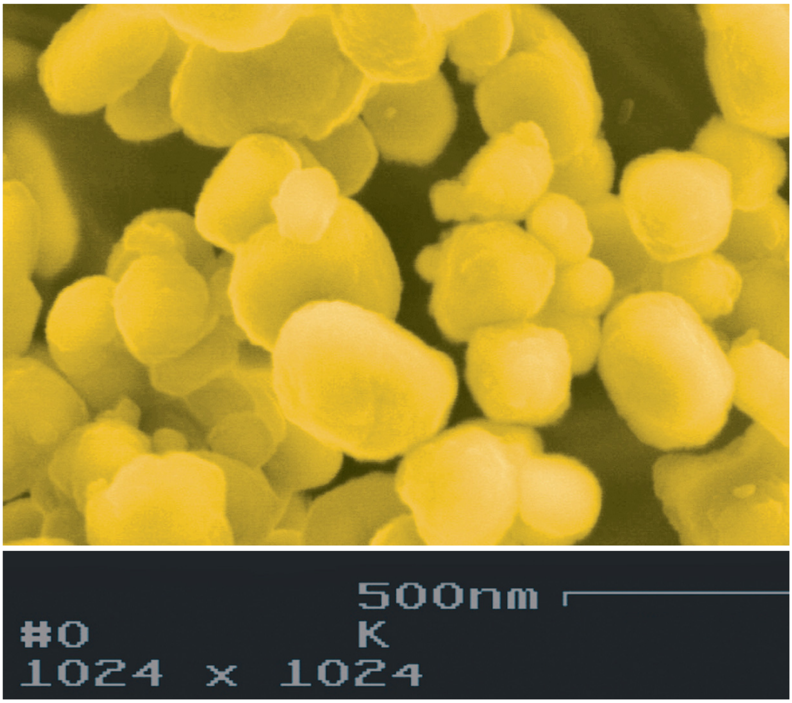
Michael Schiller

PVC Additives

Performance, Chemistry, Developments, and Sustainability



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Preface

I thought a long time about what I should write in this preface for the English and revised edition of my book, *PVC Additives*. From my perspective, only a little has changed in the PVC industry during the last five years, although there has been some progress on switching from lead stabilizers to calcium-zinc in Europe, which is discussed in the last chapter of the book. I hope that the English edition gives the reader an insight into the world of PVC. I intend for the book to be understandable for the layman; that is, the person who is not a chemist, a plastics engineer, or a PVC processor. I hope even more that one or more accountants read the book. I have attempted to consistently maintain an entertaining writing style for the scientific topics, though not always with success, so for that, I ask for leniency. I do not believe that the book reads nor will sell like "Harry Potter"!

I want to use the preface as a way to express my gratitude to all the people who have supported me directly or indirectly. Again, I want to thank my love and wife, Annette. She has always has my back as she supports me in word and deed, even if it is not always easy because I am often working thousands of miles away from her. I also want to thank my children. I am very proud of both of my pretty and smart daughters, Sarah and Maria, who are both successful students. Of course, I again thank my parents and my grandmother; I look forward to giving them copies of this book. After all, I owe them for all that I have become.

Apart from the people who I mentioned in the preface of the German edition, I want to thank others who have influenced and taught me and are perhaps unaware of their impact. The order of mention is, of course, not to be understood as ranking. First, I want to thank Mr. Ünal Heris, who founded Akdeniz Kimya thirty-eight years ago and who has run the company since. I thank him for my position at Akdeniz Kimya, not only for bringing me into an excellent and interesting company, but also for getting me to Turkey, a country full of culture and wonderful people. It was a giant step for me, although for humanity, it was probably barely noticeable. In Izmir, Turkey, I have worked for years with Mr. Tarkan Uysal, a very good and trusted friend, as we work together in application technology. To him I owe much of my knowledge and understanding, along with many new experiences with respect to the lubricants and their influence on rheology. It may seem to the reader that my new colleagues and friends mainly learned from my experience, my knowledge, and my understanding of PVC technology. But this impression is incorrect. Without their support, and of course many others who are not mentioned here, I would not have had time to revise and supplement this book and still be able to do my job at Akdeniz Kimya successfully.

Added to the list of people I want to thank is “iTouch,” his real name being Mr. Aytac Sahin; I thank you wholeheartedly for your collaboration in developing new one-packs and for assistance in resolving many difficulties. And to Mr. Bugra Aldanmaz, you are indeed quite new in our industry and in our company, but you are like a sponge: you absorb knowledge, asking many good questions, and are always as positive as my other friends Aytac, Mahir, and Özge; I want to thank them as well.

Theoretically, nothing would connect me to Mr. Mahir Dadas because Mahir speaks little more English than I do Turkish. (My Turkish is still very limited and I find it somewhat embarrassing that I do not speak the language of the country where I spend much time.) But with Mahir, I share a friendship that does not need a common language. Mahir was a huge support when he was working as a production manager and later as a QC Manager, and as a surfer and wall climber.

Dr. Özge Aksin-Artok, who is not only an excellent chemist and a good friend, how can I thank you? You are systematic, creative, critical, and reliable. A truly great scientist, wife, mother, and friend. So keep it up, Özge!

Actually, although my list of friends and managers has ended, there are many more in the application technology group, such as Alptug, Kemal, Süleyman, Ercan, Serkan, Tugfan and furthermore Müserref and Türkhan in the analytical lab and QC; Mehmet, Deniz, Begüm in the chemical laboratory; Volkan, who takes care of the most exciting matters, such as SDSs and REACH; logically, also a heartfelt thanks to Mr. Gerd Pack for many years of friendship even in difficult times; special thanks are due as he has helped me much more in technical matters that he acknowledges. In your line of work, Gerd, which also is one of Volkan's and my areas for a few years, I can still learn much from you.

Many thanks also to Dr. Herbert Schrunner, whose friendship I gained after I left Chemson, as well as to Hanser Publishers, especially to Dr. Nadine Warkotsch and Ms. Cheryl Hamilton, who are named in addition to those already mentioned in the preface to the German edition.

I would like to thank Dr. Mark Everard, who coauthored the fifth chapter in the German edition, which I translated to German, and that chapter is now again translated back into English for this book; many, many thanks for all our years of friendship and collaboration. Dear Dr. Jörg-Dieter Klamann, I thank you for the translation into English, as well as some meaningful additions.

Well, I hope that I have not forgotten anyone who is dear to me. If I have, I sincerely beg your pardon.

My last sentence in this preface: Ladies and Gentlemen at Akdeniz Kimya, even if you do not read your name here, it is an honor and a pleasure to work, to live, and to learn with you!

Arnoldstein (Austria) / Izmir (Turkey), January 2015 *Dr. Michael Schiller*

Preface to the German Edition

When I joined the PVC industry, after completing my university studies in 1992, I thought to myself: “How boring, but at least it is a job in research and development.” One of my colleagues told me that I would certainly not stay in my PVC job until retirement. My colleagues in sales and marketing often said that “PVC is different” and that many phenomena would never be explained. We were all wrong. Despite having an 80-year history of industrial application, this raw material is anything but boring. During the past eighteen years of my work I have been confronted with new and interesting challenges almost on a daily basis. Not only new technologies (“away from lead and tin – on to alternative stabilizer systems”) were developed. Not only did the stabilizer one-packs become better and more cost efficient. We also scientifically explained several previously mystical phenomena, such as photo bluing and plate out, and by this destroyed the myth that “PVC is different.” We explained structure/properties relationships and interactions of (co)stabilizers from the perspective of a chemist and scientist. Our approach was always: “We want to understand!” and not only solve a short-term problem. Like others in our industry, we have also contributed our small part to the sustainability of PVC products.

My biggest problem turned out to be that there was only very little literature written to assist the researcher and developer in solving everyday problems. Most articles are written by plastics technologists for plastics technologists and often are not very helpful to the chemist; or the articles are more fundamentally scientific, therefore not helping the plastics technologists, but assisting the chemist in the understanding of problems. The PVC-seminars offered by the Hanser Verlag have proven to be a good compromise. According to participants’ feedback they strike a good balance between theoretical knowledge and the needs of actual practice. Admittedly, every now and again “too much chemistry” has still been a point of criticism. But, our PVC industry also belongs to the chemical industry. Building on the experiences from the seminars, the idea to write this book evolved. The first chapter in particular is still teeming with formulas and chemistry. I have made a special effort to ensure these are understandable to the layman and I hope I was successful in doing so. The other chapters are also scientifically based but are less “burdened with chemistry.”

Sadly, I am not so gifted a writer that I could consistently maintain an entertaining writing style for the scientific topics. For that, I ask for leniency.

Of course all the information is not based on only my own experiences. If facts have been taken from the literature, they are properly quoted. But at this point, I would also like to thank many people.

Firstly I thank my family, my wife Annette and my daughters Sarah and Maria, for supporting my work with their companionship and love, and also, in the most positive sense, for distracting me from it. I, of course, also thank my dear parents and my dear grandmother for making my education possible and for being there for me and my family, when we needed them far away from their home. I also want to thank my former colleagues of the Chemson Group for their support, the exchange of our experiences and the many, sometimes heated, discussions. Namely, I would like to thank Dipl.-Ing. Alfred Egger for his support, especially in the section of "guide formulations," Dr. Walter Fischer for his contributions to the section "additives for drinking water and food contact" and Dr. Bernhard Pelzl for his friendship and the fun we had while solving various "PVC problems." Furthermore, I want to thank my friend, the ecologist, rock musician, fisherman, and book author Dr. Mark Everard for contributing the chapter on "sustainability." I also want to thank Petra Ziegler of the Carl Hanser Verlag for the friendship and the excellent organization of the PVC seminars. Last but not least I want to cordially thank my patient editor from the Carl Hanser Verlag, Monika Stüve, for our open cooperation.

Izmir (Turkey) / Arnoldstein (Austria) October 2010 *Dr. Michael Schiller*

Contents

1 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.

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 (Fig. 1.1). The left-hand side of Fig. 1.1 depicts the cracking of petroleum or natural gas to make ethylene. On the right-hand side of Fig. 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.

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 (Formula 1.1).

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.

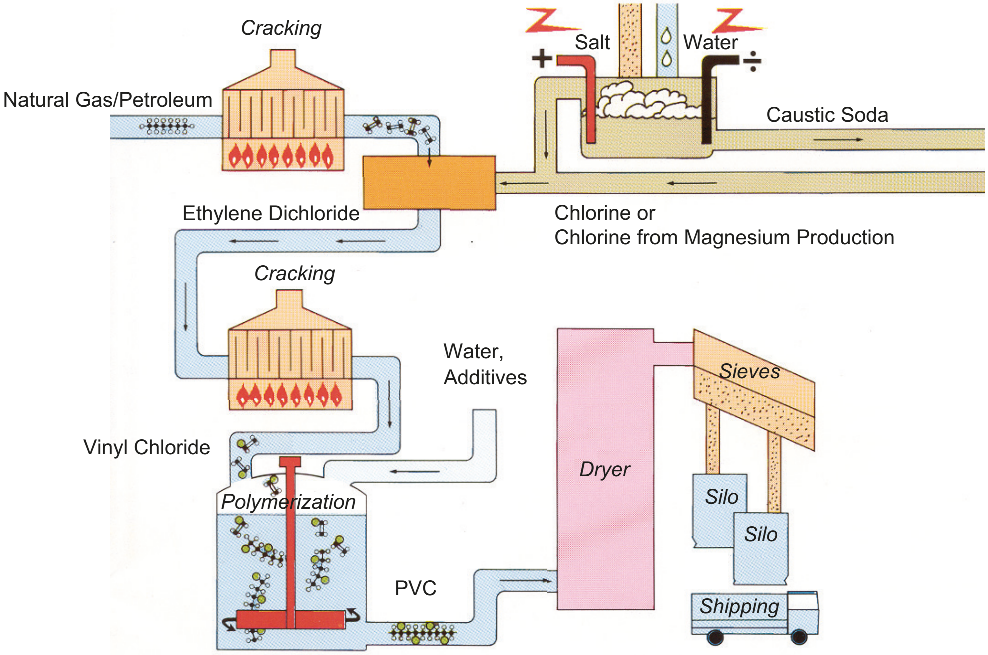
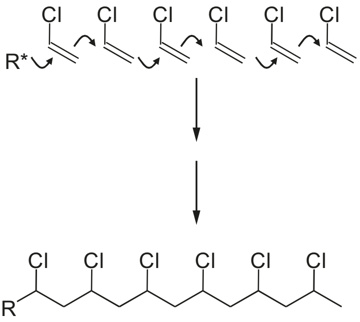


Figure 1.1 Schematic representation of the production of PVC [1]



Formula 1.1 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 Tables 1.1 and 1.2.

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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 1.1 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

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

Application Area	k-Value of S-PVC			
	57–60	63–65	65–68	70–74
Pipes (compact pipes or outer skin layer)		+++	++	
Pipes (foam layer)	+++			
Pipe fittings (injection-molded products)	+++			
Ceiling/wall panels, roller shutters	+	+++	++	
Edge banding (0.4 mm sheet)	+++			
Edge banding (2 mm profile)		+++		
Foamed technical profiles	+++	++	+	
Foam sheets	+++	+		
Geo membranes and water stops			++	+++
Door/window profiles		+	+++	
Siding		+	+++	
Cables, hoses, tablecloth, shoe soles				+++
Cable channels		+++	++	
Rain gutters		++	+++	

+ recommended ++ very recommended +++ highly recommended

Other polymers, 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. 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.

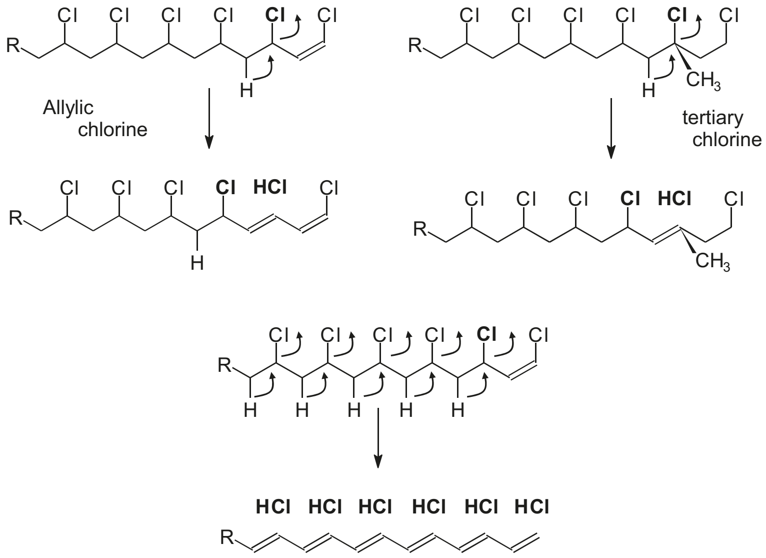
1.2 Thermal Degradation of PVC

If the production of PVC progressed ideally, as represented in Formula 1.1, 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 (Formula 1.2), and
- allylic chlorine atoms, which form for example by termination of the polymerization reaction (Formula 1.2).

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 (Formula 1.2). 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 Formula 1.2 a radical degradation process can also be considered.



Formula 1.2 Degradation of PVC at allylic and tertiary carbon atoms due to heat or shearing

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 (Fig. 1.2). Liquid stabilizers, excluding tin stabilizers, are often a complex solution of additives in solvents and are mostly used in plastisol and calender applications.

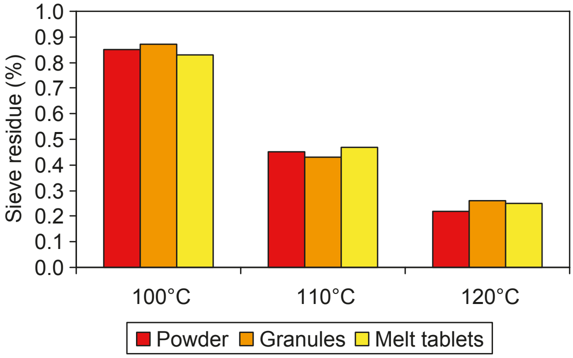


Figure 1.2 Studies on dispersion as a function of delivery form and mixing temperature

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.

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?

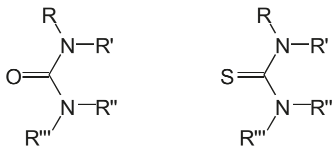
Scots have a multitude of expressions for rain [56]. Eskimos have 27 words for snow [57]. It is similar with heavy metals. Mankind has currently more than 40 definitions for this term, heavy metal [58]:

- 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] (Formula 1.3). In addition to the "normal" urea, the sulfur-containing thiourea (Formula 1.3) 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.



Formula 1.3 General structure of ureas (left) and thioureas (right); R, R′, R″, and R‴ can be identical or different substituents

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

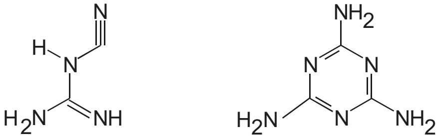
As the results in Table 1.3 show, various (thio-)ureas improve early color and color hold but decrease long-term thermostability in combination with zinc. It should also be noted that thioureas form black discolorations in combination with lead stabilizers. The reason for this is the formation of black lead sulfide (Formula 1.4).

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

Formula 1.4 Formation of black lead sulfide

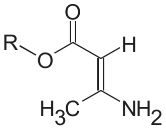
Dicyandiamide is the dimer of cyanamide. Dicyandiamide was used as a PVC stabilizer as early as 1942 [65]. From a chemist's perspective, dicyandiamide (Formula 1.5) can be seen as a derivative of urea. It shows structural similarities to guanidine and also to 4-aminouracil. Dicyandiamide is also a chemical precursor of melamine (Formula 1.5), 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.

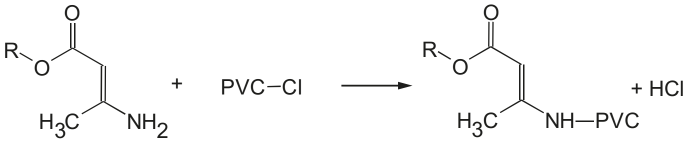


Formula 1.5 Structures of dicyandiamide and melamine

β-Aminocrotonic acid derivatives (Formula 1.6) 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 Formula 1.7 [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 Formula 1.29. 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].



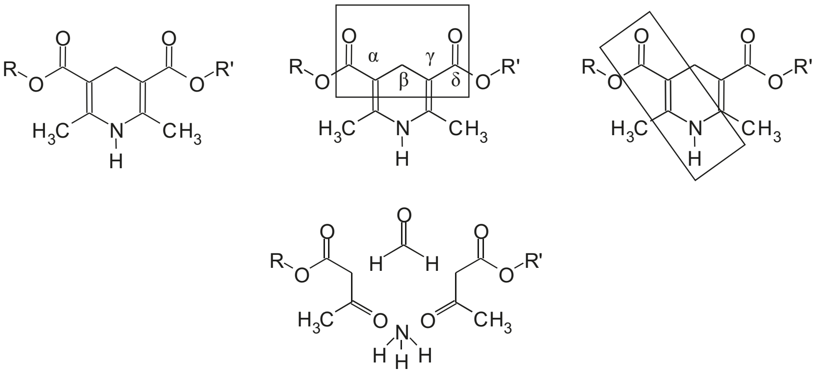
Formula 1.6 Structure of aminocrotonates



Formula 1.7 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

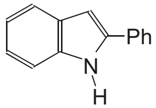
- *δ*-diketones,
- *β*-aminocrotonates, or
- derivatives of 1,3-dicarbonyl compounds (due to their synthesis from 1,3-dicarbonyl compounds, formaldehyde, and ammonia); see Formula 1.8.



Formula 1.8 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)

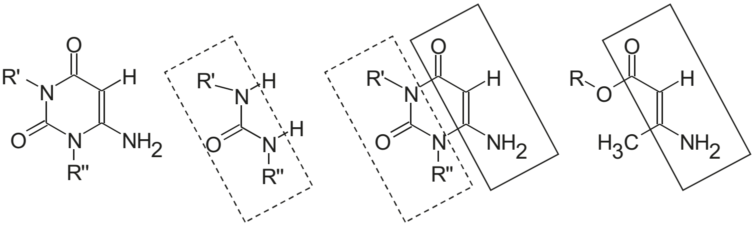
They probably stabilize PVC in a way similar to aminocrotonates or uracils; see Formula 1.7 and Formula 1.11.

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 Formula 1.9. 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.

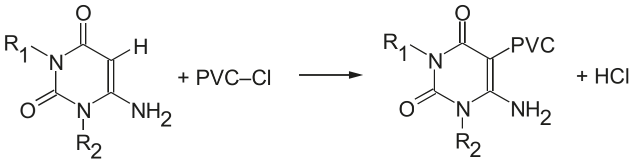


Formula 1.9 Chemical structure of 2-phenylindole

The uracils depicted in Formula 1.10 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 Formula 1.10. 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] (Formula 1.11).

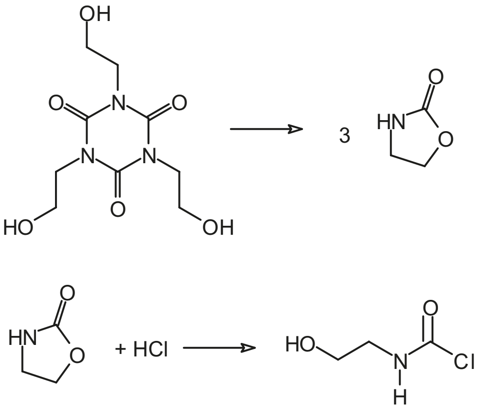


Formula 1.10 General structure of uracils depicted as "internal synergism" of urea and aminocrotonate; R, R′, and R″ can be identical or different substituents



Formula 1.11 Stabilizing mechanism of 1,3-substituted 4-aminouracils

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 Formula 1.12.



Formula 1.12 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 triethanol-