Michael Schiller

PVC Additives

Performance, Chemistry, Developments, and Sustainability

2nd Edition

HANSER

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The Author:

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Preface

For my three blondes …

January 7th, 1992 was my first day of work in the PVC industry, which I have never left since. During the first few weeks, a former colleague, later boss, even later employee in my small company and coauthor of the “VinylPedia” said to me: “You will certainly not retire with PVC.” It was 30 years ago. Either he lied to me or I will probably have to work for a long time …

It is approximately 110 years since Dr. Friedrich Heinrich August (Fritz) Klatte’s patent application, “Polymerization of vinyl chloride and use as a substitute for horn, as films, artificial threads and for paints” (DRP 281877A). A year before that patent was granted (1912), Klatte submitted a patent application for a “Process for the preparation of hydrogen halide addition products of acetylene,” greatly simplifying the production of vinyl chloride monomer (VCM) (DRP 278249). Now we are in 2022, two years into a pandemic. This gave me enough time to work on the second edition of this book and on another project, the “VinylPedia”. That is how I found out more about Klatte. He spent his last weeks in Klagenfurt, Austria, where he died and was also buried (St. Georgen cemetery, class I, field 6, row 01, number 8). That really touched me because I live and work about 65 km from Klagenfurt, and is why I wanted to visit his grave. Furthermore, I have to mention here Dr. Adolf Rollett, who was nearly forgotten. Rollett (b. 1885, December 10, in Moscow) was an Austrian chemist. He attended St. Peter & Paul High School in Moscow until June 1903, studied chemistry in Vienna and Leipzig, and received his PhD at the University of Berlin in 1908. He started his industrial career at Griesheim Elektron in Frankfurt. Together with the chemists Klatte and Zacharias, he developed a production process for PVC. He died in World War 1.

What is new in the second edition? I have only deleted a few things: In Chapter 1, a few substances have been added that played a relatively insignificant role about 10 years ago. I have also added a few test methods and various guide formulations for dry blends that will probably be of interest to the interested reader. Regarding Chapter 2, I actually wanted to go into plasticizers based on renewable resources in the first edition, but I did not have the necessary specialist knowledge (it is not much different today.) Fortunately, Dr. Peter Frenkel and Dr. Bharat Chaudhary have taken over for me to cover this topic in Chapter 2 of the new edition. For this I thank both esteemed colleagues from the bottom of my heart. I have also added my modest knowledge of chemical blowing agents and antistatic agents. The rest of the chapters have changed little. On the one hand, this is because I have not been able to work on these topics personally since 2015 and, on the other hand, because either no one else has done it or, if they have, have not published it.

In Chapter 5 I added the progress of the European PVC industry since 2015 and complemented the worldwide platforms, conferences and publications.

I would like to take this opportunity to thank a number of people. First, of course, my wife, partner, and friend, really the best of all wives: for over 32 years much more harmony than arguments. Secondly, my two favorite daughters Sarah and Maria, both of whom are already leading full and successful professional lives as a fire brigade trainer and doctor, respectively. The next to be mentioned would be the Carl Hanser Verlag, which gives me the opportunity of the second edition and there especially Dr. Mark Smith patiently editing the second edition. Without the “PVC Additives” my small company would probably not be so well known.

During my time in Izmir, Turkey, a team member asked me who had the most influence on my scientific career. That was probably my teacher and mentor Prof. Dr. Hans-Joachim Timpe from my technical university in Merseburg, Germany. Also, I have to mention Dr. Wolfgang Wehner, who unfortunately has already left us. I knew him from almost the beginning of my career in the PVC industry and consider him one of the brightest minds in our industry as a whole and not just because he is one of the masterminds of organic based stabilizers.

Regarding the cover photo I have to go back a little and sincerely thank several people. The object, an epicyclic gearing, is made of PVC and 3D printed. And it even moves! Our industry owes this development to Dennis Planner and Greg Harrison, a longtime personal and business friend, who both worked for a stabilizer manufacturer in Sydney. The photo was taken and colored for me by Ms. Mahsa Saffaripour, a professional photographer and personal friend in Tehran. I would like to thank Mahsa from the bottom of my heart for the picture and for our long-standing friendship.

February 2022 *Dr. Michael Schiller*

About the Author

Dr. Michael Schiller has about 30 years of experience in the international PVC industry in R&D. His experiences include: development of new PVC stabilizers and other additives, research in unusual phenomena (plate-out, photo effects, etc.), understanding sustainability aspects of the PVC industry, and technical product management. Michael is the author of "PVC Stabilizers" (available in Russian, Chinese, and German) co-author of the "VinylPedia" (which is an online platform coming soon), author and coauthor of approx. 200 papers, coeditor of the "Plastic Additives Handbook" in English, Russian, and German, and the inventor of more than 50 patents. He was the Head of Group R&D of Chemson (1992–2009) and the Head of the Innovation and Sustainability Center for Akdeniz Kimya, in Izmir, Turkey (2009–2015). In 2015 he founded HMS Concept e.U., a consulting company in chemical, environmental, and plastic technology. HMS Concept acts worldwide together with ~50 customers in a dozen countries on five continents. In December 2020 Michael became shareholder of the Indian stabilizer producer Platinum Industries Pvt. Ltd. He is happily married, the proud father of two daughters, and he enjoys the music from the band "Queen."

Arnoldstein (Austria), 4th August 2021

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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. 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.

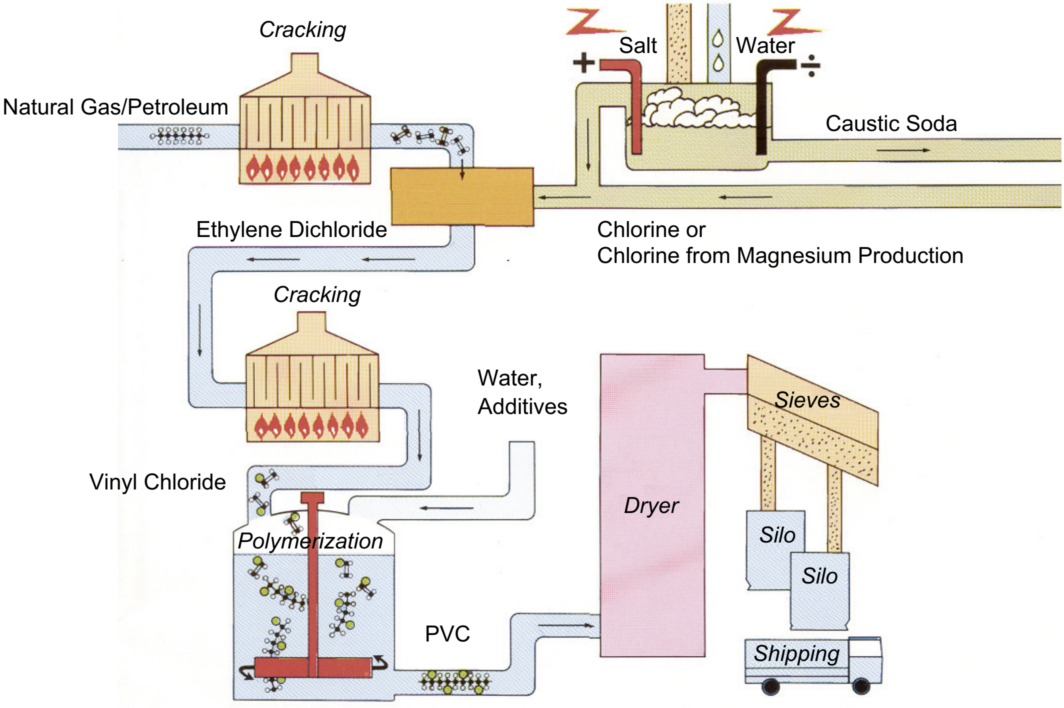

Figure 1.1 Schematic representation of the production of PVC [1]

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. Pre-stabilizers, mostly antioxidants, are often added before drying the reaction product. After drying, the PVC is ready to be shipped.

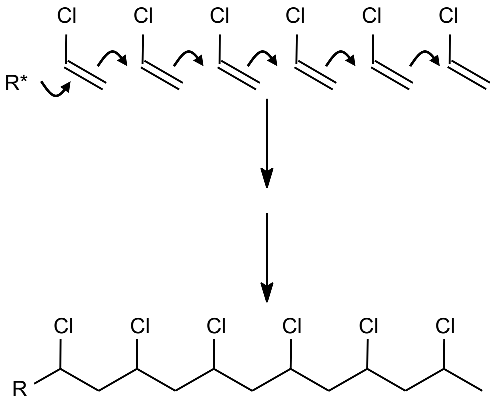

Figure 1.2
Polymerization of vinyl chloride monomer (VCM) to PVC

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

---

[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).

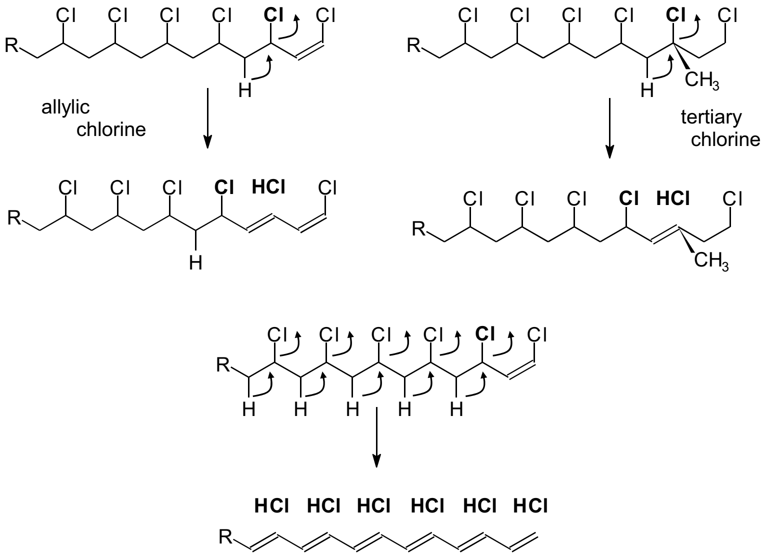

Figure 1.3 Degradation of PVC at allylic and tertiary carbon atoms due to heat or shearing

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.

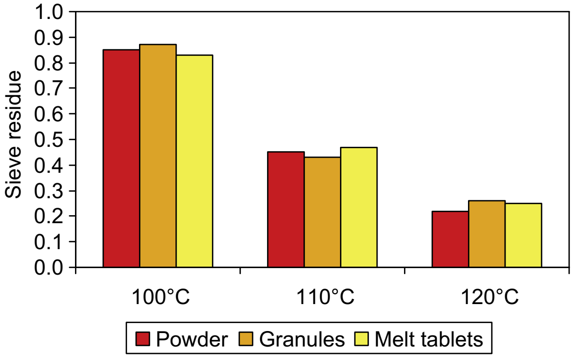

Figure 1.4
Studies on dispersion as a function of delivery form and mixing temperature

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

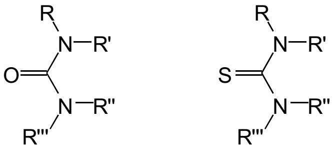

Figure 1.5 General structure of ureas (left) and thioureas (right); R, R', R'', and R''' can be identical or different substituents

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

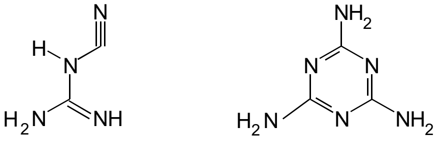

Figure 1.7 Structures of dicyandiamide and melamine

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].

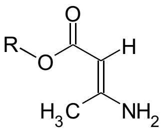

Figure 1.8 Structure of aminocrotonates