acetylene as a next step, and the modern process based on ethylene generated from petroleum or natural gas by cracking. As the carbide process is no longer of importance in Europe, though still utilized for example in China, it will not be covered in this section. The modern production of PVC can be described in a simplified manner (Figure 1.1). The left-hand side of Figure 1.1 depicts the cracking of petroleum or natural gas to make ethylene. On the right-hand side of Figure 1.1, chlorine and sodium hydroxide (caustic soda) are produced by electrolysis of rock salt. Previously, the chlorine was considered to be a waste by-product whereas the caustic soda, a raw material for glass manufacture, was the target product. Today, chlorine is considered a target product in its own right.

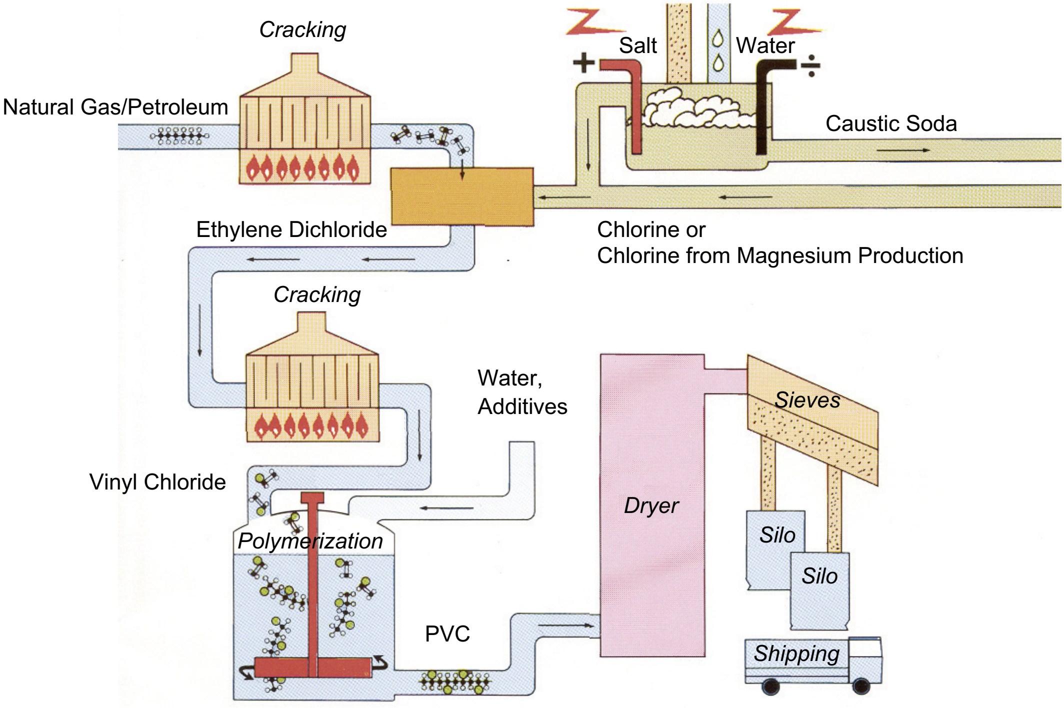

Figure 1.1 Schematic representation of the production of PVC [1]

Ethylene and chlorine are reacted to give ethylene dichloride. In a second step, the ethylene dichloride is processed to vinyl chloride monomer (VCM). The VCM is then polymerized in an autoclave under pressure, with the addition of initiators and further additives, to form PVC. The initiator forms radicals R*, which start the polymerization reaction (Figure 1.2).

Temperatures range from 50 to 70 °C and pressures range from 7 to 12 bar. Prestabilizers, mostly antioxidants, are often added before drying the reaction product. After drying, the PVC is ready to be shipped.

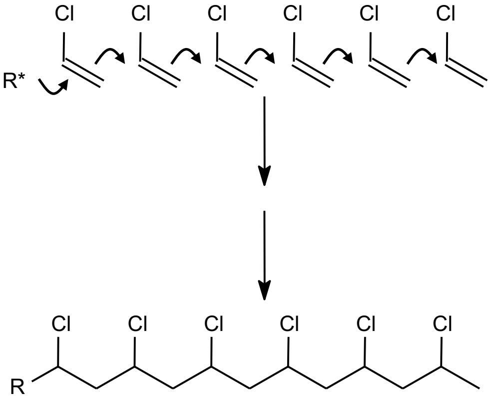

Figure 1.2
Polymerization of vinyl chloride monomer (VCM) to PVC

As for all polymerization reactions, the resulting products are not uniform. They have different chain lengths and chain branching. The k-value was introduced as a simple reference value for the average chain length of the polymer: the shorter the average chain length, the smaller the k-value. The average chain length is determined by the reaction conditions during polymerization. In general, it can be stated that the k-value of PVC decreases with increased polymerization temperature and pressure. On the one hand, the k-value is related to the molecular weight of the polymer chains. On the other hand, it is also related to polymer properties such as softening temperature, stiffness, hardness, intrinsic stability, and modulus of elasticity.

There is a simple rule: the higher the k-value, the more viscous and tough the melt, the harder and stiffer the resulting product (for example, profile, pipe, film) will be, the more energy will be needed for processing, and the closer the processing conditions will be to the degradation temperature of PVC. With increasing k-value it becomes more difficult to process PVC. It is therefore not possible to process PVC with k-values in the range of 70 to 74 without prior addition of plasticizers. After the addition of plasticizers, the resulting end products are called “flexible” or “plasticized” PVC (p-PVC or PVC-P) products. It is possible to process PVC with k-values of 54 to 68 without addition of plasticizers. Such products are called “rigid” or “unplasticized” PVC (u-PVC or PVC-U).

VCM is not soluble in water. In order to disperse the monomer evenly in water, auxiliary additives have to be used. Historically emulsion polymerization is the oldest process and was first used in 1929. The initiators (for example peroxides and other per compounds) used in this case are water soluble. Emulsion polymerization can be run as a continuous or a batch process. In the batch process about 1% of emulsifier is added; the continuous process requires 2.5 to 3.0%. The emulsifiers are surface-active substances such as alkyl sulfonates, alkyl sulfates, or ammonium salts of fatty acids. These emulsifiers remain in the PVC after drying.

The resulting polymerization product is the so-called E-PVC, and consists of very small particles in the range of 1 to 2 µm. The remaining amount of emulsifiers acts as an external lubricant and also gives the E-PVC good antistatic properties in the final products.

During the suspension polymerization process, the VCM is distributed in the water by intensive stirring. The radical initiators, for example azobisisobutyronitrile (AIBN), are soluble in the monomer. Suspending agents (used at 0.05 to 0.5%), such as polyvinyl alcohol or water-soluble cellulose, are added to prevent the agglomeration of the VCM droplets. This discontinuous process produces PVC particles of the size 50 to 200 µm, which are called S-PVC. If 0.01 to 0.03% of emulsifiers is used in addition to the suspending agents, the VCM is dispersed even finer, as a microsuspension, during the polymerization process. The resulting MS-PVC has particle sizes from 5 to 10 µm and is much finer than S-PVC. Pure S-PVC has a high purity, low water absorption, and good electrical properties.

If no water is used in the polymerization, the resulting polymer is called bulk or mass PVC, or M-PVC.[1] Because the initiator is dissolved in the VCM, the process steps of filtration and drying are no longer necessary. Products made from M-PVC appear more transparent and more brilliant than those made from S-PVC. The different PVC types are used in differing applications, according to their particle sizes and k-values; see Table 1.1 and Table 1.2.

Table 1.1 PVC Types and Their Applications

PVC Type	Particle Size	Predominant Applications
E-PVC	1 to 2 µm	Plastisols, rigid and flexible applications
MS-PVC	5 to 10 µm	Plastisols
MS/S-PVC	~50 µm	Extender PVC in plastisols
S-PVC	50 to 200 µm	Rigid and flexible applications
M-PVC		Transparent applications, various special applications

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[1] In English the abbreviation m-PVC is also used for (impact) modified PVC. The designation o-PVC (or PVC-O) for oriented PVC pressure pipes is also commonly used.

Table 1.2 k-Values of S-PVC and Application Areas

Application	k-Value of PVC			
	57–63	63–65	65–68	70–75
Automotive crash pad			***	**
Blow film	***	**		
Cable channel		***	**	
Calendered automotive (low fogging)			***	*
Calandered GP			***	*
Ceiling, roller shutter, wall panel	*	***	**	
Compact sheet	***			
Door and window profiles		*	***	
Drainage pipe		**	***	
Edge bending (0.4 mm sheet)	***			
Edge bending (2 mm profile)		***		
Flexible hoses			***	**
Flexible injection moldings	***			
Foam sheet	***	*		
Furniture foil	***			
Foamed technical profile	***	**	*	
Geo membrane, water stops			**	***
Injection moldings	***			
Office film			***	*
o-PVC pipes			***	
Pipe, compact or skin layer		***	**	
Pipe, foam layer	***			
Rain gutter		**	***	
Rigid film, calendered	***			
Shoe sole			***	**
Siding		*	***	
Spread coating of CV flooring			***	*
Spread coating of automotive applications (low fogging)				***
Table cloth			***	***
Transparent film, outdoor	***	***		
Transparent packaging film	***			
Transparent profiles	***			
Windowsill profiles	**	***		
Wire, cable insulation and sheathing				***

* recommended ** very recommended *** highly recommended

Other monomers, such as vinyl acetate or acrylate, can be polymerized with vinyl chloride. The resulting products are called copolymers. Different polymer chains can also be grafted onto the PVC chains (grafted PVC). A further possibility for modifying PVC is to add more chlorine to the polymer by a postproduction chlorination process. These PVC types with higher chlorine content than pure PVC are called C-PVC (chlorinated PVC). They have a higher softening point, which results in more difficult processing behavior.

Another important criterion of PVC quality is the morphology of the PVC particles. The particles should be porous and irregular; the surface area should be as large as possible. Given these properties, a good absorption and dispersion of stabilizer one-packs and other additives is guaranteed. A too-even surface area of the PVC particles cannot properly absorb the additives, resulting in local decomposition of the PVC, thereby causing surface defects (pit marks, pitting, specks).

Furthermore, PVC should be free of any impurities. A standard test method is available to determine the number of black spots (impurities) in a given PVC sample: TSE EN ISO 1265. According to this standard, a maximum count of 60 black spots per sample is acceptable. However, this is considered too high for most applications, and a count of less than 25 spots is preferred. Moreover, a simpler, more practical test method exists for spotting impurities. A transparent glass beaker is filled with some water or ethanol or a mixture of these. Then a small representative sample of the PVC powder to be tested is added and the mix stirred to disperse the powder completely. Then the PVC is allowed to settle at the bottom of the beaker. The black spots in the settled PVC, viewed from below (observation is made easier by using a mirror, or even better, a magnifying mirror), are counted to assess the PVC quality. A few runs should be made to achieve higher statistical certainty. This average “black spot” score should then be compared to an approved standard PVC grade, previously tested by the same method.

■ 1.2 Thermal Degradation of PVC

If the production of PVC progressed ideally, as represented in Figure 1.2, and resulted in linear polymer chains without any defects, processing of PVC powder would be much easier [2]. During polymerization, defects may occur [3]. The most important defects are

- tertiary chlorine atoms, which result from branch formation during polymerization (Figure 1.3), and
- allylic chlorine atoms, which form for example by termination of the polymerization reaction (Figure 1.3).

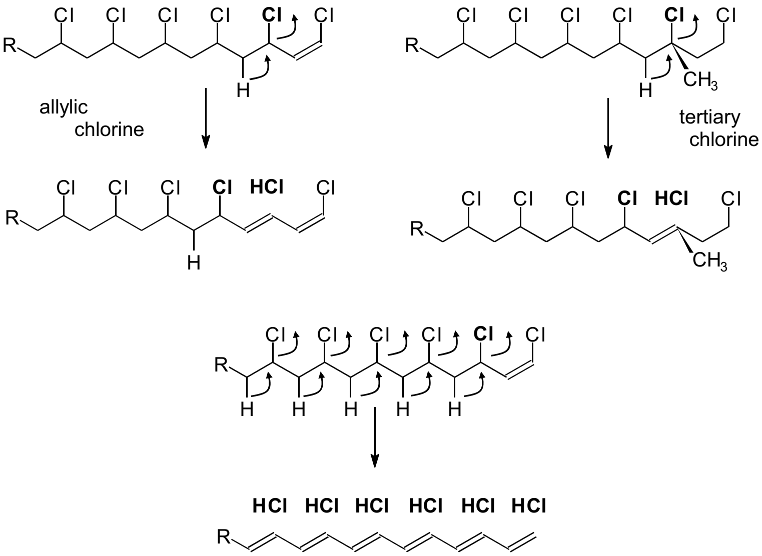


Figure 1.3 Degradation of PVC at allylic and tertiary carbon atoms due to heat or shearing

The degradation of PVC starts at these defect sites [4, 5]. Therefore, these chlorine atoms are also called labile chlorine atoms, and the site of the defect is called the initiation site of degradation. The degradation of PVC is called dehydrochlorination because hydrochloric acid (hydrogen chloride, HCl) is split off during the process. The split-off of HCl generates new defects. If no stabilizer intervenes, this process continues in a zipper-like fashion. Hydrochloric acid and conjugated double bonds form; the latter are also called polyene sequences. Once six to seven conjugated double bonds have formed, a slight yellowing of the PVC can be observed. This yellow discoloration grows darker with increasing length of conjugation, from red to brown and finally to black (Figure 1.3). The PVC is then called *burnt*.

In addition to the simplified mechanism discussed here, several others have been discussed. It should be noted, for example, that in addition to the ionic mechanism depicted in Figure 1.3 a radical degradation process can also be considered.

The influence of oxygen on the autocatalytic activity of the generated hydrochloric acid was investigated. It is further being discussed that longer conjugated double-bond systems can bind hydrochloric acid to form onium salts. This results in a deepening of the discoloration and is called halochromism. In addition to thermal degradation of PVC, shearing during processing and outdoor use of the finished products under the influence of light, air, and weather will also result in the degradation of the polymer.

These effects and mechanisms are most likely of secondary interest to the plastics processor. A detailed scientific discussion can be found in the relevant literature

[2–55]. Of essential importance to the processor is that additives can counteract these degradation processes by preventing them or at least slowing them down, partially even reversing them.

This is what PVC stabilizers are for. Unfortunately, one universal stabilizer cannot fulfill all requirements. In most cases, stabilizers are blends of single additives that complement each other, often increasing the joint effect (synergism) and sometimes counteracting each other (negative synergism). Therefore, the following will give the reader a basic understanding of the single components that play, have played, and maybe will play a role in PVC processing.

1.3 One-Packs

In most instances stabilizer blends are required to achieve the optimal PVC processing performance and the best properties for the final product. Further functions of the additives are

- substitution of labile chlorine atoms,
- shortening of polyene sequences,
- neutralization of HCl, and
- prevention of autoxidation.

In addition to the possibility of developing their own stabilizer solutions, the processor has the option to rely on formulated stabilizer-lubricant one-packs. These one-packs have the following advantages:

- All components (primary stabilizer, lubricants, flow modifiers, and other components) are included. In many instances, the one-packs are tailor-made, individual solutions.
- The cost of quality control is significantly lower because only one raw material, the one-pack, and not the individual additives, have to be tested.
- The stock-keeping is much simpler, as is the dosing and mixing in production.
- Any variability of the blends is reduced due to the fact that the minor components, the single additives, are preblended. A weighing error of the preblend has a much smaller effect compared to an error made with a highly lubricating single additive.
- Low-dust or dust-free one-packs improve plant hygiene for transport and mixing.
- Less packaging material is generated.

- The costs for new developments are lowered.
- In addition to one-pack deliveries, the one-pack supplier also ensures competent service.

Apart from having varying compositions adapted for specific requirements, one-packs are also delivered in various forms. The simplest one-packs are powder blends of individual additives. This allows virtually any combination of additives, and the powder is easily dispersed with nearly any mixing technique. Even liquids can be incorporated to a certain degree. A disadvantage is the dust generation during transport and dosing. This problem can be drastically reduced by some simple measures. One possibility is to pack the powder blends into bags. Very often the bag weight is adapted to the weight of the mix, and the complete bag can be dumped into the mixer. The bag material is chosen to be compatible with and remains in the final product. Another option is to compact the powders to granulates. This significantly reduces the dust issue. Granulating conditions are chosen to give a low dusting but easily dispersible product. Quite clearly, this product form is not suitable for slow-running mixers. Pastes are powder blends that are mixed with plasticizers until a stable, often highly viscous mass is achieved. Consequently, the dosing of pastes requires special techniques.

In the case where dust-free products are required, tablets, flakes, and microgranulates are the delivery forms of choice. Of these, tablets are the most appealing. In most cases, these one-packs are based on a melt process. Because of this, the raw material combinations and the total amount of nonmelting products are more limited than in powder blends. The dispersion is done in high-speed mixers (Figure 1.4). Liquid stabilizers, excluding tin stabilizers, are often a complex solution of additives in solvents and are mostly used in plastisol and calender applications.

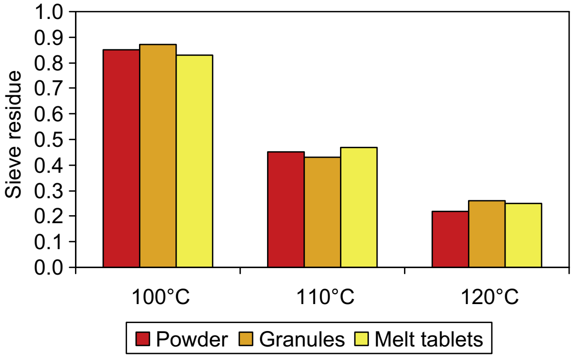


Figure 1.4
Studies on dispersion as a function of delivery form and mixing temperature

1.4 Heat Stabilizers for PVC

Heat stabilizers are based on

- metal-free, organic compounds,
- alkaline earth metal salts (mainly calcium or barium) in combination with cadmium or zinc salts (mixed-metal stabilizers),
- organotin compounds,
- rare earth metal salts, mainly based on lanthanum, and
- basic and neutral lead salts which are becoming less and less important worldwide. They were phased out in Europe at the end of 2015; see Section 5.10,
- antimony- and bismuth-based stabilizers.

The 1990s saw fairly extensive discussions about the use of heavy metals for stabilizing PVC. We therefore want to examine the question here in more detail: What actually is a heavy metal?

Scots have a multitude of expressions for rain [56]. Eskimos have 27 words for snow [57]. It is similar with heavy metals. Mankind has currently more than 40 definitions for this term, heavy metal [58]:

- The general public sees heavy metals as materials dangerous for humans and for the environment as a whole.
- There are currently 13 definitions based on the density of metal. These mention densities in the range of 3.5 to 7.0 g/mL. The most commonly used (scientific) definition is: a metal with a density > 4.5 g/mL is a heavy metal [59]. In this case even titanium, having a density of 4.506 to 4.508 g/mL, would be considered a heavy metal.
- Eleven definitions are based on the atomic weight. In the extreme, everything with an atomic weight higher than sodium is considered a heavy metal [60]. By this definition magnesium, aluminum, and calcium would be heavy metals.
- There are five definitions from the perspective of a chemist, and two in a biologist’s view, which relate to the positions in the periodic table, the atomic number.
- Another five definitions of this term relate to various other chemical properties.
- Two definitions refer to toxicological principles.
- Probably the oldest definition was coined in 1884 and is quite graphic: “guns or shot of large size.”
- Based on the definition of Directive 67/548/EEC, the elements antimony,

arsenic, cadmium, chromium-(VI), copper, lead, mercury, nickel, selenium, tellurium, thallium, tin, and their compounds are heavy metals.

- “Heavy Metal” is also a style of music.

The term *heavy metal* is misleading. Not every heavy metal is poisonous. Iron and zinc are essential, vital elements.

1.4.1 Metal-Free Base Stabilizers

Metal-free stabilizers have enjoyed something of a renaissance in recent times. The reason for this was the discussion of stabilizer systems containing heavy metals (see above). Metal-free, organic stabilizers were suggested for PVC at about the same time as lead stabilization [61, 62]. Urea and its derivatives were already published in 1937 [63] (Figure 1.5). In addition to the “normal” urea, the sulfur-containing thiourea (Figure 1.5) was also investigated. Years later, diphenylthiourea gained commercial importance as a stabilizer for producing E-PVC films by the Luvitherm process. Various (thio-)ureas were compared in a calcium-zinc test formulation. The calcium-zinc formulation was chosen to give the PVC a minimum basic stability. As the results in Table 1.3 show, various (thio-)ureas improve early color and color hold but decrease long-term thermostability in combination with zinc. It should also be noted that thioureas form black discolorations in combination with lead stabilizers. The reason for this is the formation of black lead sulfide (Figure 1.6).

Table 1.3 Comparison of Several Substituted (Thio)ureas for Thermostability, Early Color (YI 0), and Color Hold (YI 30). (Dosage was 0.1 phr in a Formulation of 100 phr PVC [k = 68], 2 phr Chalk, 1 phr Titanium Dioxide, 1 phr Calcium Stearate, 1 phr Zinc Stearate, 0.5 phr Pentaerythritol, 1 phr Paraffin Wax [64]. Oven Stability in Minutes; YI 0 and YI 30 = Yellowness Index after 0 and 30 min (in a Thermo Oven))

Urea	Oven Stability [min]	YI 0	YI 30
None	60	18.4	44.6
Urea (unsubstituted)	45	17.0	35.5
N-Ethyl-	25	20.6	
N,N'-Dimethyl-	30	12.3	59.6
N-Benzyl-	30	13.5	68.4
N-Phenyl-	40	9.7	41.2
Morpholinyl-	30	18.1	64.2
N,N'-Diphenyl-	35	18.5	41.2
N,N'-Diethylthio-	15	31.8	
N,N'-Dibenzylthio-	20	16.5	
N,N'-Diphenylthio-	25	11.4	
N,N'-Di-n-butylthio-	20	22.4	
Dicyandiamide	45	11.4	55.1

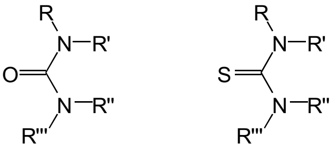


Figure 1.5 General structure of ureas (left) and thioureas (right); R, R', R'', and R''' can be identical or different substituents

$Pb^{2+} + S^{2-} \rightarrow PbS$ (black)

Figure 1.6 Formation of black lead sulfide

Dicyandiamide is the dimer of cyanamide. Dicyandiamide was used as a PVC stabilizer as early as 1942 [65]. From a chemist's perspective, dicyandiamide (Figure 1.7) can be seen as a derivative of urea. It shows structural similarities to guanidine and also to 4-aminouracil. Dicyandiamide is also a chemical precursor of melamine (Figure 1.7), which is the trimer of cyanamide. In PVC it behaves similar to urea; see Table 1.3. Also, melamine derivatives are used as costabilizers for PVC, especially in flooring applications.

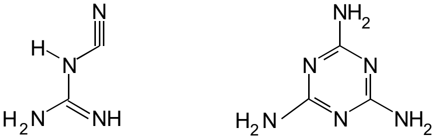


Figure 1.7 Structures of dicyandiamide and melamine

β-Aminocrotonic acid derivatives (Figure 1.8) were probably already mentioned as PVC stabilizers before 1961 [66]. They stabilize not only E-PVC but also S- and M-PVC. According to theoretical modeling, aminocrotonates substitute labile chlorine atoms at the PVC-chain; see Figure 1.9 [67]. Further literature [68] shows that, in addition to the effects mentioned before, aminocrotonates can also bind escaping hydrochloric acid. The effectiveness of aminocrotonates as stabilizers is relatively good, but the early color stability is only modest. Theoretically, aminocrotonates can be viewed as nitrogen-containing 1,3-dicarbonyl compounds; see also Section 1.5.3 and Figure 1.38. Typical examples are butyleneglycol diaminocrotonate (BGAC) and thioethyleneglycol diaminocrotonate (TGAC). The efficiency of aminocrotonates can be improved significantly in combination with synergists like calcium-zinc soaps or epoxides. A potential disadvantage of aminocrotonates is that small amounts of ammonia can be generated during processing [69].

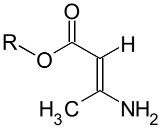


Figure 1.8 Structure of aminocrotonates

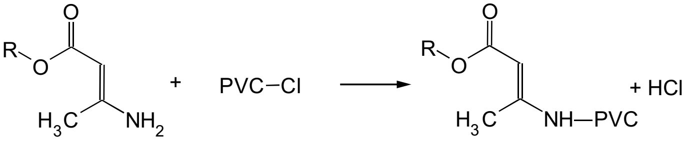


Figure 1.9 Stabilizing mechanism of aminocrotonates

Historically, dihydropyridines (DHP) are relatively “young” metal-free basic stabilizers for PVC [70]. Depending on the chemical perspective applied, they can be identified as

- *δ*-diketones,
- *β*-aminocrotonates, or
- derivatives of 1,3-dicarbonyl compounds (due to their synthesis from 1,3-dicarbonyl compounds, formaldehyde, and ammonia); see Figure 1.10.

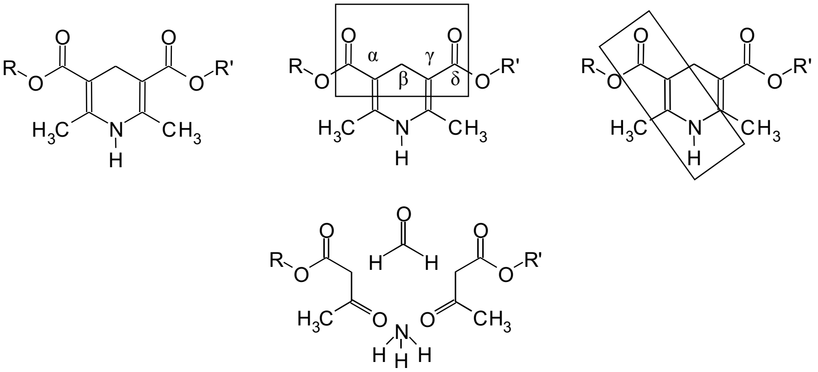


Figure 1.10 General structure of dihydropyridines (top left), as *δ*-diketone (frame, top middle), as *β*-aminocrotonate (frame, top right), and as *β*-diketone (“exploded” display, bottom)

They probably stabilize PVC in a way similar to aminocrotonates or uracils; see Figure 1.9 and Figure 1.13.

In the early days, the thermostability of calcium-zinc stabilizers alone was not sufficient for the production of mineral water bottles. Because of this, *α*- or 2-phenylindoles (2-PI) were added as costabilizers, especially in France [71]; see Figure 1.11. 2-Phenylindole requires no further catalyst to substitute the labile chlorine atoms of the PVC polymer. A disadvantage of this compound, though, is that it has a tendency to strongly discolor after only a short period under radiation, for example in sunlight. The migration of 2-phenylindole can also cause issues. In contrast to the light sensitivity, the migration problem can easily be resolved by introducing alkyl substituents into the molecule.

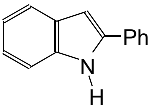


Figure 1.11
Chemical structure of 2-phenylindole

The uracils depicted in Figure 1.12 were first mentioned as stabilizers for PVC in 1966 [72]. In a way they are fascinating compounds, because they combine the structural elements of urea and those of aminocrotonates; see Figure 1.12. A pessimist would expect a negative synergism: the bad early color of the aminocrotonates and the weak long-term thermostability of urea. In reality the system retains the positive properties of each: the good early color of the urea and the good long-term thermostability of the aminocrotonates. The uracils constitute an intramolecular, or, expressed in simpler terms, an internal synergism of two molecules. Uracils are able to substitute unstable chlorine atoms in the polyvinyl chloride chains, similar to aminocrotonates. This mechanism was proven in the literature [73] (Figure 1.13).

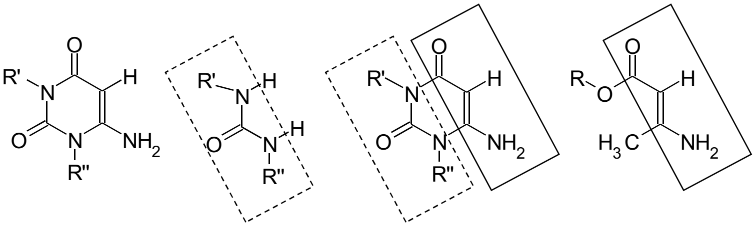


Figure 1.12 General structure of uracils depicted as “internal synergism” of urea and aminocrotonate; R, R′, and R″ can be identical or different substituents

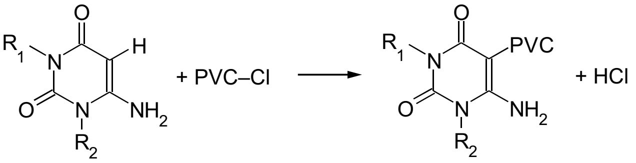


Figure 1.13
Stabilizing mechanism of 1,3-substituted 4-amino-uracils

Although not a classical polyol, tris-hydroxyethyl isocyanurate (THEIC) is often referred to as a polyol. The three OH groups are the reason for this classification. The stabilizing mechanism described below has not been scientifically proven. Nevertheless, it is known that THEIC reacts to oxazolidone in the presence of base. It is further assumed that the oxazolidone then reacts with free hydrochloric acid in a ring-opening reaction [74]; see Figure 1.14.

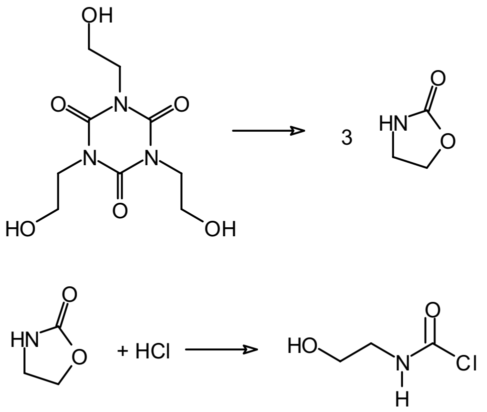


Figure 1.14
Stabilizing mechanism of THEIC

The costabilizing properties of true polyols are based on a different mechanism that will be discussed in Section 1.5.6.

For many years amino compounds were not considered as PVC stabilizers because they were known to decompose PVC [75]. Nevertheless, in recent years triethanolamine and its “structural derivatives” (Figure 1.15) have been found to be quite useful stabilizers for flexible as well as rigid PVC [76, 77]. Most notably, in combination with perchlorates, excellent stabilizer systems can be designed as solids or liquids. An interesting combination presents itself in the Greenstab TEAP stabilizers. The unique feature of TEAP is that the liquid triethanolamine, in high concentrations, forms a new crystalline compound with perchlorates. The TEAP triethanolamine as well as the TEAP complex show distinct advantages in lead-free and zinc-free formulations. They have also proven their worth for the processing of p-PVC, in plastisol and artificial leather formulations. Their use is limited as cable stabilizer because TEAP imparts inferior electrical properties. Surprisingly, highly transparent and water-insensitive products can be produced that avoid the problem of hazing in humid and warm climates, the so-called humidity or moisture whitening. If one or two of the ethoxy groups in the TEAP molecule are exchanged for long-chain alkyl substituents, the resulting triethanolamines show reduced stabilizing properties but gain antistatic properties (Figure 1.15). These stabilizers are so inherently antistatic that often no further antistatic agents are needed in a given formulation. Last but not least, triethanolamine and derivatives are said to have “antipinking” properties [78] in organic based stabilizer systems; see Section 4.3. Finally, it should be mentioned that many of the above ideas, compounds, and formulations are protected by patents. This should be considered before utilizing them in processing. Because this more recent area of stabilization development is constantly evolving, the previously mentioned literature citations only represent a selection and are not claimed to be complete or up-to-date. It is the responsibility of the user to get a sufficient overview of the patent situation.

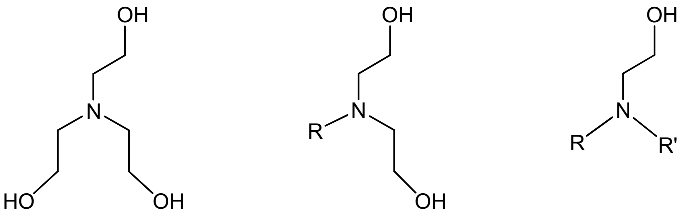


Figure 1.15 General structure of triethanolamine and its derivatives; R and R' can be identical or different substituents

1.4.2 Metal Soaps as Base Stabilizers

The following section does not describe single stabilizer components but mixtures of salts derived from reaction of organic acids with metals. The metals in question are barium or calcium on one hand, and zinc or cadmium on the other. Table 1.4 sums up some chemical and physical data of various metal soaps.

Table 1.4 Chemical and Physical Data of Various Neutral, Technical Metal Soaps

Metal Soap	m.p. [°C]	Molecular Weight [g/mol]	[%]	Metal	[%]	Acid
Technical stearic acid	64	260.0 to 275.0	Depending on the source			
Barium benzoate	100	379.3	36.2	Ba	64.3	Benzoic acid
Barium octanoate		367.3	37.4	Ba	63.1	Octanoic acid
Barium laurate	260	535.3	25.6	Ba	74.7	Lauric acid
Barium oleate		680.3	20.2	Ba	82.9	Oleic acid
Barium stearate		685.3	20.0	Ba	80.3	Technical stearic acid
Calcium benzoate	110	282.0	14.2	Ca	86.5	Benzoic acid
Calcium octanoate		326.0	12.3	Ca	88.3	Octanoic acid
Calcium laurate	183	438.0	9.1	Ca	91.3	Lauric acid
Calcium oleate	84	602.0	6.6	Ca	93.7	Oleic acid
Calcium stearate	180	588.0	6.8	Ca	93.2	Technical stearic acid
Magnesium laurate	150	422.0	5.7	Mg	94.8	Lauric acid
Magnesium oleate		586.0	4.1	Mg	96.2	Oleic acid
Magnesium stearate	88	572.0	4.2	Mg	96.2	Technical stearic acid
Sodium adipate	>400	190.0	24.2	Na	76.8	Adipic acid

Metal Soap	m.p. [°C]	Molecular Weight [g/mol]	[%]	Metal	[%]	Acid
Sodium formate	261	68.0	33.8	Na	67.6	Formic acid
Sodium fumarate	>300	160.0	28.8	Na	72.5	Fumaric acid
Sodium maleate	>300	160.0	28.8	Na	72.5	Maleic acid
Sodium malonate		148.0	31.1	Na	70.3	Malonic acid
Zinc benzoate		307.4	21.3	Zn	79.4	Benzoic acid
Zinc octanoate		351.4	18.6	Zn	82.0	Octanoic acid
Zinc laurate	128	463.4	14.1	Zn	83.6	Lauric acid
Zinc oleate	70	627.4	10.4	Zn	89.9	Oleic acid
Zinc stearate	130	613.4	10.7	Zn	89.7	Technical stearic acid

Combinations like these were patented as solid PVC stabilizers at the beginning of commercial use of PVC [79]. Liquid combinations of metal salts were developed later [80]. In general, the organic acids can be aliphatic or aromatic; phenols are also possible. In practice, mainly benzoic acid, n-octanoic acid, lauric acid, and technical stearic acid are used in solid stabilizer combinations. In liquid systems, ethylhexanoic acid, technical oleic acid, alkylbenzoic acids, and phenols are preferred.

Zinc soaps and cadmium soaps impart a good early color to PVC because, according to Frye [81], they are able to substitute labile chlorine atoms (Figure 1.16). Also worth mentioning in this context are the results of Onozuka [82], who could prove that only allylic chlorine atoms and not tertiary chlorines are substituted by carboxylic acid groups. These findings strongly support an ionic reaction mechanism. In the reaction zinc chloride or cadmium chloride are formed. Both of these chlorides are known to the chemist as Lewis acids; these metals are also able to bind more than two chlorine atoms (Figure 1.17). The compounds then formed are called complexes. Due to this mechanism, both chlorides also catalyze the degradation of PVC and reduce the long-term thermostability.

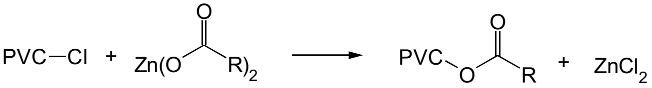


Figure 1.16 Substitution of labile chlorine atoms in PVC by zinc soaps and the resulting formation of zinc chloride

$$ZnCl_2 + 2HCl \rightarrow H_2(ZnCl_4)$$

Figure 1.17 Reaction of zinc chloride with hydrochloric acid (HCl)

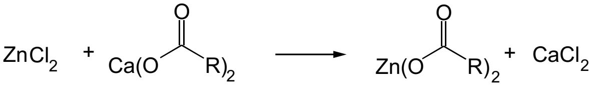


Figure 1.18 Reaction of zinc chloride with calcium soap to calcium chloride and a “regenerated” zinc soap

A further reaction of the alkaline earth metal soaps is the substitution of the fatty acid in the metal salt by hydrochloric acid (Figure 1.19). This phenomenon is well known to chemists: the stronger acids (HCl) replace the weaker acids (fatty acid) in the salt.

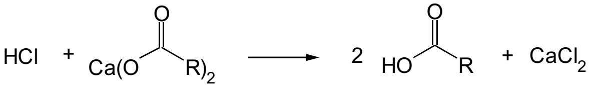


Figure 1.19 Reaction of hydrochloric acid (HCl) with calcium soap to calcium chloride and fatty acid

In principle, all long-term thermostability and early color requirements can be achieved by adjusting the ratios of alkaline earth metal soaps and zinc/cadmium soaps; see Figure 1.20. If the alkaline earth metal soaps dominate, good long-term thermostability is achieved with only moderate early color. The more zinc/cadmium soaps are used, the better the early color combined with often acceptable long-term thermostability. The true reaction mechanisms are much more complicated than described here and are similar to the ones explained for tin stabilizers (Figure 1.22). Several scientists have studied the mechanism and the synergisms of these reactions [83–87].

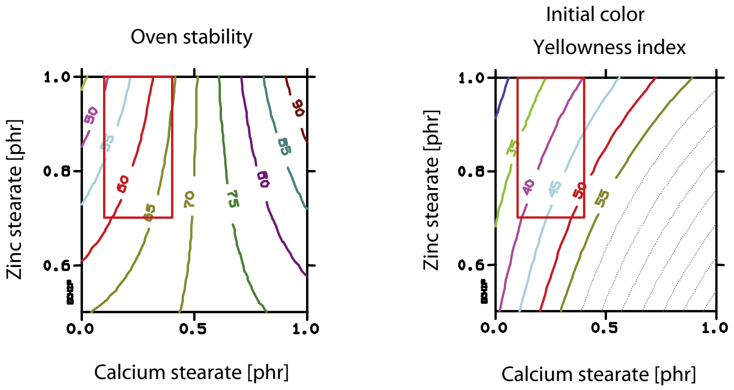


Figure 1.20 Dependency of oven stability and early color on the ratio of calcium stearate to zinc stearate (100 phr PVC [k = 68], 2 phr chalk, 0.25 phr magnesium stearate, 0.25 phr dipentaerythritol, 1 phr paraffin wax [64])

The formation of zinc chloride, according to Figure 1.16 and Figure 1.17, supports the degradation of PVC and results in the need to use costabilizers. The costabilizers bind either the hydrochloric acid or the Lewis acids, in this case the zinc chloride. Scientists also call this reaction complexation. The costabilizers used have positive and negative properties (Table 1.5). Their modes of action will be discussed in more detail in Section 1.5.3.

Table 1.5 Common Costabilizers; Their Advantages and Disadvantages

Type	Advantage	Disadvantage/ Possible Problems
Hydrotalcites	Stability booster	Expensive, early color worse
Zeolites	Better long-term stability	Early color worse, water absorption
Metal (hydr)oxides	Better long-term stability	Early color worse, water absorption, often caustic
Polyols	Better long-term stability	Early color worse, plate-out, water absorption
β-Diketones	Early color improvers	Very expensive
Organic phosphites	Early color improvers	Cause plate-out, odor
Antioxidants	Stability booster	Some are irritating
Epoxides	Stability booster	Some are irritating
Combination of costabilizers	Synergisms	Patented by third parties

Cadmium-based stabilizer systems have completely lost their importance in the European Community since the turn of the millennium (see also Chapter 5). From then on, no more cadmium-containing stabilizer products have been produced or used in the European Community. Detailed information on these stabilizers and their history can be found in the literature [88]. Meanwhile, liquid barium-zinc systems have been developed that match the stabilizing properties of barium-cadmium stabilizers.

Stabilizers based on strontium are only of academic interest and have no commercial relevance. Barium can also be seen as controversial due to its inherent chemical properties, irrespective of its positive use in PVC stabilization. On one hand, barium with a density of 3.65 g/mL is considered a heavy metal under very few of the heavy metal definitions. On the other hand, the barium chloride, formed in a reaction analogous to the calcium chloride by the stabilization process (as in Figure 1.18 and Figure 1.19), is often classified as toxic. The toxicity of barium compounds depends on various factors: some are classified as toxic, others only as harmful. Highly insoluble compounds, such as barium sulfate, are nontoxic. Barium sulfate is used as a contrast agent in X-ray imaging.

Liquid barium-zinc salts, in combination with costabilizers, are mainly used in plastisols. PVC-plastisols are used for the production of PVC wallpaper, artificial leather, foils, and tarpaulins, and for calendered flexible and semirigid films. Initially, commercial considerations hindered the substitution of liquid barium-cadmium and barium-zinc stabilizers by equivalent calcium-zinc products. Today, because of toxicological considerations and the emergence of modern, cost-competitive combinations, a tendency to use liquid calcium-zinc stabilizers can be observed.

The combination of calcium and zinc has been described as rather unimportant and ineffective in the past [89]. Today, liquid as well as solid calcium-zinc one-packs have gained significant market importance (see also Chapter 5).

However, some time ago there were some new developments in metal soaps, which gained a market relevance. The most important is sodium adipate. It is used as a food additive (E356) as a complexing agent and acid regulator. It is also used as a stabilizer for PVC. Sodium adipate is the sodium salt of adipic acid. It neutralizes the HCl with formation of sodium chloride. EP0492803 [90] claims the combination of sodium adipate and a metal-based stabilizer. In this patent tin stabilizers are mainly mentioned. This shows that sodium (and potassium) salts of adipic acid function as a stability booster for tin stabilizers. However, a wide range of calcium-zinc and zinc-free stabilizers have been developed and sold, especially for injection molding applications.

EP2083044 [91] claims the combination of sodium adipate and sodium perchlorate. This shows that sodium adipate not only works in combination with zinc soaps but also in zinc-free PVC stabilizers.

Furthermore, EP2363431 [92] claims the combination of sodium adipate and an alkali metal salt of a carboxylic acid having from 1 to 22 carbon atoms.

Apart from adipic acid, other dicarboxylic acids found the interest of product designers of different stabilizer producers. In WO2011054537 [93] Schiller et al. claimed a sodium salt of either fumaric or malonic acid as PVC stabilizer. This type of sodium salt has a better initial color than sodium adipate but a slightly inferior long-term heat stability depending on the entire composition of the stabilizer one-pack.

Berna et al. claim in EP2151475 [94] sodium formate as a PVC stabilizer. Reichwald et al. claim in EP2978805 [95] the combination of sodium (or potassium) salts of a (di)carboxylic acid like formic acid, adipic acid, fumaric acid, succinic acid, etc., and polyols.

In 1994, 5 phr of a one-pack based on calcium and zinc was still necessary to produce a white window profile. Five years later, on average only 4 phr was needed to achieve the same properties. Another two years later, the market was offering stabilizer products that only required 3.5 phr. In 2003, the additional cost compared to lead stabilization (= 100%) was

- per kilogram dry blend, about 7%,
- per meter of extruded profile, considering the density changes, about 3%, and
- per finished window, about 0.1%.

So the true cost difference is minimal. The changeover from lead to calcium-zinc stabilization could be achieved in Austria in the 1990s without significant cost disadvantages because most profile-extruding companies also build the windows. Therefore, 90% of the window profiles produced in Austria were lead-free at the turn of the century. The situation in Germany is different, though: several profile producers only produce and sell the window profiles.

The situation for foamed sheets and foamed profiles can be summarized as follows: depending on the requirements for the extrudates, calcium-zinc or organic-based, lead-free alternatives are available and cost-neutral.

For cable sheathing and insulation with lower requirements, calcium-zinc stabilizers can substitute for lead stabilizers at no extra cost. This is only applicable for cables that do not require low water absorption, though.

What is new and improved with calcium-zinc and organic stabilization today, compared to 20 years ago? Chemists have applied statistical experimental planning to find more effective and “intelligent” combinations of well-known raw materials. New raw materials are more of an exception. Whereas it was true for lead stabilizers that high lead content resulted in high stability, for calcium-zinc and organic systems the chemistry and understanding of stabilization mechanisms is most important. (The rule of thumb “much lead equals good stability” has been challenged by Schiller et al., who have developed lead stabilizers for window profiles and pipes that require only half (or even less) of the lead content of commonly sold products. These stabilizers nevertheless allow production of the highest quality profiles and pipes [96].)

Metal salts not only influence the long-term stability and color hold; they also strongly influence the rheology, the flowing behavior, of the polymeric melt. Zinc and cadmium stearate behave similar to neutral lead stearate: they delay plastification and lower the torque in extrusion. Calcium stearate acts in the opposite way: plastification is faster. These properties commonly cause no problems because the rheological behavior of the metal soaps can be compensated for by adjusting the lubricants in a one-pack system. In North America (and some other parts of the world) tin stabilizers are the most commonly used. Many converters have either developed their own lubricant compositions or use external lubricant one-packs provided for tin systems. A changeover from tin to calcium-zinc stabilizers may cause issues with the rheological behavior of the metal soaps because often only the tin stabilizer is exchanged and the (tin-based) lubrication is retained. Schiller et al. developed calcium-zinc core-packs that have no or only a small influence on the overall rheology (see also Section 1.4.3).

Metal salts influence transparency, gloss, plate-out tendencies, weathering performance, fogging, recycling, and many more properties, due to their varying compatibility in PVC, their solubility at processing temperatures, their volatility, their diffraction index, and by the overall stabilizer one-pack formulation.

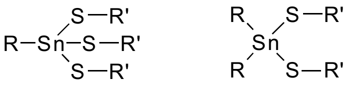
Zinc and cadmium salts also work as kickers in foamed applications by activating the decomposition of blowing agents, for example azodicarbonamide. Decomposition temperature as well as decomposition speed can be varied within limits. Because of this property, foamed formulations can often do without a separate kicker if zinc-containing systems are used.

1.4.3 Tin Stabilizers

The use of tin compounds as PVC stabilizers was first suggested in the 1930s [97]. Tin is located in the periodic table in the same main group as lead and therefore should have similar properties. And yet, there are significant differences for their use as stabilizers:

- Lead occurs in the oxidation state +2, tin in +4.
- The core lead stabilizers are mostly basic, inorganic, and solid. Tin stabilizers are mainly neutral, organic, and liquid.
- Lead systems react with sulfides to form gray or black discolorations whereas many tin stabilizers contain sulfur components. These are called organotin mercaptides or sulfur-containing organotin stabilizers [98].
- While lead-based stabilizers were dominant in Europe until 2010, the majority of stabilizers in North America and some other parts of the world remain tin-based. Lead stabilizers were phased out in Europe at the end of 2015.
- Tin stabilizers started to come under legal pressure in Europe too [99].

Organotin mercaptides are a very effective and universally applicable group of tin stabilizers. The general formula of these heat stabilizers is represented in Figure 1.21. A distinction can be made between monoalkyl and dialkyl tin compounds. The alkyl groups may be methyl (CH_3-), n-butyl (C_4H_9-), n-octyl (C_8H_{17}-), and n-dodecyl radicals. The latter is also known as lauryl ($C_{12}H_{25}$-).



Methyl- (CH_3-)
n-Butyl- (C_4H_9-)
n-Octyl- (C_8H_{17}-)
Lauryl- ($C_{12}H_{25}$-)

-CH_2-CO-O-Alkyl	Thioglycolate, (often i-Octyl- or ethylhexyl)
-CH_2-CH_2-CO-O-Alkyl	β-Mercaptopropionate
-CH_2-CH_2-O-CO-Alkyl	Mercaptoethanolester (“reverse esters”)
-Alkyl	Alkylmercaptide

Figure 1.21 Common structures of sulfur-containing organotin stabilizers

The sulfur-containing component is most often based on the 2-ethylhexyl ester of thioglycolic acid or the slightly longer-chain *β*-mercapto propionic acid. In both cases the tin is bound to the sulfur of the mercapto acid. Also, oleic acid esters of 2-mercapto ethanol (HS-CH_2-CH_2-OH) are used. In these cases the tin is bound to the sulfur of an alcohol component.[2]

Next to these compounds, other chemical groups are possible as acid or alcohol components. Such variations are not discussed here due to their lesser commercial importance. The function of tin stabilizers is displayed in Figure 1.22.

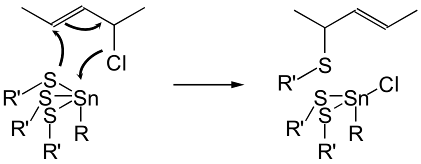


Figure 1.22
Substitution of labile chlorine atoms of PVC by tin stabilizers

- Tin stabilizers bind the escaping hydrochloric acid.
- They substitute unstable chlorine atoms in the polymer chain [27] and thereby prevent discoloration and further degradation of the polymer.
- The thio compounds, generated when neutralizing the hydrochloric acid, can add onto polyene sequences. They thereby disrupt the color-causing conjugated double bond system and improve the color of the PVC object.
- In addition, they prevent the autoxidation of PVC [100].

It is interesting to note that the dialkyltin compounds provide the PVC with good long-term stability and a rather modest initial color. The monoalkyl derivatives have a different effect: their long-term stability is not as good as that of the dialkyltin compounds, but the initial color is significantly better. To a layperson it may seem surprising that in their combination the positive characteristics of each are retained and the negative properties “forgotten” (Figure 1.23). This phenomenon is called a synergistic effect. In this context the trialkyltin compounds should also be mentioned. Their content in stabilizers has to be very low (< 0.1%) due to their very high toxicity. Such small amounts are often hard to detect analytically or to characterize quantitatively in the mixtures, which can cause difficulty in meeting these limits.

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[2] These products are also referred to as reverse esters because the chemical “order” within the tin stabilizer is tin-alcohol-acid. For the first-mentioned, more common tin stabilizers the molecular arrangement is tin-acid-alcohol.

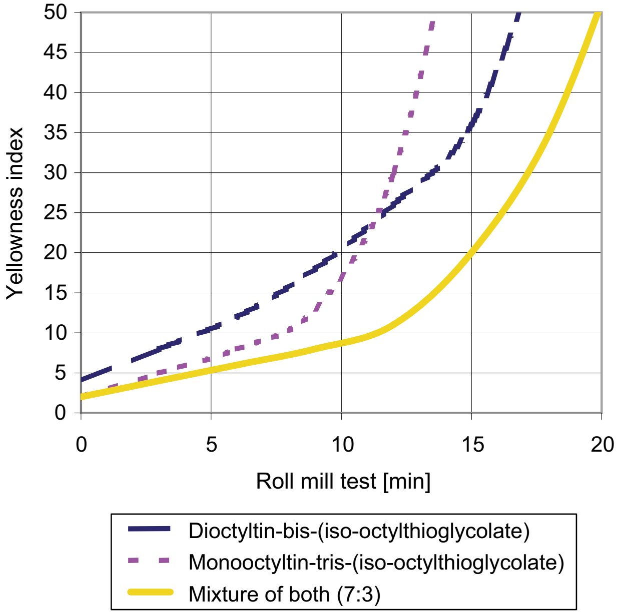

Figure 1.23
Synergistic effect of monoalkyltin and dialkyltin iso-octylthioglycolates in a long-term milling trial on a two-roll mill at 205 °C

In the following we will look at the applications of individual alkyltin mercaptides. Methyl-substituted derivatives are more volatile than the longer chain compounds (homologs). Because of this, the legal maximum air concentration permissible in the workplace, the MAK-value of 0.1 mg tin/m^3, is important to note. Methyltin compounds have always been used in the USA and have been introduced in Japan for the extrusion of pipes a time ago. In the USA these stabilizers also play a role for the extrusion of profiles. It has not yet been finally determined whether during stabilization using methyltin compounds highly toxic dimethyltin dichloride is released. There are currently still countless arguments for and against this.

Butyltin derivatives are used in many technical applications, such as sidings, injection molded products, films, sheets, flooring, wallpaper, and pipes, mainly within the USA and increasingly also in Asia. An exception is the use in food contact and drinking water contact applications because dibutyltin mercaptides have never been toxicologically classified as harmless. Due to the European reevaluation of the risk potential of dibutyltin compounds, the market share of butyltin stabilizers has been decreasing in significance.

Organotin stabilizers have a low migration tendency in u-PVC [101–103]. Therefore, several mono- and dialkyltin compounds have worldwide approvals for use in applications in contact with drinking water and food. Among these are methyltin, octyltin, and dodecyltin compounds, with the methyl- and octyltin stabilizers more or less dominating the respective markets. This situation has recently changed in Europe: several alkyltin stabilizers are currently undergoing a reassessment and change of their classifications with the introduction of the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) [104].

An alternative to tin stabilizers are calcium-zinc stabilizers. These are complex blends of products that also influence rheology, even if they do not contain lubricants (see Section 1.4.2). As many producers have either developed their own lubricant compositions or use external lubricant one-packs provided for tin systems, a changeover from tin to calcium-zinc stabilizers may cause issues with the rheological behavior of the metal soaps. This is because often only the tin stabilizer is exchanged and the lubrication should be retained. Schiller et al. have developed calcium-zinc core-packs [105] which have no, or only a small, influence on the overall rheology (see Table 1.6).

Table 1.6 Comparison of Window Profiles Extruded with Tin and Calcium-Zinc Stabilizer Systems and Identical Lubricant One-Packs (100 phr PVC (k = 68); 9 phr Titanium Dioxide; 5 phr Acrylic Impact Modifier) [98]

Stabilizer	phr	Gloss	DHC	*L* Value	*a* Value	*b* Value	Charpy Impact
Low-Speed Extrusion							
Butyltin	3.8	65	55	91.2	−0.6	1.3	62
Ca/Zn II	3.4	71	69	91.3	−0.7	1.2	61
High-Speed Extrusion							
Butyltin	3.8	51	57	91.6	−0.6	0.8	63
Ca/Zn II	3.4	57	70	91.4	−0.7	0.8	63
Best Color Retention under Dynamic Conditions							
Butyltin	3.8	51	57	91.4	−0.6	0.8	63
Ca/Zn III*	4.2	57	70	91.6	−0.7	0.8	63

* Non-optimized laboratory development

In addition to the linear mercaptides, cyclical mercaptides also play a role in PVC stabilization. These are the reaction product of 3-thiopropionic acid and organo thiostannoic acids (Figure 1.24).

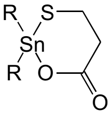

Figure 1.24
Cyclic tin mercaptides

Tin stabilizers distinguish themselves by providing excellent transparency to the final products. Their light resistance, though, is generally inferior to that of other stabilizer systems (Figure 1.25). This requires the addition of a higher dosage of titanium dioxide or of UV stabilizers. Another disadvantage during recycling in combination with lead-stabilized materials can be the so-called "sulfur cross-stain-

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