Richard P. Krock
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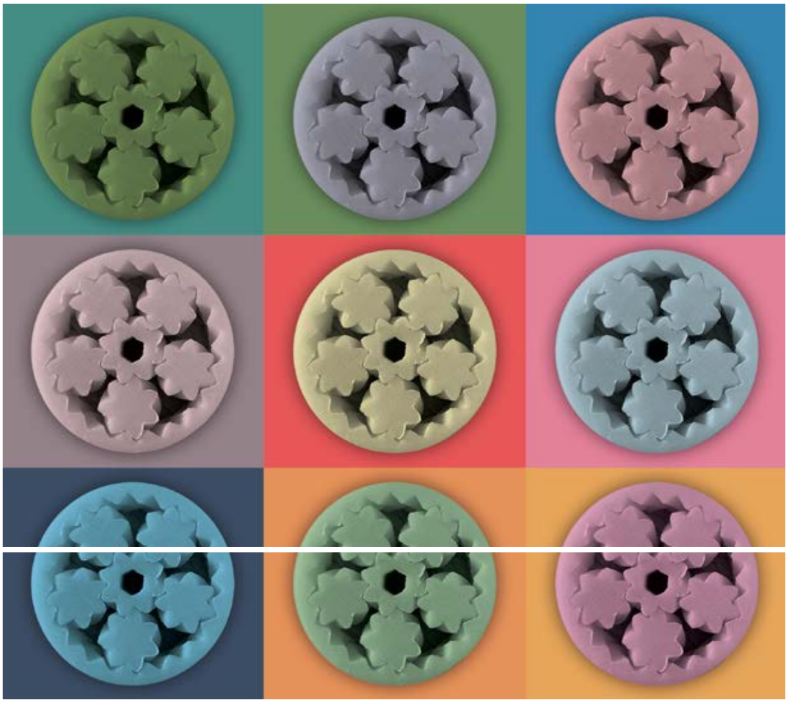
Peter Frenkel
James W. Summers
Charles A. Daniels (Eds.)

PVC
Handbook



2nd Edition

HANSER

Krock / Schiller / Frenkel /
Summers / Daniels

PVC Handbook

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Preface

In the spirit of the 1st edition of PVC Handbook, we as editors of the 2nd edition have aimed to maintain the overall book structure as far as practically possible, and continue providing a comprehensive account of all aspects of PVC – from the monomer manufacture to polymerization, compounding, and processing. It includes the most complete review of the main PVC additive categories, such as heat stabilizers, lubricants, plasticizers, flame retardants, smoke suppressants, impact modifiers, processing aids, fillers, and reinforcing agents; polymer blends and alloys; polymer characterization; compound performance testing and weatherability; product engineering design; applications; environmental, health, and safety aspects; sustainability, recycling, and decarbonization; and finally the PVC industry dynamics. Since many of the fundamental technological developments related to PVC were made after the 1st edition was published in 2005, all chapters of the 1st edition of the Handbook have been revised and updated by an international team of leading industry experts.

Major advancements on the 1st edition of PVC Handbook include the following:

a) A substantially reworked Chapter 4 (by Gianluca Sarti, Peter Frenkel, Yashodhan Kanade, and Michael Schiller) on heat stabilizers and lubricants for both PVC and CPVC, emphasizing new product and formulation compositions as well as additional details about the mechanisms of their action in these polymers.

b) Chapter 5 (by Michael Schiller, Peter Frenkel, and Patrick Harmon) on plasticizers now contains technical information on commercial bio-attributed plasticizers produced from renewable feedstocks as well as a regulatory status review of commercially viable plasticizers.

c) Flame retardancy of PVC materials and flame retardants are now covered by two separate chapters: Chapter 13 (by Marcelo Hirschler) updates PVC material fire performance with contemporary standards for comprehensive comparisons with other materials for product designers, and the new Chapter 14 (by Gianluca Sarti) presents new advantages of PVC materials in terms of their fire performance when compounded with modern generations of flame retardants and smoke suppressants.

d) Chapter 19 (updated by Michael Schiller, Arjen Sevenster, and Richard Krock, and Michael Schiller) provides the latest regulations on chlor-vinyl manufacturing, and protection of workers, compounding, applications, the evolving microplastics criteria, and with a special section on hazardous environmental incidents during transport of VC process hazard and program safety.

Following the industry trends, the 2nd edition of the PVC Handbook also includes new chapters on sustainability (Chapter 20 by Mark Everard, Jason Leadbitter, and Sophi MacMillan), PVC recycling (Chapter 21 by Jason Leadbitter, Sophi MacMillan, and Richard Krock), and decarbonization (Chapter 22 by Peter Frenkel, Domenic DeCaria, and Jason Leadbitter). The book concludes with an updated perspective on the global industry (Chapter 23 with summaries by Anna Lopez on global production and by Ned Monroe, Chair of the Global Vinyl Council on regional initiatives, and by Richard Krock).

The handbook contains both a lot of practical formulation information as well as theoretical and mechanistic considerations based on experimental data that explain why PVC and the PVC additives behave as they do.

As co-editors and co-authors, we were fortunate to connect and coordinate chapter preparations with experienced authors who generously shared their knowledge and expertise in their respective fields. We greatly appreciate Mark Smith of Carl Hanser Publishers for his commitment to and unwavering support of the project especially during preparation of the manuscript. We also gratefully acknowledge the encouragement and guidance provided by James Summers and Charles Daniels, editors of the 1st edition.

We hope that this compilation of published, patented, and systematized knowledge will demonstrate once again the resilience and versatility of PVC materials over the years, even under pressure from not fully informed sources, and result in many new applications and continued growth of the mature industry associated with this polymer.

Regarding the cover photo: We chose this image for several reasons. The object depicted is an epicyclic gearing 3D printed from PVC, and it even moves! Our industry owes this development to Dennis Planner and Greg Harrison, who both worked for a stabilizer manufacturer in Sydney. Furthermore, it resembles a planetary screw extruder, which was invented by L. Wittrock in the early 1950s and was initially widely used in the PVC films and sheet goods manufacturing industry. It also symbolizes that a small change in the compound can change the entire picture of characteristics when you turn a wheel. Last but not least, it connects to Hanser’s 2nd edition of the book “PVC Additives,” by Michael Schiller, which also features this epicyclic gearing on its cover.

We would like to thank our families (Richard to his wife Marilyn; Michael to his wife Annette; Peter to his wife Elena) for their patience and support throughout the preparation of this book.

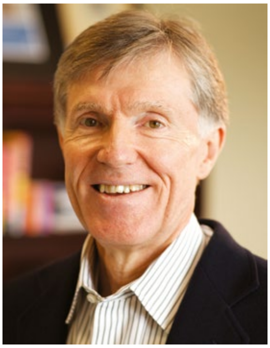
July 2025

Richard Krock Michael Schiller Peter Frenkel

The Authors

The Editors

Richard Krock



Richard Krock is Principal, VyChlor Advisors LLC, a consulting company he formed in 2022 to assist manufacturers, recyclers, suppliers, and trade associations in advancing their positions in the PVC value chain. He retired as Senior Vice President for Regulatory and Technical Affairs at the Vinyl Institute and has worked in the PVC industry for 37 years beginning with BFGoodrich in 1988. He joined the Vinyl Institute in 2009 to advocate for the PVC industry, and advance its strategic positions related to regulatory and technical affairs, and sustainability. He is co-author of many technical papers and presenter at numerous industry association meetings related to PVC recycling, sustainability, and other PVC technical matters and topics related to petroleum refining technologies. A registered professional engineer, Mr. Krock holds a Bachelor of Science in Chemical Engineering from the University of Cincinnati in Ohio and a Master in Business Administration from Marshall University in Huntington, West Virginia.

Michael Schiller

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Dr. Michael Schiller born in 1959, is a German chemist, scientist, author, editor, and inventor. Michael has more than 30 years of international experience in the PVC industry, with a strong focus on research and development. His expertise includes the development of new PVC stabilizers and additives, investigation of unusual phenomena, sustainability aspects of the PVC industry, and technical product management. Michael considers himself more a student than an expert, always eager to learn.

He is the author of the book PVC Additives (Hanser Verlag, two editions, also available in Russian and German). Additionally, he is co-author of "PVC from A to Z" in the PVC eSolution by Hanser Verlag, author and co-author of around 200 scientific papers, co-editor of the Plastic Additives Handbook in English, Russian, and German, co-editor of the 2nd edition of the "PVC Handbook", and inventor on more than 50 patents.

Michael served as Head of Group R&D at Chemson from 1992 to 2009 and as Head of the Innovation and Sustainability Center at Akdeniz Kimya in Izmir, Turkey, from 2009 to 2015. In 2015, he founded HMS Concept e. U., a consulting company specializing in chemical, environmental, and plastics technology, which serves approximately 50 clients across more than a dozen countries on five continents.

Privately, Michael has been happily married for more than 35 years, is the proud father of two adult, well-educated, and accomplished daughters, and is grandfather to two wonderful grandsons. He enjoys listening to the music of Queen.

Peter Frenkel

Dr. Frenkel has over 40 years in technical management, leading international technical teams, and conducting industrial and basic research on new chemical product & process technologies.

Dr. Frenkel has been serving as the Vice President of Technology at Galata Chemicals. He has over 30 years of experience in the field of polymer additives, focusing on product innovation and advocacy, with an emphasis on PVC. Dr. Frenkel drives innovation that concentrates on sustainable technologies related to bio-based plasticizers, heat stabilizers, polymer modifiers and catalysts. Together with his teams, he conducted fundamental studies and made major contributions to establishing the Universal Mechanism of PVC stabilization with binary heat stabilizer systems, proposing the mechanism of C-PVC stabilization, developing and market introduction of high efficiency primary bio-based plasticizers, modifying reactivity of organic peroxide initiators and accurately determining the mechanism of in-vitro metabolism of selected alkyltin heat stabilizer components that based on these results were discovered to be non-reprotoxic.

Dr. Frenkel has co-authored over 40 patents, several book chapters and dozens of scientific journal and conference publications; played a critical role in numerous new product launches. He has a broad educational background, holds a Ph.D. in Inorganic Chemistry from Belarus Institute of Technology and a Master of Science degree in Organic Chemistry from Belarus University. Dr. Frenkel was named the Fellow of The Society of Plastics Engineers.

James Summers

Dr. James Summers was co-editor and a major contributor of information for the First PVC Handbook published in 2005, a capstone project led by him. Through his work at BFGoodrich, The Geon Company, PolyOne Corporation, and P3 Consulting, and his devoted participation in the Society of Plastics Engineers, Dr. Summers' legacy stands as a respected technical educator for thousands of individuals involved with polymerizing PVC resins, formulating and compounding PVC materials, processing PVC into finished parts, and designing PVC products to perform at their best for their entire useful life.

Charles Daniels

Dr. Charles Daniels was co-editor and a significant contributing author for the First Edition of the PVC Handbook as a capstone to his career spanning over four decades in PVC with BFGoodrich, The Geon Company, and PolyOne Corporation. Dr. Daniels is currently the President of Materials Performance Consulting LLC and utilizes his expertise in polymer analytics to consult in plastics performance programs, and to contribute as an expert witness in a number of legal cases involving patents and polymer failure analyses.

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1

Introduction

Peter Frenkel, Richard Krock, Michael Schiller

Early History

Around 1835, Henri Victor Regnault, a French chemist, physicist and photographer, obtained vinyl chloride by dehydrohalogenation of EDC (1.2-dichloroethane, also called ethylene dichloride) with alcoholic potassium carbonate. He noticed that prolonged exposure to sunlight produced a white powder – polyvinyl chloride (PVC) – but did not recognize the significance of his discovery [1]. The German pharmacist, chemist and biochemist Eugen Albert Georg Baumann synthesized PVC in 1872 after extended investigation and experimentation [2].

In 1912, the German chemist “Fritz” Friedrich Heinrich August Klatte, together with the German chemist Adolph Emil Zacharias and the Austrian chemist Adolf Rollett developed a method for the synthesis of vinyl chloride from acetylene (ethyne) and hydrogen chloride at the Griesheim-Elektron chemical factory [3]. They also exposed glass vessels containing vinyl chloride and various additives to sunlight. In doing so, they laid the foundations for the production of PVC. In 1913, Klatte et al. patented the “polymerization of vinyl chloride and its use as a horn substitute, as films, synthetic threads and for varnishes” [4].

Ivan Ivanovich Ostromislensky, a Russian-born chemist, also patented his early work on the synthesis of polyvinyl chloride in the U.S. [5].

Structure, Polymerization and Manufacture

PVC [CAS Number: 9002-86-2] has a chemistry and a physical structure that makes it broadly unique in the polymer world. PVC (often referred to as vinyl) is produced commercially by the free-radical polymerization of vinyl chloride monomer (VCM) in different ways; Figure 1.1.

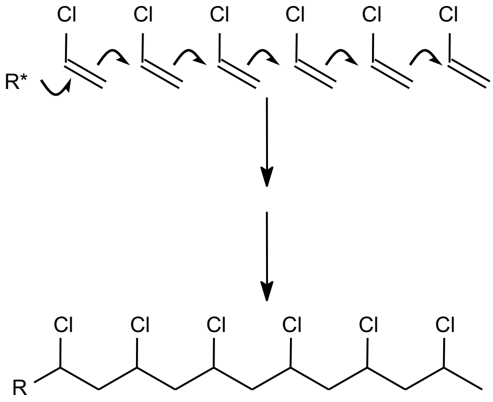

Figure 1.1 Polymerization of vinyl chloride monomer (VCM) to PVC

PVC is made commercially in several molecular weights, depending on the intended applications: from Mw = 39,000 g/mol (inherent viscosity = 0.51 dL/g, K value = 49, weight average degree of polymerization = 625) used for injection molding of thin-walled parts [6, 7], to Mw = 168,000 g/mol (inherent viscosity = 1.60 dL/g, K value = 91, weight average degree of polymerization = 2700) used for plasticized PVC requiring outstanding compression set [8]. More information on PVC polymerization is found in *Chapter 3*.

VCM can be produced in two different ways. The EDC (ethylene dichloride) method is more modern and described in detail in *Chapter 2*. Conversion of EDC into vinyl chloride is widely practiced around the world because of its efficiency and widespread availability of chlorine and ethylene. The carbide method is an older and more energy-intensive route to vinyl chloride. It is considered to be less sustainable because of its higher energy consumption and use of mercury-based catalysts. Therefore, it is no longer used in the Western world. However, it is still practiced in many regions of China because of their abundant supplies of locally produced coal, the primary raw material used to manufacture acetylene. The carbide process, also known as the acetylene route, is based on the hydrochlorination of acetylene. In this method, acetylene reacts with hydrogen chloride at temperatures of 140–200 °C and atmospheric pressure, utilizing mercury(II) chloride as a catalyst. The reaction occurs in the gas phase within tube bundle reactors, where the exothermic reaction ($\Delta H_R = -98.8$ kJ/mol) is controlled by an oil circulation cooling system. The acetylene conversion reaches 96–97% with a vinyl chloride selectivity of 98–99%. As a result of its 2017 entry in the Minamata Convention, the Government of China committed to a reduction in mercury emissions from all sources. Part of the Chinese government program includes transforming its carbide-based PVC industry for higher-efficiency utilization of any mercury catalyst, effectively reducing it by 50% by 2020 compared to 2010, and to achieve a further 50% reduction with eventual substitution with a similarly effective gold catalyst [9]. China has also prohibited any new construction of vinyl chloride production that employs mercury catalysis. More information on these Chinese initiatives can be found in *Chapter 24*.

Significance to World Industry

Less than 0.3% of the world's supply of gas and oil and approximately 35% of the world's production of chlorine goes into the manufacture of PVC. With a chlorine content of 56.8%, PVC is of lower carbon footprint and much less dependent on the limited supply of gas and oil than other polymers. As a main component of seawater, the supply of sodium chloride salt as a source for chlorine is virtually limitless. However, this salt is abundantly found in vast crystalline deposits in many regions around the globe and chlor-alkali plants around the world utilize salt mined from local deposits. PVC consumes roughly 30 to 50% of the chlorine output of the chlor-alkali process depending on the geographic region it is produced within. Since sodium hydroxide and chlorine are co-produced in nearly equal amounts (1.1 pounds of sodium hydroxide to 1 pound of chlorine), PVC therefore consumes roughly 15 to 25% of the total output of the chlor-alkali process. Chlorine and caustic soda (sodium hydroxide) are widely used in literally hundreds of industrial processes, intermediates, and commercial products. Thus, PVC is an important material to maintain the operational balance of chlor-alkali production. Most other polymers are largely hydrocarbons and thus are more dependent on supplies of oil and gas than is PVC. This makes vinyl a unique polymer in its sources of raw materials. As already mentioned, VCM is produced on the basis of oil, gas and coal, but bio-PVC made from ethylene derived from bio feedstocks has also been commercially available for some time; more details in *Chapter 22*.

Uniqueness of PVC

PVC is one of the few polymers that are insoluble in their monomer. PVC resin particles precipitate early on in the polymerization process [10]. This offers a rare opportunity to influence and control morphology of the particles during polymerization by using surfactants on the polymer/monomer interface [11]. This ability to control particle morphology facilitates efficient monomer removal, routinely to less than 5 ppb for resins used in applications such as thin-film-type food packaging, and to less than 1 ppm for resins used in rigid PVC pipe applications. This very low level of residual monomer concentration in the polymer is unheard of for most other polymers, and it makes PVC unique; more details can be found in *Chapters 3 and 19*.

Highly syndiotactic PVC, in which the chlorine atoms alternate from one side of the plane of carbon atoms to the other, forms a crystalline structure that is virtually unmeltable [12, 13]. Therefore, small consecutive runs of syndiotacticity in a molecule and small fringed-micelle crystallites [14] found in commercial PVC resins can make it impossible to completely melt PVC during processing [15, 16]. As PVC is processed without completely melting, it flows as bundles of about 10 million molecules (primary particle flow units at 1 µm diameter). This is discussed in more detail in *Chapter 4*. This behavior is also very rare in the polymer world, where most polymers flow as completely melted molecules. This leads to some unique advantages for PVC in extrusion die design. While other polymers have more elastic recovery and die swell at lower melt temperatures, PVC compounds have less die swell [17]. In fact, die swell can be so low for PVC compounds that sometimes the die opening is cut at the exact size of the desired profile.

The flow of PVC as molecule bundles and the ability to control the amount of melting (temperature control) and molecular entanglement makes PVC properties dependent not only on formulations but also on the previous processing conditions. At low melt temperatures, the PVC primary particle flow units move with relatively little molecular entanglement at the surface of the primary particles. At high temperatures, more crystallites melt, allowing for more chain entanglement. Upon cooling from this melt, recrystallization occurs, causing fusion (gelation) at the particle surface. This of course affects strength between the primary particles and the strength of the whole article [17]. Again, PVC is fairly unique in this strong dependence of properties on processing. More information on process and tool design is found in *Chapters 16 and 17*.

PVC is moderately polar, as judged by its Hildebrand Solubility Parameter HSP (19.6 to 20.2 MPa$^{1/2}$,depending on the reference source); see also *Chapter 4, Section 4.7.3.5; and Chapter 9, Section 9.5*. Thus, when polymers are sorted according to solubility parameter [18, 19], PVC is centrally located among polymer types, making it fairly easy to compatibilize with other polymers and therefore amenable to compounding. For example, PVC, located between polystyrene (18.4 MPa$^{1/2}$) and polyacrylonitrile (27.1 MPa$^{1/2}$), is compatible with styrene/acrylonitrile copolymers [20] such as in ABS. Also, PVC has a strong attraction to esters, where the polar carbon–chlorine bond ($C^{\delta+}$–$Cl^{\delta-}$) has a special attraction to the polar carbonyl bond ($C^{\delta+}=O^{\delta-}$) of the ester [21–28]. This attraction is particularly notable for PVC with acrylic processing aids and for PVC with ester-containing plasticizers, and is discussed in more detail in *Chapter 9, Section 9.5*. Thus, PVC is known for its ability to be compounded because so many materials can be blended with it.

Development of the PVC Industry

In 1926, Waldo Semon of BFGoodrich, seeking an adhesive to bond rubber to steel, discovered that heated tricresyl phosphate or dibutyl phthalate make PVC highly elastic at room temperature. One of the first items made this way was a golf ball. This plasticized PVC was the first thermoplastic elastomer (TPE) and represented the invention of plastisol and organosol processing techniques that resulted in the birth of the vinyl coatings industry [29, 30].

The new plasticized material made melt processing much easier. In 1928, in an attempt to make PVC processing easier, Union Carbide and DuPont each made a copolymer of vinyl chloride with vinyl acetate.

In the same year, chlorinated PVC (C-PVC) was made, which was more solvent-soluble and was used for manufacturing lacquers and fibers [31]. While C-PVC does not have a separate chapter in the 2nd edition of the Handbook, its stabilization and lubrication aspects have been added in *Chapter 4, Section 4.9* and revised *Chapter 11, Section 11.5; and Chapter 16, Section 16.4.1*.

New stabilizing additives for PVC were much needed from the very beginning of manufacturing PVC. In 1934, Frazier Groff of Union Carbide discovered that alkaline earth soaps were useful PVC heat stabilizers.

The PVC industry has a rich history of providing many other solutions to society's needs. The first PVC pipes were manufactured in 1935. However, PVC pipes were certainly not the first plastic pipes. Early literature reports on the manufacture of pipes made of vulcanized fiber, cellulose, celluloid and as well as the first thermosets, all of which predate PVC's use. However, pipes made of these plastics or modified natural materials did not find their way into pipeline construction, in which PVC pipes were used practically from the beginning. The first PVC pressure pipes were laid in Bitterfeld and Salzgitter, Germany [32].

The first significant commercial tin stabilizer was dibutyltin dilaurate, patented by Quattlebaum and Rugely at Union Carbide in 1939. Quattlebaum is often referred to as the "Father of Organotin Stabilizers."

Useful PVC solutions also included flame-resistant wire insulation materials that prevented uncontrolled fire-spread on the U.S. Navy ships during World War II. Many PVC materials often contain almost 50% chlorine. For this reason, in the event of a fire, this plastic only provides about half the fuel compared to other polymers. PVC articles with less than 50% chlorine can be equipped with flame retardants and smoke suppressants, which nowadays have a very high sustainability potential and are halogen-free. The interested reader can find out more about this in the revised *Chapter 13* and the new *Chapter 14*.

Also, when the US Navy needed a wash-down system for mine sweepers with specified tough non-magnetic piping and with delivery within 120 days, PVC piping answered the call. Use of lead-type stabilizers interfered with mine sweeping detections, so lead-free PVC pipe was developed and has been continued to be produced throughout the U.S. [33, 34]. Those who live in cities with cast iron pipes for drinking water know that cold weather and cold water bring about shrinkage of the pipes with inevitable cracks and leakage. PVC pipes are widely used for potable water and sewer today because of their durability and toughness. PVC piping has a long history of providing reliability and safety for the world's water supplies.

In the 1960s, it was speculated that PVC could not be made weather-resistant enough in terms of color retention and toughness for meeting the high demands for exterior market applications. The key to success was the use of high-quality titanium dioxide, which enabled the production of white-pigmented window profiles to be used for decades without discoloration or micro-cracks with low maintenance but not maintenance-free. Short- and long-term weathering phenomena as well as their mechanisms are explained in detail in *Chapter 15*. The development of weatherable PVC compounds at BFGoodrich in the early 1960s spawned the U.S. vinyl siding industry. Window manufacturers also began to use these weatherable PVC materials to cover wood to make more durable and low maintenance wood/vinyl windows. The development of appropriate process aids for complex extrusion profiles and advances in impact modification for holding glass under extreme weather conditions helped PVC become a material of choice for window profiles. Advancements in process aids and impact modifiers are described in more detail in Chapter 6.

Other noteworthy milestones in the production of PVC resins include the following:

- 1930: Production of 2000 Mt per year in US.
- 1932: Installation of a CPVC plant with a capacity of 10 Mt per month in Rheinfelden, Germany.
- 1935: Start of continuous production of emulsion resin (E-PVC) in Bitterfeld, Germany.
- 1936: Installation of a PVC plant with 50 Mt per month capacity in Bitterfeld.
- 1938: Start of large-scale PVC production by BFGoodrich, Monsanto, DuPont, Dow, Bakelite in the USA.
- 1939: Construction of a continuous 200 Mt per month polymerization plant in Schkopau.
- 1940: BFGoodrich built its first commercial PVC plant in Buffalo, NY, and in 1941 adopted the name Geon® for its PVC resins and compounds. Geon comes from the Latin “geo” for “from the earth” and from the Greek “eon” for “forever”.
- 1941: Publication of DIN 8061 and 8062 Plastic pipes made of polyvinyl chloride (pipe type).
- 1944: Wacker Chemie produces 2,452 metric tons of suspension PVC “Vinnol” [32].
- 1955: BFGoodrich invented rigid custom complex profile extrusion.

Further Developments Reflected in the Handbook

PVC is likely the first polymer with which people come into contact within minutes of their birth: Possibly the bracelet bearing a newborn’s name and birth date is made of PVC; the soft, flexible material fits well with babies’ small wrists. It is skin-friendly, lightweight, easy to write on and water-resistant. Or possibly the vinyl gloves worn by a healthcare worker to assist the birth, or any vinyl aspiration tubing that removes any inhaled fluids. The medical community has long relied on the sterile and functional properties of PVC medical devices and other articles.

Vinyl has also provided weatherable, flame-resistant systems for siding, windows, and flexible PVC materials for floors, roofing, wallcovering, and pool-liners. More information on PVC applications is available in *Chapter 18*.

The auto industry uses vinyl for instrument panel skins, seat upholstery, and door panel coverings (which may not be fully recognized for their outstanding fire resistance). Competitive materials that are becoming popular for use in automotive interiors, on the other hand, are hydrocarbons that have essentially the same fuel potential (once ignited) as gasoline. Other applications, where fire resistance is critical, are electrical wiring devices and their boxes (used for electrical connections in construction), electrical conduits, electrical housings for computers, appliances and business machines where safety requirements dictate the use of flame-resistant plastic materials.

Other contributions to society's safety include shatter-resistant, clear containers with handles. These extra-safe bottles were made from vinyl beginning in 1968, long before other types of plastic became popular in bottles. Vinyl blood bags are unmatched by any other polymeric material in terms of their safety, functionality, and durability.

Engineering thermoplastics are a group of polymeric materials with well-defined properties so that products can be engineered precisely to meet the needs of specific applications. PVC piping systems are a classic example in which the PVC, the process, and the properties have been tested, understood, quality checked, and engineered to meet the standards for 100 years of life at double (safety factor) the pressure of actual use. This is a very good example of engineering with PVC. Another example uses engineering data to design injection molded thin-walled parts for products such as housings for washers and dryers. Mold flow modeling considers flow length capabilities. Other engineering properties include bending limits for snap joints, strength at various temperatures, time-temperature superposition for long-term stiffness, creep, impact at various thicknesses, corner radii, compressive strength, fatigue, thermal expansion, fire properties, weatherability, and chemical resistance [35, 36]. Thus, with good data, parts are engineered with PVC, or the limits are defined at which PVC may not be the right material choice. Under these circumstances, PVC is indeed an engineering thermoplastic. Thus, we see how very significant PVC is, compared to the total range of other thermoplastics. It is compounded to attain a very wide range of properties. And with engineering data, PVC products are precisely designed to meet the needs of the market.

Health, Safety and Environmental Priorities

The PVC industry has made safety a priority, not only in products, but also within the working environment of the industry itself. When, in the 1970s, the U.S. industry realized vinyl chloride could be the cause of liver health problems in workers, the National Institute of Health (NIH) and the Occupational Safety and Health Administration (OSHA) were informed. Leading PVC producers quickly developed technology to minimize worker exposure to vinyl chloride monomer and shared the technology with the whole industry to eliminate this health issue. This illustrates how the PVC industry has been an example for continually improving for safer operations; see *Chapters 2 and 19* for more information.

PVC faced criticism from environmental organizations beginning in the 1980s. The primary concern at the time was the use of heavy-metal-containing stabilizers, particularly those based on cadmium and lead. In response, the U.S. and European PVC industries voluntarily phased out both types of stabilizer systems. This trend is now spreading to other parts of the world, such as India. Other major criticisms of PVC that have been addressed include the following:

- Environmental impacts, such as the release of chlorine-containing substances and dioxins during chlor-vinyl manufacturing: Tight regulations and voluntary practices were adopted beginning in the mid-1970s and continual improvement over the year has substantially reduced these types of emissions. More discussion on dioxins and furans regulations and industry performance is found in Chapters 2 and 19.
- Challenges in disposal and recycling: Regional recycling companies that were established in the 1990s now recycle billions of pounds of PVC materials annually. More information on PVC recycling can be found in *Chapter 22*.
- Persistence of PVC waste in the environment: Very little PVC (less than 5% on annual production in most regions) is used today in single-use disposable applications. PVC finds widespread use in durable goods and buildings because of its long-lasting performance. Additional information about microplastics can be found in *Chapter 19*.
- Health risks associated with phthalates: Alternative plasticizers with safer health characteristics have systematically replaced those in applications of most concern, in some cases voluntarily. More information on plasticizers is available in *Chapter 5*.
- Presence of VCM in PVC resin: Once polymerized, all PVC resin is steam stripped to remove residual vinyl chloride monomer (RVCM). Over the years, stripping technology has advanced in a fashion such that RVCM levels have been reduced to as low as practical without damaging the resin itself. This improvement has benefited workers who process PVC materials, and consumers who rely on PVC materials for drinking water or food packaging, both critical contact materials that require as low a levelof RVCM as possible. More information on RVCM can be found in *Chapters 18 and 19*.
- Resource consumption (high energy use in production and dependence on fossil raw materials): PVC materials have lower embodied carbon content than many other materials and often perform better based on life cycle analysis because of vinyl’s performance and durability.

Sustainability and Global Growth

While the PVC industry was primarily reactive before the turn of the century, it has since taken a proactive approach, supported by critical NGOs like The Natural Step. Since 2000, the global PVC industry has made significant efforts to address these concerns and improve PVC's sustainability. As a result, PVC has become one of the most thoroughly studied plastics in terms of sustainability.

To reflect these developments, we have included four new chapters in the 2nd edition:

- *Chapter 20*: Sustainability
- *Chapter 21*: Decarbonization
- *Chapter 22*: Recycling
- *Chapter 24*: Global Vinyl Council

These additions provide a comprehensive overview of the industry's ongoing efforts to address environmental and health concerns associated with PVC.

The result of these sustainability improvements and the growing understanding of its performance attributes has allowed the global use of PVC materials to grow exponentially (Figure 1.2). More information about the global industry and the companies that produce PVC resins can be found in *Chapter 23*.

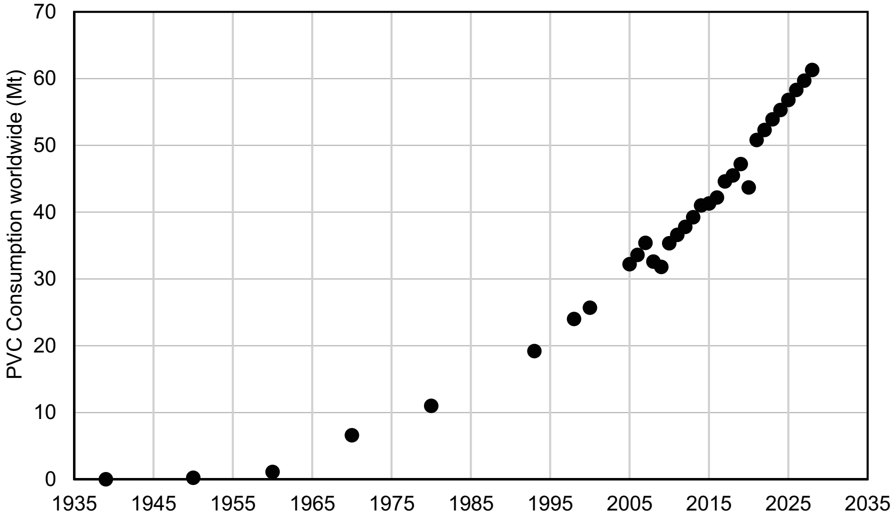

Figure 1.2 Global PVC Consumption 1939 to 2000 [37], 2005 to 2021 [38]

This astounding growth has made the PVC industry an exception among the materials industries. It continues to self-improve through the efforts of thousands of industry professionals, positively impacting lives and addressing the needs of consumers, who have benefited from its contribution to modern and healthy living around the world.

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2

Vinyl Chloride Monomer

Joseph A. Cowfer[1], Arjen Sevenster, Richard Krock

2.1 Overview

A brief history of the commercial development of vinyl chloride, tabulation of its physical properties, a discussion of its chemical reactions, detailed descriptions of the component processes currently used for its production, uses, toxicity and handling precautions and purity standards are given. Chemical reactions that vinyl chloride undergoes include polymerization, substitution at the carbon-chlorine bond, oxidation, addition, photochemistry and pyrolysis. Important manufacturing methods are described, with emphasis on the balanced process based on ethylene and chlorine feedstocks. Component processes of direct chlorination, oxychlorination and pyrolysis of the intermediate 1,2-dichloroethane are described in terms of their reaction mechanisms, operating conditions, conversions and yields and overall process integration. Oxychlorination technology comparisons are made between processes involving either fixed or fluidized-bed reactors and either air or oxygen feeds. Intermediate 1,2-dichloroethane purification requirements are described, as are by-product handling and disposal and environmental considerations. Technology trends are also briefly discussed. Economic aspects include current worldwide capacity. Quality standards are also presented, along with toxicity and handling precautions.

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[1] Joseph A. Cowfer is the First Edition Author with revisions and updates for the Second Edition completed by Arjen Sevenster and Richard Krock

2.2 Introduction

Vinyl chloride [Chemical Abstracts (CAS) number 75-01-4], CH_2=CHCl, by virtue of the wide range of applications for its polymers in both flexible and rigid forms, is one of the largest commodity chemicals in the world and is an important item of international commerce. Growth in vinyl chloride production is directly related to demand for its polymers and, on an energy-equivalent basis, rigid poly(vinyl chloride) [CAS 9002-86-2] (PVC) is one of the most energy-efficient construction materials available. Initial development of the vinyl chloride industry in the 1930s stemmed from the discovery that, with the aid of plasticizers, PVC can be readily processed and converted into a rubbery product [1]. However, it was not until after World War II that vinyl chloride production grew rapidly as a result of the increased volume of PVC products for the consumer market.

The early history of vinyl chloride has been documented [2–6]. Justus von Liebig at the University of Giessen won the distinction of being the first person to synthesize vinyl chloride when, in the 1830s, he caused "the oil of the Dutch chemists" – dichloroethane [CAS 1300-21-6] – to react with alcoholic potash to make vinyl chloride. Liebig's student, Victor Regnault, confirmed his discovery and was allowed to publish it as sole author in 1835 [7]. In 1872, E. Baumann observed that white flakes precipitated from vinyl chloride on prolonged exposure to sunlight in a sealed tube [8]. This material was further investigated in the early 1900s by Ivan Ostromislensky, who named it *Kauprenchlorid* (cauprene chloride) and gave it the empirical formula $(C_2H_3Cl)_{16}$ [9]. However, vinyl chloride was of little commercial interest until Waldo Semon's seminal work with plasticized PVC for The B. F. Goodrich Co. beginning in 1926 [10]. Some years earlier, Fritz Klatte had developed the first practical route to vinyl chloride while looking to find uses for acetylene [74-86-2] for Chemische Fabrik Griesheim-Elektron. This process, in which hydrogen chloride [7647-01-0] (HCl) is added to acetylene over a mercuric chloride [7487-94-7] catalyst, was patented in 1912 [11]. By 1926, Griesheim-Elektron had concluded that the patent held no commercial value and allowed it to lapse. Klatte's process eventually formed the basis of the vinyl chloride industry from its beginnings in the 1930s for many years, but was ultimately supplanted by a balanced process from ethylene [74-85-1] and chlorine [7782-50-5] in which vinyl chloride is made by pyrolysis of 1,2-dichloroethane [107-06-2] (ethylene dichloride, EDC).

Vinyl chloride (also known by its IUPAC name, chloroethylene) is a colorless gas at normal temperature and pressure, but is typically handled as the liquid (b. p. –13.4 °C). However, no human contact with the liquid is allowed. Vinyl chloride is an OSHA-regulated material.

2.3 Physical Properties

The physical properties of vinyl chloride are listed in Table 2.1 [12]. Vinyl chloride and water [7732-18-5] are nearly immiscible. The equilibrium concentration of vinyl chloride at 1 atm partial pressure in water is 0.276% by weight at 25 °C, while the solubility of water in vinyl chloride is 0.0983% by weight at 25 °C and saturated pressure [13]. Vinyl chloride is soluble in hydrocarbons, oil, alcohol, chlorinated solvents and most common organic liquids.

Table 2.1 Physical Properties of Vinyl Chloride[a]

Property	Value
Molecular weight	62.4985
Melting point (1 atm), K	119.36
Boiling point (1 atm), K	259.25
Heat capacity at constant pressure, J/(mol-K)	
■ Vapor at 20 °C	53.1
■ Liquid at 20 °C	84.3
Critical temperature, K	432
Critical pressure, MPa	5.67
Critical volume, cm^3/mol	179
Critical compressibility	0.283
Acentric factor	0.100107
Dipole moment, C-m	4.84 × 10–30
Enthalpy of fusion (melting point), kJ/mol	4.744
Enthalpy of vaporization (298.15 K), kJ/mol	20.11
Enthalpy of formation (298.15 K), kJ/mol	28.45
Gibbs energy of formation (298.15 K), kJ/mol	41.95
Vapor pressure, kPa	
■ –30 °C	49.3
■ –20 °C	78.4
■ –10 °C	119
■ 0 °C	175

Table 2.1 Physical Properties of Vinyl Chloride[a] *(continued)*

Property	Value
Henry's Law constant, (at 25 °C atm-m^3/gmol) [14]	0.0278
Solubility in water, ppm (at 25 °C) [14]	2,391
Vapor density, air = 1 [15]	2.16
Viscosity, mPa s	
▪ –40 °C	0.345
▪ –30 °C	0.305
▪ –20 °C	0.272
▪ –10 °C	0.244
Explosive limits in air, % by volume	
▪ Lower limit	3.6
▪ Upper limit	33
Auto-ignition temperature, K	745

[a] Ref [12].

2.4 Reactions

2.4.1 Polymerization

The most important reaction of vinyl chloride is its polymerization and copolymerization in the presence of a radical-generating initiator (see the following). More information about polymerization is provided in Chapter 3.

2.4.2 Substitution at the Carbon–Chlorine Bond

Vinyl chloride is generally considered inert to nucleophilic replacement, compared with other alkyl halides. However, the chlorine atom can be exchanged under nucleophilic conditions in the presence of palladium [7440-05-3] (Pd) – and certain other metal – chlorides and salts [16–22]. Vinyl alcoholates, esters and ethers can be readily produced from these reactions.

Use of alcohol as a solvent for carbonylation with reduced Pd catalysts gives vinyl esters [23, 24]. A variety of acrylamides can be made through oxidative addition of carbon monoxide [630-08-0] (CO) and various amines to vinyl chloride in the presence of phosphine complexes of Pd or other precious metals acting as catalyst [25].

Reaction of vinyl chloride with butyllithium [109-72-8] and then with carbon dioxide [124-38-9] (CO_2) in diethyl ether [60-29-7] at low temperatures, gives high yields of α,β-unsaturated carboxylic acids [26].

Vinylmagnesium chloride [3536-96-7] (Grignard reagent) can be prepared from vinyl chloride [27, 28] and then used to make a variety of useful end-products or intermediates by adding a vinyl anion to organic functional groups. The vinylmagnesium compound can be coupled with cuprous chloride [7758-89-6] (CuCl) at –60 °C to give 1,3-butadiene [106-99-0] [29]. Vinyl ketones and alcohols can also be prepared by the addition of vinylmagnesium chloride to organic acids [30,31]. Other products of Grignard reactions with vinylmagnesium chloride include 3,7-dimethyl-1,5,7-octatrien-3-ol [29957-43-5] [32], hexavinyldisiloxane [75144-60-4] and other organosilanes as well as organochlorosilanes [33, 34], 4-(3-methyl-2-butenyl)styrene [85964-33-6] (*p*-prenylstyrene) [35], a retinoic acid [302-79-4] precursor [36], fungicidal azole compounds [37] and fungicidal triazolyl carbinol ether precursors [38].

Vinyl chloride similarly undergoes Grignard reactions with other organomagnesium halide compounds. For example, cross-coupling with 1- or 2-phenylethylmagnesium bromide [41745-02-2 or 3277-89-2] yields 4- or 3-phenyl-1-butene [768-56-9 or 934-10-1], respectively [39, 40], while 4-(3-methyl-2-butenyl)styrene is obtained by coupling 4-(3-methyl-2-butenyl)phenylmagnesium chloride [106364-41-4] with vinyl chloride [41]. Other products of Grignard reactions with vinyl chloride include *m*- and *p*-*tert*-butoxystyrene [105612-79-1 and 95418-58-9] [42] and isomerically pure alkylethenylbenzenes [43].

Vinyllithium [917-57-7] can be formed directly from vinyl chloride by means of a lithium [7439-93-2] dispersion containing 2% by weight sodium [7440-23-5] at 0–10 °C [44]. This compound is a reactive intermediate for the formation of vinyl alcohols from aldehydes, vinyl ketones from organic acids, vinyl sulfides from disulfides and of monosubstituted alkenes from organic halides [45–47]. It can also be converted to vinylcopper [37616-22-1] or divinylcopper lithium [22903-99-7], which can then be used to introduce a vinyl group stereoselectively into a variety of α,β-unsaturated systems [48], or simply add a vinyl group to other α,β-unsaturated compounds to give γ,δ-unsaturated compounds [49]. Vinyllithium reagents can also be converted to secondary alcohols with trialkylboranes [50].

Vinyl chloride reacts with sulfides, thiols, alcohols and oximes in basic media. Reaction with hydrated sodium sulfide [1313-82-2] in a mixture of dimethyl sulfoxide [67-68-5] (DMSO) and potassium hydroxide [1310-58-3] (KOH) yields divinyl sulfide [627-51-0] and sulfur-containing heterocycles [51]. Various vinyl sulfides can be obtained by making vinyl chloride react with thiols in the presence of a base [52]. Vinyl ethers are produced in similar fashion, from the reaction of vinyl chloride with alcohols in the presence of a strong base [53, 54]. A variety of pyrroles and indoles have also been prepared by making vinyl chloride react with different ketoximes or oximes in a mixture of DMSO and KOH [55].

The carbon-chlorine bond can also be activated at high temperatures. Vinyl chloride reacts with alkanethiols and with dialkyl sulfides and disulfides at 400 °C to form vinyl sulfide compounds in low yields [56]. Aryl and thienyl vinyl sulfides can be prepared in a similar fashion via the reaction of aryl and thienyl thiols with vinyl chloride in a quartz tube at 380–440 °C [57]. Thiophene [110-02-1] and its substituted forms can be obtained by heterocyclization of vinyl chloride with hydrogen sulfide [7783-06-4] in the presence of an acetylenic reagent at 500–550 °C [58]. Reaction of vinyl chloride with germanium tetrachloride [10038-98-9] and trichlorosilane [10025-78-2] in a tubular reactor at 600–700 °C gives vinyltrichlorogermane [4109-83-5] in moderate yield [59]. Vinyltrichlorosilane [75-94-5] is obtained at yields of up to 77% reaction of vinyl chloride with trichlorosilane at 400–750 °C in a tubular reactor [60], while vinylsilanes can be made from mono-, di-, or trisilane [7803-62-5, 1590-87-0, or 7783-26-8] and vinyl chloride in a tubular reactor at 100–650 °C [61].

Finally, the reaction of vinyl chloride with hydrogen fluoride [7664-39-3] (HF) over a chromia [1308-38-9] (Cr_2O_3)-on-alumina [1344-28-1] (Al_2O_3) catalyst at 380 °C yields vinyl fluoride [75-02-5] [62].

2.4.3 Oxidation

The chlorine atom [22537-15-1]-initiated, gas-phase oxidation of vinyl chloride yields 74% formyl chloride [2565-30-2] and 25% CO at high oxygen [7782-44-7] (O_2) to Cl_2 ratios; it is unique among the chloro olefin oxidations, because CO is a major initial product and because the reaction proceeds by a non-chain path at high O_2/Cl_2 ratios [63]. The rate of the gas-phase reaction of chlorine atoms with vinyl chloride has been measured [63, 64].

The oxidation of vinyl chloride with oxygen in the gas phase proceeds by a non-radical path which, again, is unique among the chloro olefins. No C_2 carbonyl compounds are made; the major products are formyl chloride, CO, HCl and formic acid [64-18-6] [63]. Complete oxidation of vinyl chloride with oxygen in the gas phase can be achieved using a cobalt chromite [12016-69-2] catalyst [65]. At –15 to –20 °C, vinyl chloride reacts with oxygen, with ultraviolet (UV) light initiation, to give a peroxide, reported as $[OCH_2CHClO]_2$ [66]. On being heated to 35 °C, this peroxide decomposes to formaldehyde [50-00-0], CO and HCl.

Reaction with triplet oxygen $O(^3P)$ atoms [17778-80-2] gives high yields of CO and chloroacetaldehyde [107-20-0], with smaller amounts of acetyl chloride [75-36-5], HCl, methane [74-82-8] and polymer [63]. The rate of the gas-phase reaction of vinyl chloride with $O(^3P)$ atoms has also been reported [67, 68].

Oxidation of vinyl chloride with ozone [10028-15-6] in either the liquid or the gas phase gives formic acid and formyl chloride [63]. The ozone reaction with vinyl chloride can be used to remove it from gas streams in vinyl chloride production plants [69, 70].

Vinyl chloride can be completely oxidized to CO_2 and HCl, using potassium permanganate [7722-64-7] in an aqueous solution at pH 10. This reaction can be used for wastewater purification [71, 72], as can ozonolysis, peroxide oxidation and UV irradiation [73]. The aqueous-phase oxidation of vinyl chloride with chlorine yields chloroacetaldehyde [74, 75].

The combustion of vinyl chloride in air at 510–795 °C produces mainly CO_2 and HCl, along with CO. A trace of phosgene [75-44-5] also forms [76].

2.4.4 Addition

Chlorine adds to vinyl chloride to form 1,1,2-trichloroethane [79-00-5] [77–79]. Chlorination can proceed by either an ionic or a radical path. In the liquid phase and in the dark, 1,1,2-trichloroethane forms by an ionic path when a transition metal catalyst, such as ferric chloride [7705-08-0] ($FeCl_3$), is used. The same product forms in radical reactions at up to 250 °C [80]. Photochemically initiated chlorination also produces 1,1,2-trichloroethane by a radical path [81]. Above 250 °C, the chlorination of vinyl chloride gives unsaturated chloroethylenes produced by dehydrochlorination of 1,1,2-trichloroethane. The presence of small amounts of oxygen greatly accelerates the rate of the radical-chain chlorination reaction at temperatures above 250–300 °C [82, 83]. Other halogens can be added to vinyl chloride to form similar 1,2-addition products, but these reactions have not been thoroughly studied. Vinyl chloride can be halofluorinated in the sulfur tetrafluoride [7783-60-0]-HF-Cl_2 system [84].

Hydrogen halide addition to vinyl chloride in general yields the 1,1-adduct [85–87]. The reactions of HCl and hydrogen iodide [10034-85-2] (HI) with vinyl chloride proceed by an ionic mechanism, while the addition of hydrogen bromide [10035-10-6] (HBr) involves a chain reaction, in which a bromine atom [10097-32-2] is the chain carrier [87, 88]. In the absence of a transition metal catalyst and/or antioxidants, HBr will form the 1,2-adduct with vinyl chloride [85]. HF reacts with vinyl chloride in the presence of stannic chloride [7646-78-8] ($SnCl_4$) to form 1,1-difluoroethane [75-37-6] [89].

Various vinyl chloride adducts can be formed under acid-catalyzed Friedel-Crafts conditions. Vinyl chloride can add tertiary alkyl halides [90]. It can be condensed with ethyl chloride [75-00-3] to yield 1,1,3-trichlorobutane [13279-87-3] and l,l-dichloroethane [75-34-3] [91]. The reaction of 2-chloropropane [75-29-6] with vinyl chloride yields 1,1-dichloro-3-methylbutane [625-66-1] [91]. At 0–5 °C, vinyl chloride reacts with benzene [71-43-2], yielding a mixture of 1-chloroethylbenzene [672-65-1] and 1,1-diphenylethane [612-00-0] [92, 93]. Reaction with toluene [108-88-3] leads to 1,1-ditolylethane [29036-13-3], whereas reaction with anisole [100-66-3] (methoxybenzene) gives 1,1-di-*p*-anisylethane [10543-21-2] [94, 95]. Phenol [108-95-2] also reacts to give *p*-vinylphenol [2628-17-3] [96].

Vinyl chloride forms a photo [2+2] cycloadduct with 1-isoquinolone [491-30-5] and its *N*-methyl derivative [97].

Condensation of vinyl chloride with formaldehyde and HCl (Prins reaction) yields 3,3-dichloro-1-propanol [83682-72-8] and 2,3-dichloro-1-propanol [616-23-9] [98, 99]. The 1,1-addition of chloroform [67-66-3] as well as the addition of other polyhalogen compounds to vinyl chloride are catalyzed by transition metal complexes [100]. In the presence of iron pentacarbonyl [13463-40-6], both bromoform [75-25-2] ($CHBr_3$) and iodoform [75-47-8] (CHI_3) add to vinyl chloride [101-103]. Other useful products of addition reactions involving vinyl chloride include 2,2-difluoro-4-chloro-1,3-dioxolane [162970-83-4] [104], 2-chloro-1-propanol [78-89-7] [105], 2-chloropropionaldehyde [683-50-1] [106], 1-thiocyanato-1-chloro-2-arylethanes [107], 4-nitrophenyl-β,β-dichloroethyl ketone [31689-13-1] [108], β,β-dichloroethyl phenyl sulfone [3123-10-2] [109], β-chloroethylphosphonic acid [16672-87-0] [110] and various polychloropolyfluoroalkane sulfides [111].

Sodium β-chloroethanesulfonate [15484-44-3] can be obtained through reaction of vinyl chloride with sodium bisulfite [7631-90-5] [112]. Reaction with nitronium tetrafluoroborate [13826-86-3] yields 1-chloro-1-fluoro-2-nitroethane [461-70-1] [113].

Vinyl chloride reacts with ammonium chloride [12125-02-9] and oxygen in the vapor phase at 325 °C over a cupric chloride [7447-39-4] ($CuCl_2$) catalyst to make 1,1,2-trichloroethane and ammonia [7664-41-7] [114].

Vinyl chloride can be hydrogenated over a 0.5% platinum [7440-06-4] (Pt) on alumina catalyst to ethyl chloride and ethane [74-84-0] [115]. This reaction is zero order in olefin and first order in hydrogen [1333-74-0].

2.4.5 Photochemistry

Vinyl chloride is subject to photo-dissociation. Photoexcitation at 193 nm results in the elimination of HCl fragments and Cl atoms in an approximately 1.1 : 1 ratio [116]. Both vinylidene ($^3B_2$) [2143-69-3] and acetylene have been observed as photolysis products [117], as have H_2 fragments [118] and H atoms [12385-13-6] [119]. HCl and vinylidene appear to be formed via a concerted 1,1 elimination from excited vinyl chloride [117]. While a difference between HCl fragment rotational populations in vibrational states $\nu'' = 0$ and $\nu'' > 0$ may seem to confirm the existence of a dual mechanism for HCl elimination [120], further investigation using partially deuterated vinyl chloride shows that both (1,1 and 1,2) elimination pathways yield the same HCl fragment rotational energy distributions, with about 75% of the HCl fragments produced by three-center 1,1 elimination [119]. The dichotomy in rotational state distributions may be due to a hydrogen-bonded π complex between HCl ($\nu'' > 0$) and acetylene [119]. An adiabatic recoil mechanism appears likely for Cl atom elimination, since 89% of the Cl atoms were observed in the ($^2P_{3/2}$) spin-orbit state [120]. Bimodal energy distributions are seen for both spin-orbit states, with the Cl($^2P_{1/2}$) fragment having more kinetic energy than Cl($^2P_{3/2}$), suggesting competitive reaction on two potential energy surfaces [121]. As expected from the relative stabilities of the 1- and 2-chlorovinyl radicals [50663-45-1 and 57095-76-8], H atoms are preferentially produced by detachment from the β carbon [119]. Finally, a migration mechanism appears to play a significant role in H_2 elimination [118].

2.4.6 Pyrolysis

Vinyl chloride is more stable than saturated chloroalkanes to thermal pyrolysis, which is why nearly all vinyl chloride made commercially comes from thermal dehydrochlorination of EDC. When vinyl chloride is heated to 450 °C, only small amounts of acetylene form [122]. Little conversion of vinyl chloride occurs, even at 525–575 °C and the main products are chloroprene [126-99-8] and acetylene. The presence of HCl lowers the amount of chloroprene formed [122].

Decomposition of vinyl chloride begins at approximately 550 °C and increases with increase in temperature. Acetylene, HCl, chloroprene and vinylacetylene [689-97-4] are formed in about 35% total yield at 680 °C [123]. At higher temperatures, tar and soot formation becomes increasingly important. Vinyl chloride pyrolysis is a free-radical chain process, in which Cl atoms are important carriers. Abstraction of H atoms from vinyl chloride by Cl atoms leads to 2-chlorovinyl and 1-chlorovinyl radicals, respectively. The former lose Cl atoms to form acetylene, while the latter add to vinyl chloride, ultimately resulting in chloroprene. Addition of HCl increases the acetylene/chloroprene product ratio, probably due to reversal of the reaction leading to the 1-chlorovinyl radical through H atom transfer from HCl [123].

When dry and in contact with metals, vinyl chloride does not decompose below 450 °C. However, if water is present, vinyl chloride can corrode iron [7439-89-6], steel [12597-69-2] and aluminum [7429-90-5], because of the presence of trace amounts of HCl. This HCl may result from the hydrolysis of the peroxide formed between oxygen and vinyl chloride [66].

2.5 Manufacture

vinyl chloride monomer was first produced commercially in the 1930s from the reaction of HCl with acetylene derived from calcium carbide [75-20-7]. As demand for vinyl chloride increased, more economical feedstocks were sought. After ethylene became plentiful in the early 1950s, commercial processes were developed to produce vinyl chloride from ethylene and chlorine. These processes included direct chlorination of ethylene to form EDC, followed by pyrolysis of EDC to make vinyl chloride. However, because the EDC cracking process also produced HCl as a co-product, the industry did not expand immediately, except in conjunction with acetylene-based technology. The development of ethylene oxychlorination technology in the late 1950s encouraged new growth in the vinyl chloride industry. In this process, ethylene reacts with HCl and oxygen to form EDC. Combining the component processes of direct chlorination, EDC pyrolysis and oxychlorination provided the so-called balanced process for production of vinyl chloride from ethylene and chlorine with no net consumption or production of HCl.

Although 80% of China's vinyl chloride capacity is still based on acetylene feedstocks produced from calcium carbide, nearly all the rest of the world's production is conducted by the balanced process based on ethylene and chlorine [124]. The reactions for each of the component processes are shown in Equation 2.1–Equation 2.3 and the overall reaction is given by Equation 2.4:

Direct chlorination

$$CH_2 = CH_2 + Cl_2 \longrightarrow ClCH_2CH_2Cl \tag{2.1}$$

EDC pyrolysis

$$2\,ClCH_2CH_2Cl \longrightarrow 2\,CH_2 = CHCl + 2\,HCl \tag{2.2}$$

Oxychlorination

$$CH_2 = CH_2 + 2\,HCl + 1/2\,O_2 \longrightarrow ClCH_2CH_2Cl + H_2O \tag{2.3}$$

Overall reaction

$$2\,CH_2 = CH_2 + Cl_2 + 1/2\,O_2 \longrightarrow 2\,CH_2 = CHCl + H_2O \tag{2.4}$$

In a typical balanced plant producing vinyl chloride from EDC, all the HCl produced in EDC pyrolysis is used as the feed for oxychlorination. On this basis, EDC production is about evenly split between direct chlorination and oxychlorination and there is no net production or consumption of HCl. The three principal operating steps used in the balanced process for ethylene-based vinyl chloride production are shown in the block flow diagram in Figure 2.1 and a schematic of the overall process for a conventional plant is shown in Figure 2.2 [125]. A typical material balance for this process is given in Table 2.2 [126].

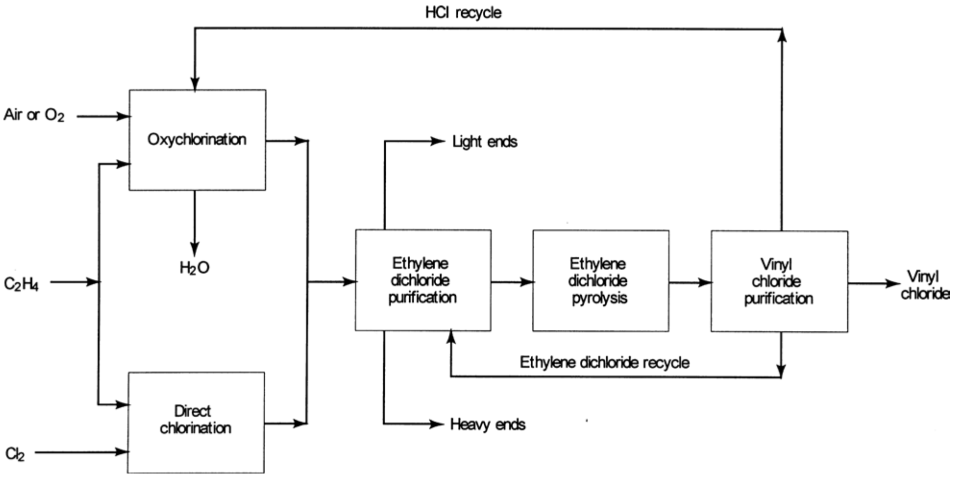

Figure 2.1 Principal steps in a balanced VCM process

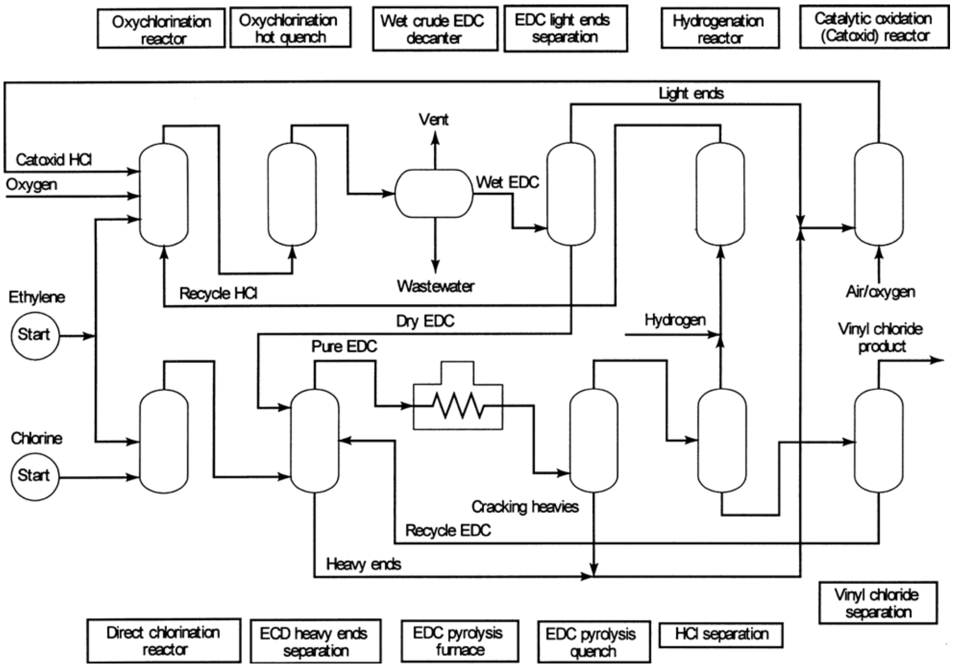

Figure 2.2 Typical balanced VCM process with oxygen-based oxychlorination

Table 2.2 Typical Material Balance for Vinyl Chloride Production by the Air-Based Balanced Ethylene Process[a]

Components (kg)	Raw Materials	Intermediates	By-products	Aqueous Streams	Vent Streams			Product
					Direct chlorination[b]	Oxychlorination	Distillation columns	
C_2H_4	0.4656				0.0025			
Cl_2	0.5871				0.0001		0.0001	
N_2	0.5782					0.5779	0.0003	
O_2	0.1537					0.0214		
CO_2	0.0003					0.0116		
CO						0.0032		
$ClCH_2$-CH_2Cl		1.6370[c]	0.0029		0.0016	0.0017	0.0045	
HCl		0.6036						
H_2O	0.0171		0.1438	0.1196		0.0413		
NaOH				0.0008				
NaCl				0.0014				
lights			0.0029		0.0003	0.0025		
heavies			0.0023					
CH_2=CHCl			0.0008		0.0001	0.0012	0.0024	1.0000
Total, kg/kg vinyl chloride	*1.8020*	*2.2406*	*0.1527*	*0.1218*	*0.0046*	*0.6608*	*0.0073*	*1.0000*

[a] Ref [126].

[b] Inerts present in chlorine feed are emitted in this vent stream.

[c] Represents EDC necessary for a stoichiometric balance, including that converted to by-products, but no recycled EDC.

2.5.1 Direct Chlorination of Ethylene

Direct chlorination of ethylene is generally conducted in liquid EDC in a bubble column reactor. Ethylene and chlorine dissolve in the liquid phase and combine in a homogeneous catalytic reaction to form EDC. Under typical process conditions, the reaction rate is controlled by mass transfer, with absorption of ethylene as the limiting factor [127, 128]. Ferric chloride is a highly selective and efficient catalyst for this reaction and is widely used commercially [129]. Ferric chloride and sodium chloride [7647-14-5] mixtures have also been utilized for the catalyst [130], as have tetrachloroferrate compounds, e. g., ammonium tetrachloroferrate [24411-12-9] (NH_4FeCl_4) [131]. The reaction most likely proceeds through an electrophilic addition mechanism, in which the catalyst first polarizes chlorine, as shown in Equation 2.5. The polarized chlorine molecule then acts as an electrophilic reagent to attack the double bond of ethylene, thereby facilitating chlorine addition (Equation 2.6):

$$FeCl_3 + Cl_2 \leftrightarrow FeCl_4^- - Cl^+ \tag{2.5}$$

$$FeCl_4^- - Cl^+ + CH_2 = CH_2 \longrightarrow FeCl_3 + ClCH_2CH_2C \tag{2.6}$$

The direct chlorination process may be run with a slight excess of either ethylene or chlorine, the choice between these depending on how effluent gases from the reactor are subsequently processed. For example, the non-condensables could easily be routed to an oxychlorination process in the case of excess ethylene [132]. Conversion of the limiting component is essentially 100% and selectivity to EDC is greater than 99% [129]. The main by-product is 1,1,2-trichloroethane, which most likely forms through radical reactions, beginning with homolytic dissociation of a small fraction of the chlorine. However, oxygen, which is frequently present as an impurity in chlorine and is sometimes intentionally added to the process, tends to increase selectivity to EDC by inhibition of free-radical reactions that produce 1,1,2-trichloroethane. Amides, e. g., *N,N*-dimethylformamide [68-12-2], also increase selectivity to EDC [133], as do aromatic hydrocarbons and phenols [134].

The direct chlorination reaction is very exothermic ($\Delta H = –180$ kJ/mol for Equation 2.1 [135],) and requires heat removal for temperature control. Early direct chlorination reactors were operated at moderate temperatures of 50–65 °C to take advantage of lower by-product formation and utilized conventional water cooling for heat removal. As energy costs became more significant, various schemes for recovering the heat of reaction were devised. A widely used method involves operating the reactor at the boiling point of EDC, allowing the pure product to vaporize and then either recovering heat from the condensing vapor or replacing one or more EDC fractionation column reboilers with the reactor itself [136–141]. An alternative method entails operation of the reactor at higher pressure to raise the boiling point of EDC; in this case, the reactor operates without boiling, but at higher temperatures (75–200 °C) to allow more efficient heat transfer to some other part of the process [142, 143]. For reactors equipped with liquid product removal, the EDC is usually treated to remove ferric chloride. The latter, which would lead to rapid fouling of the EDC cracking reactor, can be removed by washing with water or by adsorption on a solid [144, 145]. With dry feedstocks (< 10 ppm water) and good temperature control, carbon steel can be used in the direct chlorination reactor and auxiliary equipment [146].

2.5.2 Oxychlorination of Ethylene

When compared with direct chlorination, the oxychlorination process is characterized by higher capital investment, higher operating costs and slightly less pure EDC product. However, use of the oxychlorination process is dictated by the need to consume the HCl generated in EDC pyrolysis.

In oxychlorination, ethylene reacts with dry HCl and either air or pure oxygen to produce EDC and water. Various commercial oxychlorination processes differ to some extent, because they were developed independently by several different vinyl chloride producers [129, 135, 147], but, in each case, the reaction is carried out in the vapor phase in either a fixed or fluidized-bed reactor containing a modified Deacon catalyst. Unlike the Deacon process for chlorine production, oxychlorination of ethylene occurs readily at temperatures well below those required for HCl oxidation [148].

Oxychlorination catalysts typically contain cupric chloride as the primary active ingredient, impregnated on a porous support, e. g., alumina, silica-alumina [37287-16-4], diatomaceous earth [7631-86-9], and may also contain numerous additives [149–156]. Although the detailed catalytic mechanism is not known, $CuCl_2$ is widely recognized as the active chlorinating agent. The CuCl produced during the ethylene chlorination step is rapidly reconverted to $CuCl_2$ under reaction conditions and the presence of some CuCl is thought to be advantageous, because it readily complexes with ethylene, bringing it into contact with $CuCl_2$ long enough for chlorination to occur [129]. A very simple representation of this heterogeneous catalytic cycle is given in Equation 2.7–Equation 2.9, while the overall, net reaction was given in Equation 2.3.

$$\mathrm{CH_2 = CH_2 + 2\,CuCl_2 \longrightarrow 2\,CuCl + ClCH_2CH_2Cl} \tag{2.7}$$

$$\mathrm{1/2\ O_2 + 2\,CuCl \longrightarrow CuOCuCl_2} \tag{2.8}$$

$$\mathrm{2\,HCl + CuOCuCl_2 \longrightarrow 2\,CuCl_2 + H_2O} \tag{2.9}$$

Other mechanisms, involving initial formation of ethylene oxide [75-21-8] as the possible rate-limiting step [149], complexation of $CuCl_2$ with HCl [150] and Cl_2 as the chlorinating agent [151], have been suggested.

Since commercial oxychlorination processes differ with respect to catalysts (composition, morphology and physical properties), catalyst-contacting method (fluidized or fixed-bed reactor) and oxygen source (air or pure oxygen feed), the operating conditions, feed ratios, conversions and yields also vary with the particular combination of technology used as well as with the methods employed for secondary recovery of feedstock and product. For any particular combination of reactor type and oxygen source, however, good temperature control of this highly exothermic reaction ($\Delta H = -239$ kJ/mol for Equation 2.3 [135],) is essential for efficient production of EDC. Increasing reactor temperatures lead to increased by-product formation, mainly through increased oxidation of ethylene to carbon oxides and increased cracking of EDC. Cracking, i. e., dehydrochlorination of EDC, results in the formation of vinyl chloride and subsequent oxychlorination and cracking steps lead progressively to byproducts with higher levels of chlorine substitution. High temperatures (greater than 300 °C) can also cause catalyst deactivation through increased sublimation of $CuCl_2$.

Fluidized-bed reactors typically are vertical cylindrical vessels equipped with a support grid and feed-sparger system for adequate fluidization and feed distribution, internal cooling coils for heat removal and either external or internal cyclones to minimize catalyst carry-over [152]; superfine filtration may also be used to retain catalyst fines in the reactor [157]. Fluidization of the catalyst assures intimate contact between feed and product vapors, catalyst and heat-transfer surfaces and results in a uniform temperature within the reactor [129]. Reaction heat can be removed by the generation of steam within the cooling coils or by some other heat-transfer medium. An operating temperature of 220–245 °C and reactor gauge pressures of 150–500 kPa (22–73 psig) are typical for oxychlorination with a fluidized catalyst. Given these operating conditions, fluidized-bed reactors can be constructed with a carbon steel shell and with internal parts made from a corrosion-resistant alloy [146].

While fluidized bed oxychlorination reactors are generally well-behaved and operate predictably, under certain (usually upset) conditions, they are subject to a phenomenon known, appropriately, as catalyst stickiness. This can be described as catalyst particle agglomeration, which is characterized by declining fluidization quality and, in severe cases, can result in a slumped or collapsed bed. Oxychlorination catalyst stickiness is brought on by adverse operating conditions that promote the formation of dendritic growths of cupric chloride on the surface of individual catalyst particles, which leads to increasing interparticle interactions and agglomeration. All fluidized bed oxychlorination catalysts normally exhibit some level of catalyst particle agglomeration/deagglomeration dynamics and the severity of stickiness depends on catalyst characteristics as well as process operating conditions. Stickiness can be largely avoided by using catalyst formulations that exhibit excellent fluidization characteristics over a wide range of operating conditions [152, 153].

Fixed-bed reactors resemble multi-tube heat exchangers, with the catalyst packed in vertical tubes held in a tubesheet at top and bottom. Uniform packing of catalyst within the tubes is important to ensure uniform pressure drop, flow and residence time through each tube. Reaction heat can be removed by the generation of steam on the shell side of the reactor or by some other heat-transfer fluid. However, temperature control is more difficult in a fixed bed than in a fluidized-bed reactor, because localized hot spots tend to develop in the tubes. The tendency to develop hot spots can be minimized by packing the reactor tubes with active catalyst and inert diluent mixtures in proportions that vary along the length of the tubes, so that catalyst activity is low at the inlet, but steadily increases to a maximum at the outlet [129]. Another method for minimizing hot spots is to pack the tubes with catalysts having a progressively higher loading of $CuCl_2$ to provide an activity gradient along the length of the tubes. Multiple reactors are also used in fixed bed oxychlorination, primarily to control heat release by staging the air or oxygen feed. Each successive reactor may also contain catalyst with a progressively higher loading of $CuCl_2$. These methods of staging the air or oxygen feed and of grading the catalyst activity tend to flatten the temperature profile and allow improved temperature control. Compared with the fluidized bed process, fixed bed oxychlorination generally operates at higher temperatures (230–300 °C) and gauge pressures (150–1400 kPa (22–203 psig)). Given these operating conditions, a corrosion-resistant alloy is needed for the reactor tubes and the steel tubesheets and reactor heads need to be clad with nickel [7440-02-0], while the reactor shell itself can be constructed of carbon steel [146].

In the air-based oxychlorination process with either a fluidized or a fixed-bed reactor, ethylene and air are fed in slight excess of stoichiometric requirements to ensure high conversion of HCl and to minimize losses of excess ethylene that remains in the vent gas after product condensation. Under these conditions, typical feedstock conversions are 94–99% for ethylene and 98–99.5% for HCl with EDC selectivities of 94–97%. Downstream product recovery involves cooling the reactor exit gases by either direct quench or with a heat exchanger and condensation of the EDC and water, which are then separated by decantation (Figure 2.2). The remaining gases still contain 1–5% by volume EDC and so they are further processed in a secondary recovery system involving either solvent absorption or a refrigerated condenser. In air-based processes operating at high ethylene conversion, the dilute ethylene remaining in the vent is generally incinerated but, in those operating at lower conversion, various schemes are first used to recover unconverted ethylene, usually by direct chlorination to EDC [158–161].

The use of oxygen instead of air in the oxychlorination process with either a fixed or a fluidized-bed reactor permits operation at lower temperatures and results in improved operating efficiency and product yield [147, 162, 163]. Unlike the air-based process, ethylene is generally fed in somewhat larger excess over stoichiometric requirements. The reactor exit gas is cooled, purified from traces of unconverted HCl, separated from EDC and water by condensation, recompressed to the reactor inlet pressure, reheated and recycled to the oxychlorination reactor. Recycle of the effluent gas permits lower ethylene conversion per pass through the reactor, with minimal loss in overall ethylene yield. A small amount of reactor off-gas, typically 2–5% by volume, is continuously purged from the system to prevent accumulation of impurities, e. g., carbon oxides, nitrogen [7227-37-9], argon [7440-37-1] and unreacted hydrocarbons, which either form in the oxychlorination reactor or enter the process as impurities in the feed streams. An important advantage of oxygen-based oxychlorination technology over air-based operation is the drastic reduction in volume of the vent gas discharge. Since nitrogen is no longer present in the reactor feed streams, only a small amount of purge gas is vented. On a volume comparison, the reduced purge gas stream typically amounts to only 2–5% of the vent gas volume for air-based operation. Air-based processes release significant quantities of vent gases to the atmosphere, generally after treatment by thermal oxidation and scrubbing. Typically, for every kilogram of EDC produced by oxychlorination, 0.7–1.0 kg of vent gas is emitted from the air-based process (see Table 2.2). Therefore, for an air-based, balanced vinyl chloride plant with a rated capacity of 450,000 metric tons per year of vinyl chloride, the total vent gas volume released to the atmosphere would be 70–100 m^3/s (2,450–3,530 ft^3/s). However, the vent gas consists mainly of nitrogen, some unconverted oxygen and small amounts of carbon oxides. In line with the type of oxychlorination process involved, however, there are differing levels of undesirable impurities, ethylene and chlorinated hydrocarbons in the oxychlorination vent gas.

Chlorinated by-products of ethylene oxychlorination typically include: 1,1,2-trichloroethane; chloral [75-87-6] (trichloroacetaldehyde); trichloroethylene [79-01-6]; 1,1-dichloroethane; *cis*- and *trans*-1,2- dichloroethylenes [156-59-2 and 156-60-5], 1,1-dichloroethylene [75-35-4] (vinylidene chloride); 2-chloroethanol [107-07-3]; ethyl chloride; vinyl chloride; mono-, di-, tri- and tetrachloromethanes (methyl chloride [74-87-3], methylene chloride [75-09-2], chloroform and carbon tetrachloride [56-23-5]); and higher-boiling compounds. The production of these compounds should be minimized to lower raw material costs, lessen the task of EDC purification, prevent fouling in the pyrolysis reactor and minimize by-product handling and disposal. Of particular concern is chloral, because it polymerizes in the presence of strong acids. Chloral must be removed to prevent the formation of solids, which can foul and clog operating lines and controls [129].

Oxychlorination reactor feed purity can also contribute to by-product formation, although the problem usually is only with low levels of acetylene, which are normally present in HCl from the EDC cracking process. Because any acetylene fed to the oxychlorination reactor will be converted to highly chlorinated C_2 by-products, selective hydrogenation of this acetylene to ethylene and ethane is widely used as a preventive measure [129, 164–168].

2.6 Purification of Ethylene Dichloride for Pyrolysis

By-products contained in EDC from the three main processes must be largely removed prior to pyrolysis. These include by-products from direct chlorination and oxychlorination and in the recovered, unreacted EDC from the cracking process. EDC used for pyrolysis to vinyl chloride must be of high purity, typically greater than 99.5% by weight, because the cracking process is highly susceptible to inhibition and fouling by trace quantities of impurities [129, 169]. It must also be dry (less than 10 ppm water) to prevent excessive corrosion downstream. Inadvertent moisture pickup, however, is always possible. In such cases, the corrosion of steel equipment tends to be greatest in reboilers, the bottom section of distillation columns, bubble caps, plates, condensers, water separators, valves, pumps and fittings [146].

Direct chlorination usually produces EDC with a purity greater than 99.5% by weight, so that, except for removal of the $FeCl_3$, little further purification is necessary. Ferric chloride can be removed by adsorption on a solid, or the EDC can be distilled from the $FeCl_3$ in a boiling reactor, as noted earlier. Alternatively, the $FeCl_3$ can be removed by washing with water, usually in conjunction with EDC from the oxychlorination process.

EDC from the oxychlorination process is less pure than EDC from direct chlorination and requires purification by distillation. It is usually first washed with water and then with caustic solution to remove chloral and other water-extractable impurities [170]. Subsequently, water and low-boiling impurities are taken overhead in a first (light ends or heads) distillation column and, finally, pure, dry EDC is taken overhead in a second (heavy ends or product) column (see Figure 2.2).

Unreacted EDC recovered from the pyrolysis product stream contains a variety of cracking by-products. A number of these, e. g., trichloroethylene, chloroprene and benzene, are not easily removed by simple distillation and require additional treatment [129]. Chloroprene can build up in the light ends column, where it can polymerize and cause serious fouling. Benzene boils very close to EDC, as does trichloroethylene, which also forms an azeotrope with EDC. If allowed to accumulate in the recovered EDC, these by-products can inhibit the cracking reaction and increase coking rates. Since they are all unsaturated, they can be converted to higher-boiling compounds for easy separation by subjecting the recovered EDC stream to chlorination prior to distillation [170–176]. Chloroprene can also be removed by treatment with HCl and by hydrogenation [177–180].

2.7 Ethylene Dichloride Pyrolysis to Vinyl Chloride

Thermal pyrolysis or cracking of EDC to vinyl chloride and HCl occurs as a homogeneous, first-order, free-radical chain reaction. The accepted general mechanism involves the four steps shown in Equation 2.10–Equation 2.13 [181-183]:

Initiation

$$ClCH_2CH_2Cl \longrightarrow ClCH_2C\cdot H_2 + Cl\cdot \tag{2.10}$$

Propagation

$$Cl\cdot + ClCH_2CH_2Cl \longrightarrow ClCH_2C\cdot HCl + HCl \tag{2.11}$$

$$ClCH_2C\cdot HCl \longrightarrow CH_2 = CHCl + Cl\cdot \tag{2.12}$$

Termination

$$Cl\cdot + ClCH_2C\cdot H_2 \longrightarrow ClCH = CH_2 + HCl \tag{2.13}$$

The overall, net reaction was given in Equation 2.2. Reactions in Equation 2.11 and Equation 2.12 are the chain propagation steps, because each elementary step consumes one of the two chain carriers and simultaneously produces the other. The net effect of Equation 2.11 and Equation 2.12 is continuation of the chain by conversion of EDC to vinyl chloride. Thus, the two chain carriers are chlorine atoms and 1,2-dichloroethyl radicals [23273-86-1]. In general, anything that consumes a chain carrier is an EDC cracking inhibitor and anything that produces a chain carrier is a promoter. Therefore, any molecular or radical species that consumes a chain carrier without simultaneously producing either 1,2-dichloroethyl radicals or chlorine atoms is an EDC cracking inhibitor, e. g., propylene [115-07-1]. The allylic hydrogen atoms of propylene can be easily abstracted by one of the chain carriers, either 1,2-dichloroethyl radicals or chlorine atoms. The resulting allyl radical can then combine with a chlorine atom to form allyl chloride [107-05-1]. Since the same sequence can occur two more times, one molecule of propylene can consume up to six chain carriers. Reaction initiators or accelerators include carbon tetrachloride, chlorine, bromine [7726-95-6], iodine [7553-56-2] and oxygen [181], although exclusion of oxygen is claimed to result in considerably less fouling on the pyrolysis tube walls [184].

The endothermic cracking of EDC (ΔH = 71 kJ/mol EDC reacted for Equation 2.2 [135],) is relatively clean at atmospheric pressure and at temperatures of 425–550 °C. Commercial pyrolysis units, however, generally operate at gauge pressures of 1.4–3.0 MPa (200–435 psig) and at temperatures of 475–525 °C to provide for better heat transfer and reduced equipment size and to allow separation of HCl from vinyl chloride by fractional distillation at non-cryogenic temperatures. EDC conversion per pass through the pyrolysis reactor is normally maintained at 53–63%, with a residence time of 2–30 s. Cracking reaction selectivity to vinyl chloride of > 99% can be achieved at these conditions. Increasing cracking severity beyond this level gives progressively smaller increases in EDC conversion, with progressively lower selectivity to vinyl chloride, because some of the by-products generated during pyrolysis act as cracking inhibitors. Higher conversion also increases pyrolysis tube coking rates and causes problems with downstream product purification. To minimize coke formation, it is necessary to quench or cool the pyrolysis reactor effluent quickly. Substantial yield losses to heavy ends and tars can occur if cooling is done too slowly [178, 185–187]. Therefore, the hot effluent gases are normally quenched and partially condensed by direct contact with cold EDC in a quench tower. Alternatively, the pyrolysis effluent gases can first be cooled by heat exchange with cold liquid EDC furnace feed in a transfer line exchanger (TLE) prior to quenching in the quench tower. In this case, application of a TLE to preheat/vaporize incoming EDC furnace feed saves energy by decreasing the amount of fuel gas required to fire the cracking furnace and/or steam needed to vaporize the feed.

Although there are minor differences in the HCl/vinyl chloride recovery section from one vinyl chloride producer to another, in general, the quench column effluent is distilled to remove first HCl and then vinyl chloride (Figure 2.2). The vinyl chloride is usually further treated to produce specification product, recovered HCl is sent to the oxychlorination process and unconverted EDC is purified for removal of light and heavy ends before it is recycled to the cracking furnace. The light and heavy ends either are further processed, disposed of by thermal oxidation or other methods or are completely recycled by catalytic oxidation with heat recovery followed by chlorine recovery as EDC [125, 188].

By-products from EDC pyrolysis typically include acetylene, ethylene, methyl chloride, ethyl chloride, 1,3-butadiene, vinylacetylene, benzene, chloroprene, vinylidene chloride, 1,1-dichloroethane, chloroform, carbon tetrachloride, 1,1,1-trichloroethane [71-55-6] and other chlorinated hydrocarbons [129]. Most of these impurities remain with the unconverted EDC and are subsequently removed in EDC purification as light and heavy ends. The lightest compounds, ethylene and acetylene, are taken off with the HCl and end up in the oxychlorination reactor feed (as noted earlier, the acetylene can be selectively hydrogenated to ethylene). The compounds that have boiling points near that of vinyl chloride, i. e., methyl chloride and 1,3-butadiene, will co-distill with the vinyl chloride product. Chlorine or carbon tetrachloride addition to the pyrolysis reactor feed has been used to suppress methyl chloride formation [189], while 1,3-butadiene, which interferes with PVC polymerization, can be removed by treatment with chlorine or HCl, or by selective hydrogenation [190–192]. The practice of intentionally adding carbon tetrachloride (CTC) to the pyrolysis reactor has been phased out by many vinyl chloride producers in most regions around the world in an effort to comply with the provisions of the UNEP Montreal Greenhouse Gas Reduction Protocol Article 2D which directs the phaseout of CTC except for critical uses only where a substitute does not exist [193]. However, in the U.S., EPA's TSCA Final Risk Management Rule for CTC, published Dec. 18, 2024, provides an exemption for use as a processing aid in the manufacture of vinyl chloride under the condition that the facility has a Workplace Chemical Protection Program in place specifically for managing workplace CTC exposure [194].

2.8 By-Product Disposal

By-product disposal from vinyl chloride manufacturing plants is complicated by the need to process a variety of gaseous, organic liquid, aqueous and solid streams, while ensuring that no chlorinated organic compounds are inadvertently released. Each class of by-product streams poses its own treatment and disposal challenges.

Gaseous vent streams from the different unit operations may contain traces (or more) of HCl, CO, methane, ethylene, chlorine and vinyl chloride. These can sometimes be treated chemically, or a specific substance can be recovered by scrubbing, sorption, or other method when economically justified. For objectionable components in the vent streams, however, the common treatment method is either thermal oxidation or catalytic combustion, followed by removal of HCl from the effluent gas typically by liquid scrubbing and neutralization.

Organic liquid streams include the light and heavy ends from EDC purification (see Figure 2.2 and Table 2.2). The light ends typically consist of ethyl chloride, *cis*- and *trans*-1,2-dichloroethylene, chloroform and carbon tetrachloride. The heavy ends mainly comprise 1,1,2-trichloroethane, lesser amounts of tetrachloroethanes, chlorinated butanes and chlorinated aromatics and many other chlorinated compounds present in small concentrations. When there is economic justification, these streams can be fractionated to recover specific, useful components and the remainder subsequently incinerated and scrubbed to remove HCl. An alternative method involves combining all liquid by-product streams and passing them along with air or oxygen-enriched air into a fluidized bed, catalytic oxidation reactor [195-199]. The resulting combustion product stream, consisting essentially of HCl, CO_2, H_2O, O_2 and N_2, is fed directly into an oxychlorination reactor, where the HCl content is recovered as EDC. In addition, the heat of combustion is recovered as high-pressure steam in a manner similar to that in fluidized bed oxychlorination processes. In addition, there is no direct vent to the atmosphere and any unconverted chlorinated organic material is recovered in the crude EDC from the oxychlorination process and ultimately recycled back to the catalytic oxidation unit.

Process water streams from vinyl chloride manufacture are typically steam-stripped to remove volatile organics, neutralized and then treated in an activated sludge system to remove any non-volatile organics [200]. If fluidized bed oxychlorination is used, the process wastewater may also contain suspended catalyst fines and dissolved metals. The former can easily be removed by sedimentation and the latter by precipitation. To an extent depending on the specific catalyst formulation and outfall limitations, tertiary treatment may be needed to reduce dissolved metals to acceptable levels.

Solid by-products include sludge from wastewater treatment, spent catalyst and coke from the EDC pyrolysis process. These need to be disposed of in an environmentally sound manner (e. g., sludge digestion/thermal destruction, landfill).

2.9 Economic Aspects

Up-cycles in the pricing trends of vinyl chloride over the years are generally brought on by a tight chlorine supply, which raises chlorine prices. Contract prices for vinyl chloride monomer are largely determined by the prices of the two raw materials, ethylene and chlorine and by the price of the end-product, PVC. The interplay of these components, which fluctuate monthly, results in relatively stable monomer prices. In general, the price is high enough to allow monomer producers to make a profit, yet low enough so as not to place non-integrated PVC producers at a significant competitive disadvantage. The lower relative cost of PVC has allowed it to compete effectively with metals and other polymers in the construction and automobile industries.

The “shale revolution,” which began in earnest in 2007, brought about a newfound abundance in natural gas supply in the U.S. market. The convergence of hydraulic fracking and horizontal drilling allowed production of natural gas and gas liquids to grow from 18 trillion cubic feet (Tcf) in 2005 to nearly 38 Tcf in 2023 [201]. Abundant sources of “wet gas” yielded significant quantities of ethane, the basic raw material for ethylene. This abundance and relatively inexpensive cost of natural gas and ethane led to the growth in ethylene crackers in the U.S. and subsequently lowered manufacturing costs for ethylene dichloride and vinyl chloride to be among the lowest in the world. Hence, the U.S. has become one of the largest exporters of ethylene dichloride and PVC resins into the global markets.

Worldwide production capacity of major geographic regions for vinyl chloride is listed in Table 2.3 [202].

Table 2.3 Worldwide Vinyl Chloride Capacity as of December 2024[a]

Region	Capacity (Million Metric Tons/Yr)	% of Total
Americas (North and South)	11.2	18
Europe	9.3	15
Asia Pacific	38.0	61
Rest of World	3.7	6
Total	*62.2*	*100*

[a] Ref [202].

2.10 Health and Environmental Considerations

Because of the toxicity of vinyl chloride, the US EPA in 1976 enacted the following emission standards for vinyl chloride manufacture under the Vinyl Chloride National Emissions Standard for Hazardoous Air Pollutants (VC NESHAP), EPA Regulation 40 CFR 61.60 to 71, Subpart F [203]:

1. Emissions from all point sources except oxychlorination would be limited to 10 ppm vinyl chloride
2. Emissions from the oxychlorination process would be limited to 0.2 g vinyl chloride per 1 kg EDC produced by oxychlorination
3. No preventable relief-valve discharges would be allowed; (revised to any PRD release under the PVC MACT)

4. Fugitive emissions would be minimized by enclosing emission sources and routing all collected emissions to a closed vent system, upgrades to rotating equipment to minimize shaft leaks and implemention of leak detection and repair programs (LDAR)
5. Workplace ambient air monitoring for vinyl chloride; (fenceline monitoring added for HON RRT)
6. Emissions testing, reporting and recordkeeping requirements

Compliance testing began in 1978. Additional EPA and state actions were initiated in 1977 to reduce hydrocarbon emissions from vinyl chloride plants in non-attainment regions. These were aimed primarily at lowering the ethylene content of vent streams from air-based oxychlorination units [129]. Failure to comply with any U.S. EPA standard is punishable with civil penalites and daily fines as determined by EPA's Office of Enforcement and Compliance.

The VC NESHAP was one of EPA's first rules under the 1970 Clean Air Act and is unique since it regulates emissions to air and water and residual vinyl chloride in PVC resin and copolymer products, all in the same rule. In 1990, the Clean Air Act was amended and updated to include Maximum Achievable Control Teachology (MACT) and Residual Risk and Technology Reviews (RRT). MACT authorizes EPA to update all NESHAPs every 8 years which results in the emissions standards being set by the emissions levels achieved by the best performing facilities in the industry. RRTs go beyond MACT to further regulate to reduce risk from known hazardous air pollutants (HAP).

In 2012, U.S. EPA promulgated the PVC MACT and in 2024 promulgated the RRT for the Synthetic Organic Chemicals Manufacturing Industry Hazardous Organics NESHAP (HON). Dioxin and furan limits were established in each of these rulemakings. These rules set more strict requirements on emissions and plant operations than NESHAPs previously in effect. Facilities that are subject to the HON include EDC/VCM plants and standalone direct chlorination EDC plants, because they are considered continuous processes. Certain EDC/VCM plants also treat waste gas from PVC production facilities and these control devices are regulated by the PVC MACT in addition to the requirements of the HON. Significant changes are listed in Table 2.4.

Table 2.4 U.S. EPA Updates on Emissions Controls for EDC and VCM [204, 205]

Parameter	PVC MACT (Combined Units)	HON (EDC and EDC/VCM Units)
VCM to air from thermal oxidizers	1.1 ppmv	N.A.
Total organic HAP to air from thermal oxidizers	9.8 ppmv	98% reduction or to 20 ppm max.
HCl (as total chloride ion)	380 ppmv	N.A.

Table 2.4 U.S. EPA Updates on Emissions Controls for EDC and VCM [204, 205] *(continued)*

Parameter	PVC MACT (Combined Units)	HON (EDC and EDC/VCM Units)
Fenceline monitoring action levels for VCM and EDC	N.A.	VCM = 3 ug/m^3 annual avg. EDC = 4 ug/m^3 annual avg.
Dioxin (I-TEQ) from thermal oxidizers	0.051 ng/std. m^3 at 3% O_2	0.054 ng/std.m^3 at 3% O_2

These emissions limits are in effect continuously, including during startup, shutdown and malfunction events. As a consequence, U.S. producers must carefully plan and execute any startup or shutdown so that no violations occur.

In the U.S., unregulated releases of hazardous substances to the environment in quantities greater than prescribed limits under 40 CFR Ch. I, Subpart J, Section 302.4 are reportable to the National Response Center immediately and this information is publicly available.

Table 2.5 U.S. EPA National Reporting Center Release Quantities [206]

Substance	NRC Reportable Quantity (pounds)
Vinyl chloride	1
Ethylene dichoride	100
Chlorine	10
Hydrochloric acid	5,000

In 1995 the European vinyl industry, i. e. at that time all Western European VCM manufacturers, committed in their “ECVM Charters” to monitor and reduce emissions into the environment, including ethylene dichloride, vinyl chloride and dioxins, as well as having members’ performance regularly audited by an independent third party. After several such audits, updated charter versions with more stringent and wider criteria have been published since 1995 [207]. The latest version dates from 2019 and the limits committed to are listed in Table 2.5. Performance of the signatories in 2022–2023 was audited by DEKRA Assurance Services. The overall compliance rate was 99.2%.

In the European Union, the emissions of hazardous substances by industry are regulated by the Industrial Emissions Directive 2010/75/EU (IED). The IED imposes emission limits through so-called Best Available Techniques (BATs). Reference Documents (BREFs) are all publicly available [208]. EDC, VCM and dioxin emissions are covered by the BREF for the Production of Large Volume Organic Chemicals (LVOC BREF), initially adopted in 2003 and last updated in 2017 [209], as well as by the Common Waste

Gas Management and Treatment Systems in the Chemical Sector (WGC BREF) [210]. Regulated emission parameters are listed in Table 2.6.

Table 2.6 European Regulated Emissions and Voluntary Commitments for the Production of EDC and VCM, EU LVOC BREF [209]

Parameter	LVOC BREF Maximum emission level (Notes 1, 2, 3)	ECVM Charter, 2019
VCM & EDC to air from thermal oxidizers	1 mg/Nm^3	1 mg/Nm^3
EDC aqueous effluents		0.5 g/t purified EDC
HCl (as total chloride ion) to air from thermal oxidizers	10 mg/Nm^3	10 mg/Nm^3
Chlorine from thermal oxidizers	5 mg/Nm^3	N.A.
Dioxin (I-TEQ) from thermal oxidizers	0.1 ng/Nm^3	0.08 ng/Nm^3
Dioxin (I-TEQ) aqueous effluents	0.1 ng/l	0.3 ug/t EDC produced by oxychlorination

1. Maximum emission levels are averages with no single measurement higher than twice the value (except the dioxin value which is an annual average).
2. Concentrations are adjusted to: 213 K, 101.3 kPa, dry gas, 11% oxygen by volume.
3. Fugitive emissions are regulated by Leak Detection and Repair Requirements (LDARs)

Environmental concerns and government regulations have prompted a major increase in the amount of add-on technology used in U.S. and European Union vinyl chloride production plants. Primary and redundant thermal oxidation capabilities for all vinyl chloride point source and collected fugitive emissions, except oxychlorination, are now needed to ensure compliance. The incinerators are typically equipped with HCl scrubbing and neutralization or recovery units. Process sewers and sewage collection systems are closed. Larger and/or redundant strippers are used to remove trace organics from wastewater. Dual mechanical seals on pumps and agitators are required. Other common emissions control/reduction measures include vinyl chloride and EDC leak-detection systems and portable monitors, enclosed sampling and analytical systems and vapor recovery systems for vinyl chloride loading and unloading and equipment cleaning [129].

Since the early 1980s, there has been much debate between environmental activist organizations, industry and government about the impact of chlorine chemistry on the environment [211–213]. One aspect of this debate involves the incidental manufacture and release of trace amounts of hazardous compounds, such as polychlorinated dibenzodioxins, dibenzofurans and biphenyls (PCDDs, PCDFs and PCBs, respectively, but often to referred to collectively as dioxins) during the production of chlorinated compounds like ethylene dichloride, as well as during thermal oxidation of chlorinated by-products. Initial concerns were prompted by the acute animal toxicity of 2,3,7,8-tetrachlorodibenzodioxin [1746-01-6] (TCDD) and 2,3,7,8-tetrachlorodibenzofuran [51207-31-9] (TCDF). Other health effects include the potential estrogen mimic capabilities of dioxins [214]. In 1994, the EPA released a review draft of its reassessment of the impact of dioxins in the environment on human health, which prompted speculation as to the amount of dioxins that might be attributed to chlorine-based industrial processes [215].

The U.S. vinyl industry responded to this document by committing to a voluntary characterization of dioxin levels in its products and in emissions from its facilities to the environment. The results of this study to date support the vinyl industry’s position that it is a minor source of dioxins in the environment [213, 216]. In addition, studying U.S. EPA’s toxic release inventory ambient (air & water) emissions data in Figure 2.3 indicates that the production of vinyl chloride and PVC accounts for less than 7% of overall emissions from regulated sources for all of U.S. industry [217, 218].

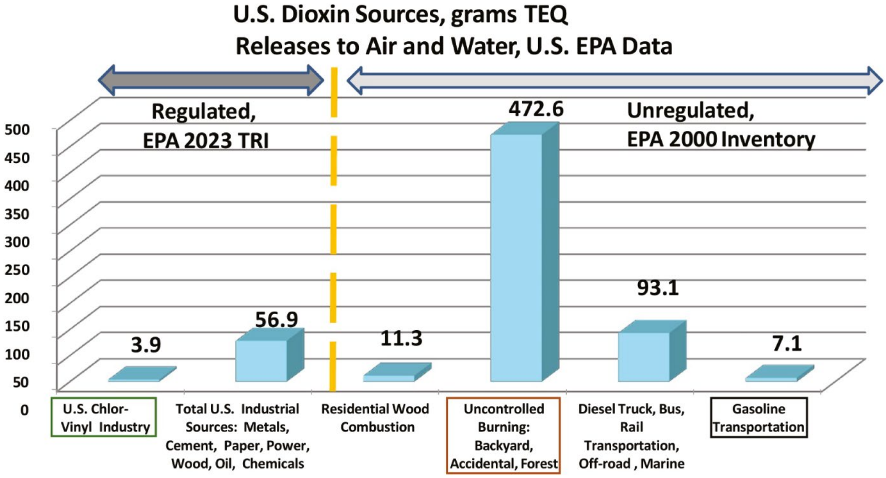

Figure 2.3 U.S. Dioxin Sources in Perspective

Based on the performance of the ECVM Charter signatories in 2022–2023, as audited by DEKRA Assurance Services, the contribution of the European vinyls industry to the total European Union dioxin emissions is also minor.

In addition, a process model analysis of a vinyl chloride purification distillation unit demonstrated that, owing to the roughly 500 °C boiling point difference between vinyl chloride and TCDD, any incidentally manufactured TCDD would be quantitatively removed from the vinyl chloride product [213]. This is confirmed by analyses of PVC samples: “Samples of virgin suspension PVC resin from eleven major manufacturer sites in Europe have been analysed for PCDDs and PCDFs using a dissolution method validated in two laboratories, down to levels of detection of less than 1 ppt (part per trillion). The results show there are no PCDDs and PCDFs in virgin PVC resin above the level of quantitation [219]. In addition, a global benchmark study released by the American Society of Mechanical Engineers found no relationship between the chlorine content of waste and dioxin emissions from combustion processes [220]. Reviews of this issue and other environmental considerations related to vinyl chloride production are available elsewhere [211, 213, 216].

Environmental concerns and government regulations have prompted a major increase in the amount of add-on technology used in U.S. and European Union vinyl chloride production plants. Primary and redundant thermal oxidation capabilities for all vinyl chloride point source and collected fugitive emissions are now needed to ensure compliance. The incinerators are typically equipped with HCl scrubbing and neutralization or recovery units. Process sewers and sewage collection systems are closed. Larger and/or redundant strippers are used to remove trace organics from wastewater. Dual mechanical seals on pumps and agitators are required. Other common emissions control/reduction measures include vinyl chloride and EDC leak-detection systems and portable monitors, enclosed sampling and analytical systems and vapor recovery systems for vinyl chloride loading and unloading and equipment cleaning [129].

2.11 Technology Trends

The ethylene-based, balanced vinyl chloride process, which accounts for nearly all capacity worldwide, has been practiced by a variety of vinyl chloride producers for more than 40 years. The technology is mature, so that the probability of major changes is low. New developments in production technology will likely be based on incremental improvements in raw material and energy efficiency, environmental impact, substance risk assessments, safety and process reliability.

Recent trends include widespread implementation of oxygen-based oxychlorination, development of two-stage and single-stage fixed-bed oxychlorination processes, further development of new catalyst formulations, a broader range of energy recovery applications, a continuing search for ways to improve conversion and minimize byproduct formation during EDC pyrolysis and chlorine source flexibility. In addition, the application of computer model-based process control and optimization is growing as a way to achieve even higher levels of feedstock and energy efficiency and plant process reliability.

Nearly all oxychlorination processes built in the 1990’s and 2000’s are oxygen-based and many existing, air-based units are being retrofitted for pure oxygen feed. This was prompted by the significant advantages of oxygen- over air-based operation, described earlier. The greatest benefit is drastic reduction (over 95%) in the volume of vent gas discharged by the process, making destruction of any environmentally objectionable compounds in this stream more manageable. Savings in ethylene and chlorine feedstock, thermal oxidation fuel consumption and air compression costs can more than offset the oxygen raw material cost [147, 162]. For existing, air-based plants, the decision whether to convert to oxygen depends on local emission standards, oxygen availability and cost, electrical energy cost and the viability of alternative, add-on processes for cleaning the vent stream, e. g., catalytic oxidation or sorption methods.

Fixed-bed reactor systems consisting of two-stage and single-stage processes have been developed to enable savings, relative to the traditional three-stage process, in capital cost and energy utilization while improving on catalyst and reactor productivity [221]. The two-stage process relies on a particular catalyst loading scheme of initial high activity, followed by low activity and finishing with high activity. The single-stage process is characterized by a catalyst gradient increasing with the direction of feed flow and operation with a large excess of ethylene relative to the hydrogen chloride feed. Fixed-bed catalysts containing highly dispersed copper metal diluent, to enhance heat transfer capability and minimize the formation of hot spots, have also been developed [222]. Fluidized-bed reactor systems with more effective cooling coil designs, for improved heat transfer and temperature control, have also been described [223].

Methods for preventing or reducing the formation of highly undesirable compounds, such as chlorobenzenes, polychlorinated biphenyls, polychlorinated dibenzodioxins and polychlorinated dibenzofurans, in the oxychlorination process have also been developed [224].

New catalyst developments have steadily progressed, especially for ethylene oxychlorination [152–156, 225], so that the remaining potential increases in reactor productivity and feedstock efficiency keep shrinking. Nevertheless, there is still room for further catalyst improvements. Direct chlorination, for example, would benefit from a catalyst, or catalyst plus a free-radical scavenger, that provides increased reaction selectivity to EDC and minimizes by-product formation at the higher temperatures required for boiling reactors [134, 226]. Catalytic dehydrochlorination of EDC, at lower temperatures than those used in thermal cracking, has also been patented [227]. A catalyst that is more resistant to poisoning by the metals content of by-product streams (e. g., iron from direct chlorination, sodium from caustic washing, tramp metals from corrosion) would improve the performance of catalytic hydrogenation and oxidation processes. Improved catalyst systems have been developed for the fluidized-bed catalytic oxidation/destruction of liquid chlorinated by-products, wherein the catalyst maintains high levels of catalytic activity for prolonged periods of operation [198]. In this catalytic “combustion” process (flameless, but complete oxidation), the heat of combustion is recovered as high pressure steam with cooling coils located within the fluidized-bed; and the reactor effluent, consisting essentially of HCl, CO_2,

H_2O, O_2 and N_2, is fed directly into an oxychlorination reactor where the HCl content is recovered as EDC.

In order to take advantage of the heat released by the reaction, most direct chlorination processes built within the past fifteen years use boiling reactors with energy recovery [228, 229]. Some alternative designs that also utilize the heat of reaction, but without boiling have likewise been developed [142, 143]. Lately, EDC pyrolysis furnaces are being built with TLEs, which use the thermal energy of the product stream to vaporize the EDC furnace feed or make steam and with air pre-heaters, which preheat the furnace air feed by exchange with the flue gas, to reduce the energy requirements for pyrolysis. Further design modifications to improve energy efficiency are likely, particularly if the cost of energy should increase significantly.

The search for new EDC cracking promoters and by-product inhibitors (e. g., refs [230–232, 237]) and for improved feed purification methods is expected to continue. Since current cracking technology limits EDC conversion to 55–65%, considerable energy and cost savings would be realized if conversion could be increased without concurrent loss of EDC to undesirable side reactions and coking [238]. Ability to continuously measure the cracking conversion from individual cracking furnaces would also help to optimize the cracking process [239]. Laser-induced EDC cracking has been studied as a way to promote thermal cracking [233–236]. At temperatures comparable to those used in commercial pyrolysis reactors, laser-induced cracking is claimed to increase conversion while decreasing by-product formation. However, commercial application at the current state of development appears unlikely. Periodic furnace decoking is still normally accomplished thermally by controlled air/steam oxidation. However, shot peen and catalytic decoking are two more recent alternative methods aimed at faster turnaround times and less thermal stress on the cracking furnaces.

Improved methods of separation and purification within the EDC cracking process and VCM purification train [240–245], as well as new or improved methods of heat transfer or energy usage, have also been developed [246, 247].

Tightness of the chlorine market, accompanied by rising chlorine prices, sparks interest in alternative sources of chlorine, i. e., HCl and EDC, where available. Some plants no longer operate in a strictly balanced mode, but instead operate with more than half of their EDC made from oxychlorination (due to importation of HCl and/or EDC as a chlorine source, thus bypassing direct chlorination). The ideal situation is one in which the plant can adapt to any feed combination, allowing operation at the optimum mix of feedstocks as determined by minimization of the sum of raw material and operating costs. Methods for recovering HCl from chlorine-based waste material, for use in the oxychlorination process, have also been developed [248].

Alternatives to oxychlorination have also been proposed as part of a balanced VCM plant. In the past, many vinyl chloride manufacturers used a balanced ethylene-acetylene process for a brief period prior to the commercialization of oxychlorination technology. Addition of HCl to acetylene was used instead of ethylene oxychlorination to consume the HCl made in EDC pyrolysis. Current relative costs of ethylene and acetylene now make this route economically unattractive, unless if acetylene can be produced from cheap coal. Another alternative is HCl oxidation to chlorine, which can subsequently be used in direct chlorination [249]. The Shell-Deacon [250] Kel-Chlor [251] and MT-Chlor [252] processes, as well as a process developed at the University of Southern California [253] are among the available commercial HCl oxidation technologies. Each has had very limited industrial application, perhaps because the equilibrium reaction is incomplete and the mixture of HCl, O_2, Cl_2 and water presents very challenging separation, purification and handling requirements. HCl oxidation does not compare favorably with oxychlorination, since it also requires twice the direct chlorination capacity for a balanced vinyl chloride plant. Consequently, it is doubtful that it will ever displace oxychlorination in the production of vinyl chloride by the balanced ethylene process.

If the production of vinyl chloride could be reduced to a single step, such as direct chlorine substitution for hydrogen in ethylene or oxychlorination/cracking of ethylene to vinyl chloride, a major improvement over the traditional balanced process would be realized. The literature is filled with a variety of catalysts and processes for single-step manufacture of vinyl chloride [254–259]. None has been commercialized, because of the high temperatures, corrosive environments and insufficient reaction selectivities encountered so far. Substitution of lower-cost ethane or methane for ethylene in the manufacture of vinyl chloride has also been investigated. The Lummus-Transcat process [260], for instance, proposes a molten oxychlorination catalyst at 450–500 °C to make ethane react with chlorine to produce vinyl chloride directly. However, ethane conversion and selectivity to vinyl chloride are too low (30% and less than 40%, respectively) for this process to become competitive. Numerous other catalysts and processes have been patented as well, but none has been commercialized, owing to problems with temperature, corrosion and/or product selectivity [261–267]. However, the potential payback, renders this a very active area of research.

Another technology first developed by European Vinyl Corporation, now part of Ineos Vinyl and a competing technolgy developed by Dow is the “ethane-to-VCM” process technology [268, 269]. Note that Dow’s patent (World Patent 01738274, May 2001) has expired. This process is promoted as a “single-step, ethane-to-VCM process” technology breakthrough wherein ethane, chlorine, hydrogen chloride, oxygen and recycled chlorine-containing by-products are fed to a high-temperature catalytic oxychlorination reactor to convert ethane to VCM. The actual process, however, contains three reactor systems: the high-temperature oxychlorination reactor; a hydrogenation reactor for hydrogenating unsaturated chlorinated by-products prior to recycling back to the oxychlorination reactor; and a direct chlorination reactor for converting by-product ethylene to EDC prior to recycling back to the oxychlorination reactor [269]. Furthermore, an in-depth evaluation of this high-temperature oxychlorination system and reaction mechanisms involved shows that, with this feed mixture, there are four different types of reaction chemistry occurring all at the same time and under the same reaction conditions in the oxychlorination reactor: chlorination, dehydrochlorination, oxidative dehydrogenation and oxychlorination. Therefore, reaction conditions must be selected to achieve the best compromise for all four types of reactions to occur in a favorable way. Although one of the initial claims was that the ethane-to-VCM technology could reduce VCM production costs by up to 30%, there is not a commercial operation using this technology as of this writing.

Even more recently, Dow has patented a process for vinyl chloride manufacture from a mixture of ethane and ethylene [270] and from methane [271]; and BASF has patented a method for the production of EDC from ethane [272].

2.12 Specifications

Polymerization grade vinyl chloride should not contain more than the amounts of impurities listed in Table 2.7 [273].

Table 2.7 Typical Impurity Levels in Monomer Grade Vinyl Chloride[a]

Impurity	Maximum level (ppm)
Acetylene	0.5–2.0
Acidity, as HCl, by wt	0.1–1.0
Acetaldehyde	0.4–1.0
Alkalinity, as NaOH, by wt	0.25
1,3-Butadiene	8–12
Ethyl chloride	35
EDC	10
Iron, as Fe, by wt	0.15–0.4
Methyl chloride	60–75
Vinylacetylene	10
Water	100
Non-volatiles	25–50
Total C4 unsaturates	40
Oxygen in vapor space after loading	200–1,000
Vinyl chloride, % by weight	99.96–99.98[b]

[a] Ref [273].

[b] Minimum vinyl chloride content

2.13 Health and Safety Factors

U.S. Occupational Safety and Health Administration (OSHA) promulgated its Vinyl Chloride Standard on Jan. 2, 1975, as 29 CFR 1910.1017 [274]. OSHA's Vinyl Chloride Standard has not changed much since 1975 except for communications requirements. The Vinyl Chloride Standard imposes a permissible exposure limit (PEL) to vinyl chloride vapors of no more than 1.0 ppm averaged over any eight hour continuous period. Short-term exposure is limited to 5.0 ppm averaged over any 15-min period. Contact with liquid vinyl chloride is prohibited. Monitoring is required at all facilities where vinyl chloride is produced, or PVC is processed. OSHA regulations also define an action level of 0.5 ppm, 8-h time-weighted average. Employers must demonstrate that monitoring results show exposure below the action level of 0.5 ppm on subsequent readings taken not less than five working days apart in order to discontinue monitoring. Where concentrations cannot be lowered below the 1.0 ppm PEL, the employer must establish a regulated area with controlled access, a respirator program conforming to Section 1910.1017(g) of the OSHA standard [274] and a written plan to reduce vinyl chloride levels. OSHA regulations require facilities that handle vinyl chloride to develop a medical surveillance program with annual physical examinations and blood serum analyses for all employees exposed at levels above the action level.

While the current OSHA limitations for EDC exposure are not as restrictive as those for vinyl chloride, OSHA included EDC in Table Z-2 beginning in January 1976. A new regulation similarly limiting EDC exposure was subsequently issued in 1997, but remanded [275]. Currently OSHA's Table Z-2 of Section 1910.1000 Subpart Z regulates EDC exposure at 50 ppm for an 8-hour time-weighted average and at 100 ppm for a 5-minute exposure during any 3-hour period which has been unchanged since 1976 [276]. The NIOSH recommended exposure limit (REL) for EDC is 1 ppm twa over a 10-hour period and 2 ppm short-term-exposure limit (STEL) over a 15-minute period [277]. The U.S. EPA is currently completing its risk evaluation for EDC and will likely influence any updates to permissible exposure limits.

In the European Union, the Binding Occupational Exposure Limits (BOELs) are respectively 1 ppm for VCM and 2 ppm for EDC, 8-h time-weighted average. The European vinyls industry committed to continuous monitoring of VCM and EDC in the workplace and to operating a medical surveillance programme for workers exposed to VCM.

Contact with liquid vinyl chloride can cause frostbite. Chronic exposure to vinyl chloride at concentrations of 100 ppm or more is reported to have produced Raynaud's syndrome osteolysis of the distal bones of the fingers and a fibrosing dermatitis. However, these effects are probably related to continuous intimate contact with the skin. Chronic exposure is also reported to have produced a rare cancer of the liver (angiosarcoma) in a small number of workers after continued exposure for many years to large amounts of vinyl chloride gas [278]. Consequently, the vinyl industry worked in conjunction with government regulatory agencies to develop the much more stringent hygiene standards that currently exist. Toxicology data on vinyl chloride, e. g., TC_{Lo} (human), TC_{Lo} (rat), LD_{50} (rat) and threshold limit values, are reported in [279]. OSHA's Hazard Communication requirements in Section 1910.1017 (l) require that in classifying the hazards of vinyl chloride at least the following hazards are to be addressed: Cancer; central nervous system effects; liver effects; blood effects; and flammability. vinyl chloride monomer is listed as a Carcinogen category 1 by the European Chemical Agency. The American Conference of Governmental Industrial Hygienists (ACGIH) calls it a confirmed human carcinogen, while the National Toxicology Program (NTP) and the International Agency for Research on Cancer (IARC) both regard it as a known (Group 1) human carcinogen [280].

Vinyl chloride also poses a significant fire and explosion hazard. It has a wide flammability range, from 3.6–33.0% by volume in air [281]. Large fires of the compound are very difficult to extinguish, while vapors represent a severe explosion hazard. Vapors are more than twice as dense as air and tend to collect in low-lying areas, increasing the risk of fire. Workers entering these low-lying areas risk suffocation, which can occur at levels above 18,000 ppm. The mild, sweet odor of vinyl chloride becomes detectable at around 3,000 ppm [282].

Vinyl chloride is generally transported via pipeline, in railroad tank cars or tanker ships [283]. Containers of vinyl chloride must be labeled “Vinyl chloride”, “Extremely flammable gas under pressure” and “May cause cancer” [284]. Because hazardous peroxides can form on standing in air, especially in the presence of iron impurities, vinyl chloride should be handled and transported under an inert atmosphere. The presence of peroxide from vinyl chloride and air can initiate polymerization of stored vinyl chloride; however, stabilizer can be added to prevent polymerization [285]. Inhibitors such as hydroquinone [123-31-9] are often added, particularly when shipping long distances in warmer climates.

Vinyl chloride is listed as “ethene, chloro-” on the Toxic Substances Control Act (TSCA) inventory and on the Canadian Domestic Substances List (DSL). It is listed as “chloroethylene” on the European Inventory of Existing Commercial Chemical Substances (EINECS), having the identification number 2008 310 [286].

U.S. EPA has established enforceable National Primary Drinking Water Regulations which include maximum contaminant levels (MCLs) for organic contaminants that apply to community and non-transient, non-community drinking water systems. Vinyl chloride has an MCL of 0.002 mg/L and EDC has an MCL of 0.005 mg/L [287]. In accordance with the Clean Water Act, EPA performs a six-year review of drinking water quality across the U.S. in which local drinking water providers are required to submit their records for testing and monitoring for listed drinking-water contaminants, such as VCM and EDC. In each of the previous four reviews, vinyl chloride was mostly non-detectable. In the EPA report for the most recent six-year period 2012-2019, VCM was detected sporadically and inconsistently above the MCL in 58 measurements out of a total of over 482,000 measurements (which is a rate of 0.012% or approximately 1.2 in 10,000 tests) provided by local water districts subject to the review. Because of these low numbers, EPA has not considered changing the MCL for VCM.

In 1988, EPA delegated authority for testing and compliance with NSF/ANSI 61: Drinking Water System Components – Health Effects to NSF International. In this test, NSF performs destructive testing of PVC pipe, fittings and other drinking water contact products to determine compliance with EPA's MCL of 0.002 mg/L standard. Drinking-water components containing PVC materials must be below 1/10th the EPA MCL which is equivalent to 0.0002 mg/L (0.2 parts per billion) vinyl chloride in order to be sold in the U.S. market [288]. NSF International audits PVC materials from manufacturers regularly and performs unannounced plant visits annually at those listed component manufacturers in order to assure continual compliance with the standard. Non-compliant materials are restricted from use for drinking water applications.

For a complete listing of vinyl chloride U.S. regulations, visit the National Institute of Health PubChem website [289]. Other environmental, health and safety concerns are discussed in Chapter 19.

2.14 Uses

Vinyl chloride has gained worldwide importance, because of its industrial use as the precursor to PVC. It is also used in a limited variety of copolymers. The inherent flame-retardant properties, wide range of plasticized compounds and low cost of polymers from vinyl chloride have made it a major industrial chemical, especially in the construction sector. About 99% of current vinyl chloride production worldwide ends up in polymer or copolymer applications [290]. The major nonpolymeric uses of vinyl chloride are in the manufacture of chlorinated solvents (primarily 1,1,1-trichloroethane), vinylidene chloride for copolymer use and ethylene diamine for conversion to resins [290].

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3

Polymerization

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This chapter on PVC polymerization is organized in three segments: First, in Section 3.1, a thorough review on organic peroxide initiators which are necessary for carrying out the polymerization of vinyl chloride monomer into PVC resin; second, in Section 3.2 to Section 3.6, a review of the suspension polymerization process, equipment, and resins; and third, in Section 3.7 to Section 3.15, an explanation of the various dispersion, emulsion and microsuspension processes and resins. Figure 3.1 depicts the essence of the chemical transformation of vinyl chloride into the polymer and highlights the importance of the free radical initiator.

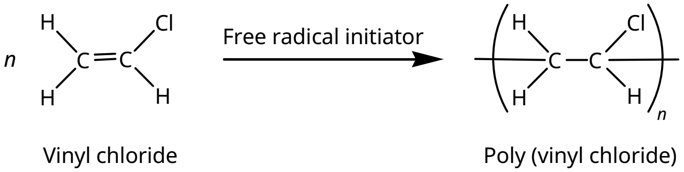

Figure 3.1 Depiction of vinyl chloride monomer and PVC repeat units, where typically n ranges from 625 to 2700 Da

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[1] Donald E. Witenhafer: Section 3.2–Section 3.6 , reviewed and edited by Allen Bodron; David J. Poledna: Section 3.7–Section 3.15 , reviewed and edited by Alan Matyger; Peter Frenkel: Section 3.1

3.1 Organic Peroxide Initiators for PVC Polymerization

3.1.1 Polymerization with the Use of Organic Peroxides

In the polymer industry, organic peroxides are used for the following processes [1]:

- Polymerization of monomers (PVC, LDPE, PS, PMMA)
- Polymer crosslinking to increase molecular weight (LDPE) and viscosity modification of polymers (PP)
- Curing of unsaturated polyesters (vinyl esters and acrylics)

The free-radical polymerization with the use of organic peroxides (and also persulfates, azo-compounds and hydrogen peroxide) is a polyaddition reaction of monomers without formation of by-products.

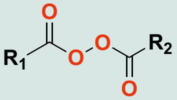
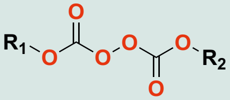
Organic peroxides are used as initiators in the manufacture of PVC from vinyl chloride monomer (VCM) by both the suspension and mass (bulk) polymerization processes.

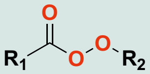
The simplified chemical structures of organic peroxides can be described as R_1OOR_2, where R_1 and R_2 are organic functional groups that can be the same or different and one of them can be hydrogen. Chemical reactivity of organic peroxides is characterized by the presence of an oxygen-oxygen (-O-O-) bond in their molecular structures. Under heating and/or activation (see Section 3.1.7), the oxygen-oxygen bond cleaves homolytically to form $R_1O\cdot$ and $R_2O\cdot$ free radicals that are highly reactive and can be used to initiate polymerization reactions.

Most common, commercially available organic peroxide types used for initiating polymerization of VCM into PVC are (Table 3.1) [1–2]:

- Peroxyesters
- Peroxydicarbonates
- Diacyl peroxides

Table 3.1 Commercially Available Organic Peroxide Types Used in PVC Polymerization

Organic Peroxide Types	Structural Formulas
Diacyl peroxides	
Peroxydicarbonates	

Organic Peroxide Types	Structural Formulas
Peroxyesters	

R_1 and R_2 are the same or different alkyl groups

3.1.2 Safety Considerations

Oxygen-oxygen bonds of organic peroxides contribute to the following characteristics of organic peroxides [3]:

- Sensitivity to heat and formation of free radicals on decomposition
- Release of heat on decomposition
- Sensitivity to contamination (relevant to selected peroxide types)
- Formation of gases and mists on decomposition (relevant to selected peroxide types)
- Limited oxidizing properties

The three primary types of hazards associated with handling of organic peroxides to be concerned with are heat sensitivity, flammability and contamination. Organic peroxides decompose at varying rates depending on the temperature. The decomposition rate increases with temperature. Therefore, the most critical aspect of storing organic peroxides is temperature control. Proper control of storage temperatures enables safe handling and use of organic peroxides. Inability to effectively remove heat and pressure buildup caused by the inadequate control of storage temperatures may result in self-heating that may accelerate and give rise to a runaway or self-accelerating decomposition reaction of the peroxides [3–5].

All peroxides burn vigorously, often with acceleration (especially in their undiluted forms) [8], and once ignited are not easy to extinguish. Flammability of organic peroxides is also affected by the nature of the decomposition by-products. Flammable vapors may cause an explosion [2, 4, 6].

Organic peroxides, including those used for polymerizing VCM into PVC, decompose rapidly at room temperature and are stored and shipped under refrigerated conditions. Due to higher surface-to-volume ratios that enable more effective heat dissipation, smaller packages are safer and commonly used for packaging these initiators [2–4].

3.1.3 Main Characteristics for Selecting Organic Peroxides

Self-Accelerating Decomposition Temperature (SADT)

The rate of decomposition of organic peroxides increases rapidly as their temperature increases. If the heat generated is not dissipated or absorbed, the decomposition may then auto-accelerate and become uncontrollable. SADT is the lowest temperature at which an organic peroxide formulation in a commercial package as used in transport undergoes self-accelerating decomposition (temperature increases ≥6°C over 7 days) [3]. Maximum storage and transportation temperatures are derived from the SADT according to the recommendations made by the United Nations Committee of Experts on the Trasport of Dangerous Goods [7].

Active Oxygen (AO) Content

While the peroxygroup is the main structural element and commercial value of organic peroxides, the functional groups at either side of the -O-O- bond also affect the relative thermal stability and reactivity of the peroxides. Each peroxygroup is considered to contain one “active” oxygen atom. The concept of active oxygen content is used for comparing the relative concentration of peroxygroups in organic peroxide formulations, and that concentration is proportional to the energy content of the specific peroxide grade. In general, energy content increases with active oxygen content. Thus, the higher the molecular weight of the organic peroxide of the same type, the lower the energy content and the hazards of that peroxide [10].

The theoretical concentration of active oxygen can be calculated as follows:

$$\mathrm{A[O]_{theoretical}}\ (\%) = 16\frac{\mathrm{p}}{\mathrm{m}} \times 100$$

where

p is the number of peroxide groups in the molecule and

m is the molecular mass of the pure peroxide

Half-Life

The efficiency of an organic peroxide as an initiator in polymerization processes depends on its ability to dissociate under prescribed reaction conditions into free radicals [6]. The decomposition rate of polymerization initiators can be expressed through their half-life. The half-life is the time required for one half of the molecules present in a defined amount of an initiator to decompose at a certain temperature. The thermal decomposition of organic peroxides generally is a first-order reaction. The half-life is determined either titrimetrically by measuring loss in the active oxygen content over time in a dilute 0.1–0.2 M solution or by differential scanning calorimetry at a given temperature. Typically, the half-lives of peroxides are measured at 0.1, 1.0 and/or 10 hours [1, 8–9]. Inert solvents used for the preparation of dilute organic peroxide solutions commonly utilized for the half-life measurements are benzene, monochlorobenzene or hydrocarbons.

Peroxides of shorter half-life offer faster rates of generating free radicals upon thermal decomposition and, therefore, can react at lower temperatures. Thus, the half-life serves as a guide for selecting the initiators intended for specific polymerization processes and process conditions. Proper selection of a peroxide initiator based on its thermal stability/decomposition rate/half-life temperature enables the polymerization to be conducted at the required process temperature and process cycle time; it may also affect physical properties of the formed polymers [1, 5].

Information about half-life temperatures and SADTs of the same organic peroxides may vary from manufacturer to manufacturer, due to variations in the test methods and tested package sizes.

3.1.4 Commercially Available Organic Peroxide Initiators for PVC Polymerization

Key characteristics of typical organic peroxides used in PVC polymerization are summarized in Table 3.2 [7]. In general, the commercially available initiators for PVC polymerization are liquid, since it is easier to handle and transfer liquids as well as control their temperature. The liquid peroxides used in PVC manufacturing are either technically pure or concentrated solutions in a solvent- or water-based emulsion. The maximum storage temperatures of liquid organic peroxides suitable for use in PVC polymerization generally range from below –5 °C down to –25 °C. Entry 7c in Table 3.2 illustrates properties of an emulsified organic peroxide grade [10].

Table 3.2 Selected Organic Peroxide Initiators for PVC [7]

	Chemical Name	Organic Peroxide Type	CAS Number	Molecular Weight	Assay, %	Calc. A.O. Content, %	Physical Form	10-hour Half-Life Temp., °C	SADT*, °C	Max. Storage Temp., °C
1	Diisobutyryl peroxide	Diacyl peroxide	3437-84-1	174.2	30	2.76	Solution	23	0	–20
2	Cumyl peroxyneodecanoate	Peroxyester	26748-47-0	306.4	75	3.92	Solution	38	10	–20
3	1,1,3,3-Tetramethylbutyl peroxyneodecanoate	Peroxyester	51240-95-0	300.5	70	3.73	Solution	40	15	–15

Table 3.2 Selected Organic Peroxide Initiators for PVC [7] *(continued)*

	Chemical Name	Organic Peroxide Type	CAS Number	Molecular Weight	Assay, %	Calc. A.O. Content, %	Physical Form	10-hour Half-Life Temp., °C	SADT*, °C	Max. Storage Temp., °C
4	Cumyl peroxyneoheptanoate	Peroxyester	130097-36-8	264.4	75	4.54	Solution	42	10	–20
5	tert-Amyl peroxyneodecanoate	Peroxyester	68299-16-1	258.4	75	4.64	Solution	43	20	–15
6a	Di-(sec-butyl) peroxydicarbonate	Peroxydicarbonate	19910-65-7	234.2	98	6.69	Liquid	47	0	–20
6b					60	4.10	Solution		0	–20
7a	Di-(2-ethylhexyl) peroxydicarbonate	Peroxydicarbonate	16111-62-9	346.5	98	4.53	Liquid	47	0	–20
7b					75	3.46	Solution		5	–15
7c					60	2.77	Emulsion		0	–20
8a	tert-Butyl peroxyneodecanoate	Peroxyester	26748-41-4	244.4	95	6.22	Liquid	46	15	–10
8b					75	4.91	Solution		20	–10
9	tert-Amyl peroxypivalate	Peroxyester	29240-17-3	188.3	75	6.37	Solution	55		
10	tert-Butyl peroxypivalate	Peroxyester	927-07-1	174.2	75	6.89	Solution	57		

* SADT for all entries except 7c is for HDPE can; SADT for entry 7c is for IBC.

3.1.5 Emulsified Organic Peroxide Initiators for PVC Polymerization

Many liquid organic peroxides used in PVC polymerization processes are available in the water-based emulsion form of improved safety characteristics to the extent that the emulsified initiators can be supplied (shipped and stored) in bulk. The water-based organic peroxide emulsions were introduced by AkzoNobel Specialty Chemicals in Europe and then in the U.S. in 2018 [11].

Non-frozen water-based peroxide emulsions usually contain an anti-freezing agent and nonionic surfactants that make it possible to maintain the emulsions in a liquid form, even under refrigerated storage conditions.

Initially, methanol, the most water-soluble alcohol of lowest molecular weight, was used as an anti-freezing agent of highest efficiency for lowering the freezing point of the emulsified peroxide formulations. Later on, due to its hazards and toxicity profile, methanol was replaced by less efficient but less hazardous anti-freezing agents to reduce risk of exposure to the emulsified peroxides during their handling and use. Options for replacing methanol in non-freezing water-based emulsions of organic peroxides are limited to small molecules, containing up to four carbon atoms, such as ethanol, iso-propyl alcohol, ethylene glycol, diethylene glycol and 1,2-propanediol. Compared with methanol, its replacements are added at higher concentrations to ensure that the emulsions remain in a liquid form and maintain their relatively low viscosity during storage [10].

The presence of water in the emulsions of organic peroxides lowers their burning rate compared with the corresponding technically pure grades and their solutions in organic solvents. It is interesting to note that the effect of water on reducing the burning rate of the emulsions is more pronounced than the presence of flammable alcohols that would be expected to increase it. This translates into improved safety of handling of the peroxide emulsions (including the methanol-free emulsions), lowers their hazard classification, requires less demanding storage conditions and enables their packaging and transportation in bulk [10]. For example, a 60% aqueous emulsion of di(2-ethylhexyl) peroxydicarbonate can be shipped and stored in IBC containers, while the technically pure peroxydicarbonate and its solutions in hydrocarbon solvents can only be shipped in plastic bottles under comparable temperatures (Table 3.2, entries 7a, 7b and 7c) [7].

For further process and safety optimization of the polymerization reactions, emulsion-based peroxides are also delivered into reactors using the Continuous Initiator Dosing (CiD) technology introduced by AkzoNobel Specialty Chemicals. CiD helps to control heat generation during polymerization in a PVC reactor by precisely dosing the peroxides into the process. It optimizes the use of cooling capacity and reduces batch process time by 20 to 40%. CiD is also capable of stopping the reaction quickly in an emergency [11–12].

3.1.6 Selecting Organic Peroxide Initiators for PVC Polymerization

The ideal optimum process of PVC polymerization targets a “square-shaped” reaction temperature profile with a relatively low peak temperature. This type of temperature profile requires minimum heat removal capacity for maintaining the consistent reaction rate at the process temperature and results in maximum output (shorter reaction time) under safe process conditions. It is achieved through the use of optimum combinations of organic peroxide initiators in the process. The combinations may contain two or three organic peroxides. One of the peroxides in the combination is of shorter half-life, decomposes most rapidly at the beginning of the reaction at lowest possible reaction temperature and is called a front-end initiator; the other one with the longer half-life decomposes more slowly and is called a back-end initiator. Initiator combinations containing both front- and back-end peroxides result in more even distribution of the heat load during the process and enable the reaction to be completed more efficiently in a shorter reaction time.

Optimization of the weight ratio between the front- and back-end initiators allows the focus to be placed either on productivity to achieve higher output at higher process temperatures or on minimizing the overall process-heat load and improve process safety at lower process temperatures. For running the reaction at lower process temperatures, the amount of front-end initiator is greatly increased and the amount of back-end initiator is reduced. This ratio and the type of peroxides used in the process also affect the content of residual monomer in the produced polymer, reactor fouling and resin whiteness. Specifically, it is known that peroxydicarbonates form higher-energy free radicals that cause PVC resins to discolor to a greater extent than is the case for peroxyesters [13]. Therefore, it is desirable to lower the peroxydicarbonate-to-peroxyester ratio in order to maximize the amount of the low-energy free radicals and enable obtaining whiter resins [14].

3.1.7 Modifying the Reactivity of Organic Peroxide Initiators

Several effective stabilizers have been identified that improve the storage stability of symmetrically-structured (relative to the -O-O- bond) dialkylperoxydicarbonates, a group of thermally unstable organic peroxides that are normally stored at –20 °C and undergo auto-accelerated self-induced decomposition above 10 °C; they are widely used as initiators in manufacturing PVC resins. The stabilizers increased the onset decomposition temperatures (dT) (as measured by differential thermal analysis that correlates directly with SADT [15]) of the peroxydicarbonates and by this means enhanced the safety margins of handling, storing and shipping of these initiators. Additionally, this approach enabled the safe replacement of non-stabilized concentrated solutions of the peroxydicarbonates by their stabilized technically pure grades (that are normally less stable in storage than the solutions), thus increasing the storage capabilities of manufacturing sites.

Tert-butyl hydroperoxide (TBHP) [16] and 2,4-pentanedione (PD) [17–18] were found to be the most cost-effective stabilizers of the commercially available dialkyl peroxydicarbonates, such as di-(2-ethylhexyl) peroxydicarbonate (Table 3.3).

Table 3.3 Onset Temperature of Decomposition and SADTs for Di-(2-ethylhexyl) peroxydicarbonate* [17]

Stabilizer	Weight, %	Onset Decomposition Temperature (dT), °C	SADT (for a 1-Gallon Bottle), °C
None	0.0	36.3	1 ± 5
TBHP**	0.5	48.6	15
PD	1.0	50.1	20

* A 75% solution in odorless mineral spirits
** A 70% aqueous solution

The stabilizers added at concentrations as low as 0.5–1.0% were effective at increasing the SADT of this peroxydicarbonate grade by about 15–20 °C. In addition to TBHP and PD, additives that were also reported to stabilize dialkyl peroxydicarbonates include beta-ketoesters [17], phosphomolybdic acid [19] and oximes [20]. The stabilized peroxydicarboates were patented in the 1990s. Commercialization of the stabilized peroxydicarbonate technology made these products the industry standard in the 2000s, improving their safety of handling, due to the delay in the onset decomposition temperatures. The stabilizers had no detrimental effect on the kinetics of polymerization and color stability of the PVC resins produced with the use of the stabilized peroxydicarbonate initiators.

All stabilizers exhibited proton-donating characteristics: for example, TBHP on account of its similarity to alcohols and PD, due to its keto-enol tautomerism. It was demonstrated that the intermolecular mechanism of stabilization of the peroxydicarbonates is attributed to the formation of hydrogen bonds between the -O-O- groups and the stabilizers.

Following the development of the stabilized peroxydicarbonate technology, it was postulated that certain proton-donating additives would have the opposite effect and destabilize asymmetrically structured (relative to the -OO- bonds) peroxide molecules, such as peroxyesters, and accelerate their rate of thermal decomposition. Phosphotungstic acid (PTA), which is safe to handle and readily soluble in many organic solvents, was found to function as an effective promoter of organic peroxides' decomposition, reducing their onset decomposition temperatures and, in turn, leading to a reduced reaction peak temperature [21–22]. As can be seen in Table 3.4, PTA reduced the onset decomposition temperature of peroxyesters used for PVC polymerization by 5–12 °C. PTA was found to accelerate the polymerization of styrene with the use of peroxyesters, ketone peroxides and hydroperoxides without discoloring the resin. It was also shown that the PTA-accelerated thermal decomposition of these peroxides is homolytic (as opposed to heterolytic) in many cases and led to the formation of free radicals required for the polymerization processes. Conceptually, increasing the reactivity of storage-stable peroxides (that normally do not require temperature-controlled storage conditions) should enable the replacement of more reactive, storage-unstable peroxides (that normally require low temperature storage conditions and relevant to the use in PVC polymerization) with more storage-stable initiators, thereby improving process control and the safety of the polymerization processes. This approach is conventionally used for curing unsaturated polyester resins with the use of cobalt naphthenate [23] and is not known to be routinely applied in the PVC polymerization process.

Table 3.4 Acceleration of Thermal Decomposition of Peroxyesters through the Use of PTA [21]

Peroxyester	Weight of PTA solution*, %	Onset Decomposition Temperature (dT), °C
tert-Butyl peroxyneodecanoate**	None	61.5
tert-Butyl Peroxyneodecanoate**	0.5	56.2
tert-Butyl Peroxyneoheptanoate***	None	62.6
tert-Butyl Peroxyneoheptanoate***	0.5	50.6

* A 50% solution in ethanol

** A 75% solution in odorless mineral spirits

*** A 75% solution in odorless mineral spirits

3.2 PVC Polymerization: Basic Considerations

Vinyl chloride monomer (VCM) is a clear, colorless liquid that boils at –13 °C. VCM is soluble in water to less than 3% and water is soluble in VCM to less than 1%. VCM is known to polymerize via free radical methods and in the liquid state only. There are gas phase” polymerizations reported in the literature. A check ther, however, will reveal that these polymerizations are actually taking place in some condensed state, such as having the VCM absorbed in some polymer, such as PVC itself. VCM has a liquid density at normal polymerization temperatures between 0.85 and 0.90 g/cm^3. The polymer has a density of 1.4 g/cm^3, meaning that large volume shrinkage takes place during polymerization. Oxygen must be excluded from the polymerization. Oxygen is an effective but undesirable shortstop for the polymerization reaction. In fact, an alternating copolymer of oxygen (peroxide) and VCM (called poly(vinyl chloride peroxide)) will form until the oxygen is consumed and the reaction starts. A dead time of several minutes before polymerization begins usually is an indication that there is oxygen contamination. It is usually easy to exclude oxygen, because VCM is stored under pressure, thus ensuring that no air can leak into the system. It is possible, however, to experience air contamination if care is not taken to purge residual air from transfer lines and tanks. Poly(vinyl chloride peroxide) is a dangerous solid chemical. It can detonate upon impact. Workers who enter monomer storage vessels in particular must be informed about the hazards of poly(vinyl chloride peroxide).Nitrogen is quite soluble in VCM, so it is generally not good practice to use nitrogen pressure to move VCM about the plant or the laboratory. Pumps should be used in the plant and a slight heating of the storage tank will generate enough pressure to transfer VCM around the laboratory. Gravity transfers can also be done. Nitrogen does not interfere with the polymerization; however, because nitrogen is soluble in the monomer and not soluble in the polymer, significant pressure can build up in the polymerization vessel during polymerizations containing nitrogen, especially if there is not a lot of headspace in the vessel.

Unlike most polymers that are soluble in their own liquid monomer, PVC is highly insoluble in VCM. This insolubility is what makes it possible to manufacture PVC as porous granules. The PVC precipitates as tiny particles during polymerization and the agglomeration of these particles produces a porous internal structure in the resin particles. VCM, however, is fairly soluble in PVC to about 30% concentration, and thus the particles of PVC precipitated during polymerization are plasticized or highly softened by the monomer. The rate of polymerization of the VCM inside the swollen particle is substantially faster than the rate of polymerization in the liquid phase, presumably because the gel prevents mobility of the growing polymer radicals and therefore results in a substantial lowering of the radical termination rate in the gel. Thus, PVC polymerizations are auto-accelerating. As conversion increases, more of the fast-polymerizing (swollen) phase is present. In fact, if a long half-life free radical initiator is used (relative to the polymerization time), the rate of reaction up to about 60% conversion is proportional to the conversion. The straight-line plot of polymerization rate versus conversion does not pass through the origin however, because the rate of polymerization is not zero at zero conversion. More details about this will be presented later.

As the PVC radical chain grows, the polymerization proceeds primarily by a head-to-tail placement of the monomer units. Theus, the molecular structure primarily consists of -CH_2- units alternating with -CHCl- units. The carbon containing the hydrogen and the chlorine is capable of tactic placement. With respect to the plane of the carbon atoms, the chlorine can add such that it is on the same side as the previous chlorine, which is called an isotactic placement, or it can add on the opposite side to that of the previous chlorine, called a syndiotactic placement. PVC shows a slight tendency to add via a syndiotactic placement, but this is a function of the polymerization temperature. Lower polymerization temperatures favor higher syndiotactic placement, as might be anticipated from energy considerations. In the normal commercial polymerization temperature range, NMR studies [24] have indicated that PVC is approx. 52% syndiotactic at a 70 °C polymerization temperature and approx. 56% syndiotactic at 50 °C. The fact that PVC is slightly syndiotactic is a very fortunate occurrence for the physical properties of flexible PVC. Because of the slight preference for random syndiotactic placement, there is the probability of finding a number of syndiotactic placements blocked together along the chain. It is this association of syndiotactic sequences with each other in a crystal-like order that gives PVC its physical crosslinks to produce its elastomeric nature when plasticized. Without these thermally reversible crosslinks, flexible PVC would not be the thermoplastic elastomer that it is. Because the crystals are small and imperfect, they have a very wide melting temperature range, from 120 °C to 260 °C [25]. An idea of what a more crystalline PVC would be like can be gained by considering the nature of urea canal complex PVC [26]. This UCC PVC is prepared by absorbing VCM into the canals located in the crystal structure of urea. The VCM is then polymerized using radiation to generate radicals. The resulting UCC PVC is just about 100% syndiotactic, because of the way the monomer is placed in the urea canals. UCC PVC shows high crystalline X-ray diffraction and has a unique infrared spectrum. It is also totally un-processable and not soluble in any solvent, even at very high temperatures. If we did not have just the right level of syndiotacticity, we might have properties more like UCC PVC. The right amount of crystallinity is needed for producing the meltable crosslinks of a thermoplastic elastomer when plasticized; too much crystallinity will make the polymer less processable. Crystallinity in commercial PVC is at a low level, based on probabilities of syndiotactic runs. The following calculation shows that long runs are of very low probability. If a mer is picked at random, it does not matter which side of the carbon atom's plane the chlorine atom is located on: the probability is 100%. The probability of a syndiotactic di-mer then computes to 100% × 56% = 56% at a 50 °C polymerization temperature. The probability of a syndiotactic tri-mer is then 100% × 56% × 56% = 31% (see Table 3.5). The probabilities of tetra-mers and penta-mers is even lower, as shown in this table. Not all of these syndiotactic structures will be able to find each other and pack into a crystallite. Thus, PVC generally has less than 10% crystallinity. Summers describes and shows the typical dimensions of a common crystallite structure of PVC, as illustrated in Figure 3.2 [27].

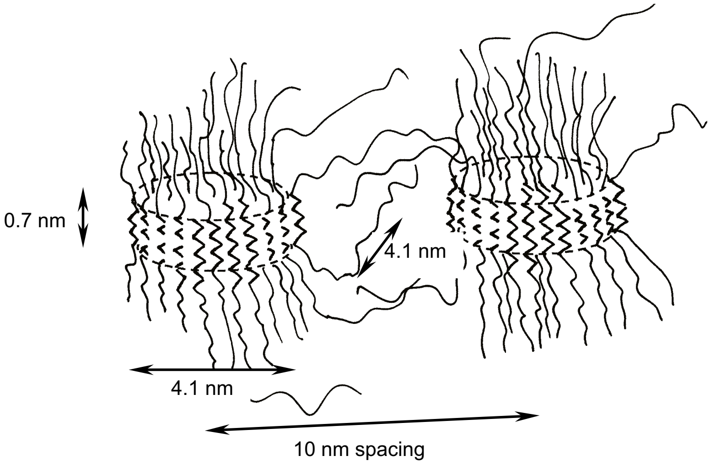


Figure 3.2 The average of a wide range of PVC crystal sizes, three syndiotactic mers in the chain direction, 10 nm spacing

Table 3.5 The Probability of Syndiotactic Runs in PVC Polymerized at 50 °C

Run length	1-mer	2-mers	3-mers	4-mers	5-mers	6-mers	7-mers	8-mers
Unit probability	100% ×	56% ×	56% ×	56% ×	56% ×	56% ×	56% ×	56%
Overall probability	100%	56%	31%	18%	10%	5.5%	3.1%	1.7%

Because of the limited amount of syndiotactic runs, Summers proposes that this common PVC crystallite has only three syndiotactic mer units in the chain direction. However, the actual crystal structures must be quite varied in terms of both size and perfection in order to explain the wide temperature range of the melting points. The small amount of PVC crystallinity plays a role in rigid PVC also. As noted earlier, the crystals melt over a temperature range up to approx. 260 °C. Because of its heat stability, the temperature at which PVC is processed is not high enough to completely melt it. Thus, the PVC "melt" is not truly a melt at all, but contains some crystalline pseudo-crosslinks that hold bundles of molecules together as primary particle flow units. It is the partial melting and re-crystallization of PVC that is responsible for the phenomenon of fusion or gelation in PVC [28]. It must be processed hot enough, or it will not develop full strength.

The molecular weight of PVC is controlled by altering the polymerization temperature. Chain transfer to monomer controls the molecular weight. In fact, a typical radical will chain transfer about ten times before it ultimately terminates. The higher the polymerization temperature, the lower is the molecular weight. As the temperature increases, the rate of chain transfer to monomer increases faster than the chain propagation rate. Normal commercial polymerization temperatures range from 50 °C to approx. 70 °C. Below 50 °C, the reactions become too slow and the molecular weight is generally too high for most processing needs. Above 70 °C, the reactor pressure becomes too high. If extremely fast polymerizations are run, however, e. g., with a total polymerization time shorter than approx. three hours, the concentration of free radicals can become high enough for the termination reaction to start playing a role in molecular weight control. Normal polymerization times run from 3 to 6 hours, but reactor design can greatly affect this. It should be pointed out that, for PVC, the term chain transfer to monomer takes on a special meaning. Mechanistically, it is not a classical chain transfer mechanism. The chain transfer process in PVC actually starts with a monomer unit adding in a head-to-head fashion. The resulting growing radical structure does not continue to polymerize fast enough and generally, before another monomer can add, the structure rearranges, inserts a double bond at the end of the chain, thereby forming another new radical, which in turn initiates a new growing chain. The process looks like chain transfer to monomer, but this mechanism is somewhat unique to PVC.

Another very important feature of PVC polymerization results from its high heat of polymerization of 106 kJ/mol (730 BTU/lb) [29]. This high heat of polymerization must be removed from the polymerization reactors. To a large extent, our ability to make PVC productively is directly related to the ability of the reactor to remove the heat. If a reaction goes out of control, the pressure rises rapidly with temperature, as does the rate of polymerization, thus increasing the problem. Since PVC does not depolymerize, as will be described in more detail later, it has no ceiling temperature. All these conditions lead to a very dangerous condition, with the possibility of an emergency discharge of monomer into the atmosphere if temperature control is lost. Heat removal is the major design consideration for PVC polymerizers. The high heat of polymerization does have a positive side: measurement of the total heat removed from the polymerizer provides an accurate method for following the conversion during the course of a polymerization.

3.3 Suspension Process Overview

In suspension polymerization, high levels of agitation and dispersant chemicals are employed to suspend drops of VCM in water during the polymerization. This produces a slurry of PVC grains in water that have an average grain size of generally between 120 and 160 µm (microns).

Figure 3.3 shows a photomicrograph of suspension PVC resin. The process consists of four basic steps: polymerization, stripping to remove residual VCM, centrifugation to remove water, and drying. Each will be described in the following.

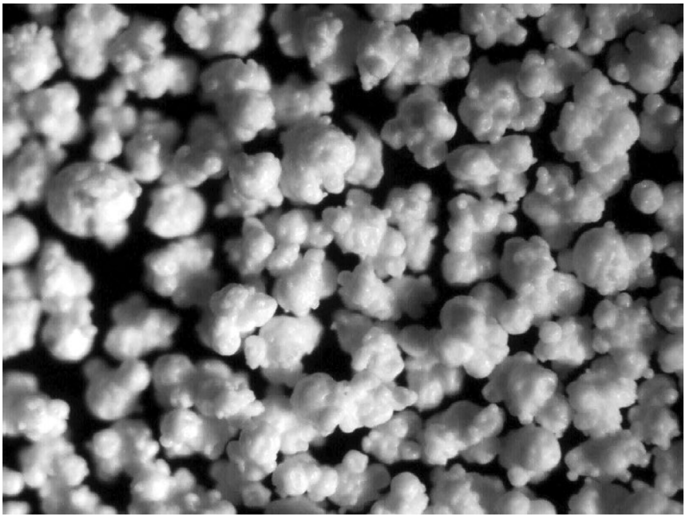


Figure 3.3 Low-magnification photomicrograph of suspension PVC resin

3.3.1 Polymerization

Polymerization is commonly done in agitated, cylindrical vessels, ranging in size from20 m^3 (5,200 gal) to 200 m^3 (52,000 gal). Figure 3.4 shows some typical suspension polymerization reactors.

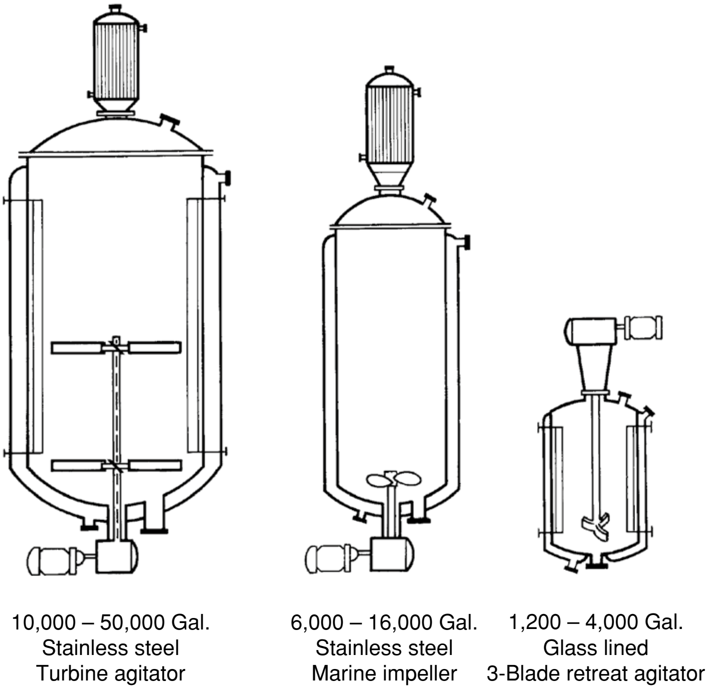


Figure 3.4 Three typical PVC suspension polymerizers

(from Langsom, M., Chapter 3, Encyclopedia of PVC, 2nd ed., Vol. I, Nass, L. and Heiberger, C. (Ed.) (1985) Marcel Dekker, with permission)

The one on the left is typical of modern large reactors, has two turbine blades, cooling baffles and is equipped with a reflux condenser for cooling. The reactor in the middle has a bottom-entering marine blade, a reflux condenser and no baffles. The small reactor on the right has a top-entering Pfaudler-type agitator with baffles and no reflux condenser. Modern plants have a high level of automation, computer control and safety-instrumented systems. The polymerization process gives off a small amount of HCl and the pH can go as low as 3.1. Thus, modern polymerizer inner surfaces are typically made of low-carbon stainless steel. Stainless steel cladding on carbon steel walls is most common. As described earlier, heat removal is very important for productivity. Stainless steel has a relatively poor thermal conductivity relative to steel, so more heat can be removed through the wall with this cladding material. Stainless steel is also substantially more expensive than steel. As the reactors become larger, the walls need to be thicker in order to safely contain the vapor pressure of the vinyl chloride, which is normally between approx. 0.9 and 1.2 MPa gauge (130 and 175 psig), depending on the polymerization temperature. This creates a design trade-off. Large reactors are inherently more economical, because the capital cost is less than proportional to the reactor size, but heat transfer is more difficult, because the surface-to-volume ratio decreases and the wall thickness increases as polymerizers get larger. Reflux condenser cooling and/or special cooling baffles are needed for heat removal in very large reactors, with only a portion of the heat being removed through the wall.

The operation of polymerizers varies substantially from manufacturer to manufacturer. The discovery that VCM is a carcinogen and the imposition of stricter environmental emission rules and regulations have led manufacturers to normally operate their reactors in what has come to be known as closed-poly mode. When operating this way, the reactors are not opened between batches, thereby preventing the possible discharge of VCM into the atmosphere. Those locations that do not operate in closed-poly mode must go to fairly extreme lengths between batches to make sure that all VCM gas is removed from the polymerizer before opening. Closed-poly operation is possible because of clean-reactor coating technology. There are many clean-reactor coatings that can be applied to the inner surface of reactor vessels between batches that allow this closed-poly operation. They can be found described in U.S. patent class 526//62. More than one thousand batches can be run before the reactor of a carefully designed reactor and coating system is opened. The closed-poly mode of operation will now be described, as it is the most common.

After a polymerization batch has reached the desired conversion, a shortstop that terminates the polymerization can be optionally added to the reactor. This is particularly useful if the batch is to sit in the reactor or downstream for any period of time before the unreacted monomer is recovered. Most shortstops are phenolic radical traps that react with any free radicals that are generated, although this is not always the case.

The reactor contents are removed, either by allowing the vapor pressure of the vinyl chloride to push it out or, as in most cases, by pumps for particularly fast removal to a downstream vessel.

After the batch is transferred or dropped, spray nozzles mounted inside the reactor rinse it with water to remove all particles of PVC. This is a critical step, because any particles going through a second polymerization cycle will become non-porous particles, which are difficult to break down later, result in “fish-eye” defects in finished products and also do not allow the residual VCM to be recovered from those particles. PVC suspension polymerizations deposit a thin coating of polymer on the walls, which continues to get thicker as more polymerizations are run. In order to prevent this, the polymerizer is coated, just after the reactor is rinsed, with a buildup-preventing coating as described previously. The coating is usually applied with a steam-driven spray through nozzles mounted in the reactor [30]. The reactor may optionally be rinsed after the steam-driven application of the coating. The amount of coating chemical used, particularly in large reactors, is very small, usually in the part per million range based on the amount of polymer ultimately produced during the batch; this makes the rinse step optional.

When the reactor has been coated, the reaction ingredients are added. The charging procedure is quite different from manufacturer to manufacturer, but this can be a very important step, because the ultimate development of the resin particle structure is determined by what happens at the very earliest conversion. Suffice to say that the ingredients are added and the reactor is brought to polymerization temperature. The key ingredients charged are the water, the VCM, the primary dispersant and the free-radical initiator. Secondary dispersants are usually used to help control the agglomeration of the monomer-swollen PVC primary particles inside each drop. Buffers to control the pH are often used. The water needs to be of very good quality and free of particulate matter, other dissolved substances and ions. Because more water is used than anything else, its quality is especially important.

Primary dispersants are used to control the polymerizing particles' agglomeration. Primary dispersants prevent the formation of a particle the size of the reactor (i. e., a solid charge, which can take weeks to clean up). Getting the right amount of primary dispersant added is absolutely critical. Typical primary dispersants are water-soluble polymers such as poly(vinyl alcohol), with a degree of hydrolysis of 70 to 88%, and low-viscosity methylcellulose polymers. The primary dispersant as well as the agitation controls the agglomeration of the initial droplets that takes place during the polymerization. Initially, the monomer droplets start out at 30–50 µm average size. As the polymerization proceeds, they agglomerate up to the 120–150 µm average grain size. Control of this in-reactor agglomeration is absolutely critical for avoiding the solid charge described earlier. The agglomeration process helps narrow the grain size distribution and dramatically lowers the amount of fines (small particles) in the batch. Fines cause the clogging of baghouses when the resin is transferred from place to place by pneumatic conveying systems.

Free-radical initiators are monomer-soluble as opposed to the water-soluble initiators usually used in the emulsion process. They partition into the liquid droplets and cause the polymerization to take place. Of primary concern is an initiator's half-life, which controls the rate at which it decomposes into free radicals, and its efficiency, which is the fraction of free radicals that actually initiate the polymerization of the VCM. Peroxydicarbonates are particularly useful because of their high efficiency. 2-Ethylhexyl peroxydicarbonate has about the right half-life and so is very often used, particularly at polymerization temperatures near 60 °C. Storage of the initiators must be handled properly, because they tend to violently decompose and release gases if allowed to warm up to near room temperature. They must be stored in a refrigerator or usually a freezer at < 0 °C. In order to help minimize this concern, initiator manufacturers offer water-dispersed initiators, where the initiator is dispersed as tiny particles in water. These initiators are much safer to handle and most will not even burn if allowed to warm up to room temperature, on account of the moderating influence of the water.

Almost all modern-day polymerizations use secondary dispersants. These are surface-active ingredients that help control the agglomeration of the monomer-swollen primary particles formed inside the monomer droplets. These ingredients can vary widely, but they all seem to have two common properties. First, they are somewhat soluble in water, thus attracting water to the internal pores within the grain to form porosity. Also, water solubility would seem to be necessary for ensuring that these secondary dispersants are partitioned properly into the VCM droplets. Second, they are soluble in VCM, and so they can work inside the droplets and thereby affect the internal structure within the grain. Secondary dispersants can be polymeric or monomeric. Perhaps the most common example is a low-molecular poly(vinyl alcohol) having a degree of hydrolysis typically between 45 and 55%. The low degree of hydrolysis reduces its solubility in water and causes it to partition into the VCM phase. There are a great many other specific examples too numerous to mention within the scope of this work. Diffusion of VCM from these primary particles is the rate-controlling process for recovering unreacted monomer; therefore, keeping the primary particles small and uniform is critical to quickly removing the unreacted VCM to below one part per million. More information about the formation and growth of the particle structure of PVC and the removal of residual VCM will be presented in later sections of this chapter.

The polymerization is allowed to continue to the desired conversion. During the course of the polymerization, it is common practice to inject water into the vessel to compensate for the volume shrinkage during polymerization, as discussed previously. The top of the liquid level is a particularly bad trouble spot for buildup on the vessel walls, which is caused by the dropping liquid level and deposition of polymer just above the liquid level. A slightly rising liquid level during the course of the polymerization solves this problem. Also, cold-water injection helps with heat removal slightly. It is important to stop at the desired conversion, because the resin particle internal structure is a function of the conversion. This is usually accomplished by following the pressure in the reactor and stopping at a particular drop in pressure. Alternatively, heat-release measurements can be used, but the pressure-drop method is much simpler. The pressure in a PVC polymerizer operating isothermally holds constant up to about 60% conversion. During this time, the liquid monomer is being consumed and turned into swollen polymer phase. Both of these phases are in equilibrium with each other and therefore have the same high vapor pressure. In other words, during the first 60% of conversion, the phase compositions remain unchanged, but the relative amount of each phase is changing. At about 60% conversion, all the liquid monomer has been consumed and only the swollen polymer phase is present. Any further polymerization now changes the amount of monomer dissolved in the polymer, creating a new composition having a lower vapor pressure and a pressure-drop starts. Reactions are commonly run to 0.03, 0.07, 0.10, or 0.14 MPa (5, 10, 15, or 20 psig) pressure-drop and then terminated by shortstopping or by removal from the reactor either before or after cooling, followed by rapid removal of the monomer, which also stops the polymerization reaction. In some instances, the monomer is partially recovered while the slurry is still in the reactor. Many variations exist, depending on the plant design.

3.3.2 Stripping

As stated earlier, it is standard practice to remove residual VCM in the final dried PVC product down to at least 1 ppm. For this job to be done reasonably well, the resin grain structure must have a good uniform internal porosity. Efficient execution requires special process equipment, such as a steam-stripping column [31]. In some instances, older plants strip VCM from the polymer using a vessel (sometimes the polymerizer) or a “blowdown” tank, into which the fresh slurry is transferred just after polymerization. Recovering the monomer down to about atmospheric pressure is relatively easy, but high temperature is required for getting to 1 ppm. Typical batch stripping temperatures approach or exceed 100 °C, with the monomer and boiled water being removed. Experience determines the time and temperature needed to reduce the monomer to the desired level. Recovered monomer is re-used in the polymerization and its quality must be continually monitored. Obviously, stripping the monomer in the polymerizer reduces polymerizer productivity substantially and a polymerizer is a relatively expensive piece of equipment to be used for this fairly simple purpose.

The most efficient stripping method involves the use of a steam-stripping column, and its use is quite extensive throughout the industry. A typical steam-stripping column unit operation may be described as follows. First, the reactor contents are blown down into a column feed tank or blowdown tank and the monomer is recovered down to approximately atmospheric pressure. This slurry is typically 30 to 40% PVC solids, < 1% VCM, and the balance is water. Recovering the monomer to this level causes the PVC particles to become rigid, because much of the plasticizing monomer is removed. This helps prevent the the soft particles from sticking together in future process steps. The resin slurry from the feed tank is passed into the top of the steam-stripping column, which is typically equipped with a stacked series of horizontally mounted sieve trays. Steam is fed into the bottom of the column and passes upward as the resin slurry flows downward through the stripping column. The top of the column removes vinyl chloride and some water, and the stripped slurry is removed from the bottom of the column. Spiral heat exchangers are used to preheat the stripping column feed with the hot column bottoms. A stripping column is an ideal piece of equipment for accomplishing this process efficiently. The resin slurry exiting the bottom is exposed to steam containing essentially no VCM, whereas the fresh slurry containing the highest level of residual VCM is exposed to the steam containing the most vinyl chloride. A high driving force for VCM removal is maintained throughout all levels of the column. Typically, a steam-stripping column operates at temperatures of 100 to 120 °C and has a residence time for the slurry of 3 to 7 minutes or longer, depending on the difficulty of stripping the resin. The difficulty of resin stripping is directly related to the uniformity of the internal resin structure (i. e., uniform porosity distribution). If the stripped resin slurry is to be held for any period of time before centrifuging and drying, it should be cooled to prevent the resin from yellowing caused by the heat history.

3.3.3 Centrifugation

The slurry, typically containing 60 to 70% water, is changed by means of a centrifuge into a sandy wet cake containing 20 to 25% water. If the slurry is centrifuged hot, above the 82 °C glass transition temperature of PVC, a lower water content results, presumably because the polymer is soft and some of the water is squeezed out of the pores by the squeezing action on the softened resin. Getting the water content as low as possible saves energy in the dryer and is quite desirable. It is generally preferred to use a solid bowl centrifuge. The screen of a screen centrifuge can be clogged by stuck PVC resin grains. The centrifuge is usually located very close to the dryer so that the sand-like wet-cake can be transferred directly to the dryer by a screw or vibratory conveyor or the like. Optionally, an anti-static agent is added to the wet-cake.

3.3.4 Drying and Screening

Typically, either fluid bed or rotary dryers are used for PVC resin. In a rotary dryer, the resin wet-cake is added to a rotating drum, which tumbles it around in the presence of hot air flowing through the drum. The resin does not typically experience any temperature above 100 °C until it is fairly dry, because the heat goes into vaporizing the water. The resin exit temperature is often used to control the amount of residual moisture in the resin. It is like walking a tightrope. Too much moisture can cause bubbling in the finished product or resin grains that freeze together in the winter. Too little moisture causes the resin particles to stick together and not flow because of static charge buildup. Fluid bed dryers work by blowing hot air upward through perforated plate decks under the PVC wet-cake and hot water plate or coil banks inside the dryer. As the resin dries, the grains become fluid because they are no longer held together by the moisture and can then be further dried and conveyed out of the dryer. Fluid bed dryers are more energy efficient, less capital intensive at scale and typically give less heat history to the resin. It is for this reason that most new dryers today are of the fluid bed type. Modern fluid bed dryers can operate at > 34 MT/hr (75,000 lb/hr).

After the resin has been dried to < 0.3% moisture, it is screened to remove large chunks or oversized grains from the resin. The resin is then transferred by a pneumatic conveying system to storage silos for loading into the appropriate shipping containers, be they bags, totes, tank trucks or railcars.

3.4 Mass Process Overview

The mass process is conceptually very similar to the suspension process, except that no water is used. The final resin has porosity and a particle size similar to the suspension process. The resin is generally cleaner, because primary dispersants are not required. The mass process work started in the 1930s with early work by the St. Gobain Corporation in France. It ultimately evolved into a commercial process by Pechiney St. Gobain in the 1950s. The key to the mass process lies in the proper use of agitation at the proper time during polymerization. When you think about it, if you want to conduct a polymerization without water you would have to agitate liquid monomer at the beginning of the process and then at the end you would have to agitate a dry powder (PVC resin). This problem was overcome by using two different vessels for the polymerization. The first stage of the polymerization, up to approx. 12% conversion, is conducted in a relatively small vessel called a pre-polymerizer. Pre-polymerizer vessels are very similar in shape and agitation conditions to those found in standard suspension reactors. At 12% conversion, the contents of the pre-polymerizer are transferred to a second vessel called the post-polymerizer. The post-polymerizer contains additional monomer and initiator. The second vessel has a very different kind of agitation, specifically designed to agitate a powder. In the early commercial version of this process, slowly rotating ribbon-blender-type agitation was used. In later versions of the technology, a vertical cylindrical vessel was used, but the agitation was still designed to agitate a powder [32].

These vertical reactors are illustrated in Figure 3.5 and have a relatively high-speed, ribbon, screw-like agitator, pumping solids upward along the vertical central axis, while at the same time having a relatively slow, scraper-like blade moving around the inside walls and bottom of the vessel. It turns out that the time in the pre-polymerizer is much shorter than in the post-polymerizer, so it is standard practice to have one pre-polymerizer feeding several post-polymerizers. The key to the process is that "seed" particles are formed in the first-stage vessel under high agitation and this seed continues to grow into the final grains in the second-stage vessel. Presumably, no new large grains are formed in the second vessel. But all the tiny primary particles that form, owing to precipitation of PVC in the liquid monomer during the second-stage polymerization, agglomerate onto the seed. This agglomeration phenomenon is what makes the process work. The mass process post-polymerizer is often operated under pressure control rather than temperature control, as is done in the suspension process. This makes no real difference for the first 60% conversion, because the pressure is directly related to the temperature. Because the process is controlled primarily by monomer reflux cooling, when the conversion reaches the point where pressure drop would occur if it were operating isothermally (60%), the efficiency of the reflux condenser decreases dramatically once liquid monomer is no longer present. By operating at constant pressure, the control system allows the resin to get hotter at the end of the polymerization in order to drive the conversion higher, produce more polymer, and have less residual VCM to recover. This is sometimes done in suspension polymerization and is called "tail peaking". At the end of the polymerization, a powder very similar to normal suspension resin, but wet with VCM, is formed.

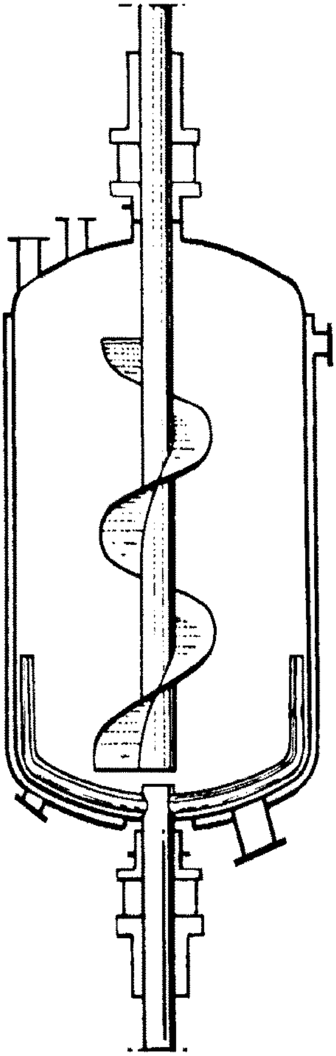


Figure 3.5

A typical vertical mass polymerizer

(*from Langsom, M., Chapter 3, Encyclopedia of PVC, 2nd ed., Vol. I, Nass, L. and Heiberger, C. (Ed.) (1985) Marcel Dekker, with permission*)

The grain size and porosity of the final resin is controlled by the agitation speed and polymerization temperature in the pre-polymerizer, respectively. Typically, about 60–70 °C is used in the pre-polymerizer. Lower polymerization temperature produces higher porosity mass resin. Higher agitation speed produces a smaller resin average grain size. Typical post-polymerizer temperatures are 50–60 °C. Because most of the total polymerization takes place in the post-polymerizer, this temperature is the primary control of the molecular weight of the finished resin. Additives for adjusting the porosity and particle size can be added to the first-stage polymerizer. Because there is no water present, only considerations about VCM solubility of these ingredients are required. Some inorganic seeds can be added as well as VCM-soluble polymeric ingredients that could not be used in the suspension process, because they have near-zero water solubility. Thus, the selection of what would be called secondary dispersants in the suspension process is much more flexible with the mass process. The heat of reaction in both the pre-polymerizer and the post-polymerizer is typically removed with reflux condensers, which are very efficient and cost effective. It is fairly important to drop the pre-polymerizer at the proper conversion. This can be done by dropping at a predetermined time or by another method called the drop-dead technique. With the drop-dead technique, a very short half-life initiator is used in the pre-polymerizer. For example, the initiator ACSP has a half-life at 70 °C of approx. five minutes. Just enough ACSP is added to the pre-polymerizer to get to the desired conversion before the initiator is essentially consumed. Thus, the final conversion in the pre-polymerizer is recipe-controlled. The contents of the pre-polymerizer can be held if, for some reason, the post-polymerizer is not yet ready when operating via this drop-dead method.

The mass process has many advantages. Because there is no water, there can be no issues involving water quality. As will be discussed later, in much more detail, suspension resins have a thin skin, called the pericellular membrane, formed at the water/VCM interface. Mass resin does not have this membrane, so it should in principle be of higher quality and able to absorb compounding ingredients more rapidly without having the skin in the way. The uniform distribution of oil soluble initiators from grain to grain is no issue in the mass process, but must be carefully controlled by charging procedure in the suspension process. The process does not require large amounts of heat energy to dry the resin. For a while, it looked as if the mass process would replace the suspension process as the preferred method for making PVC.

Today, there are a number of considerations that have caused the mass process to no longer be the process of choice. One disadvantage of the mass process is that it produces a lot of fine grains that create dusting problems when the resin is transferred pneumatically. It is quite costly to try to remove these fines with screening. I suspect that these fines are grains that, with time, would agglomerate onto the growing grains, but this agglomeration has not yet taken place. The discovery that VCM is a carcinogen created substantial problems for the mass process. In order to get the residual VCM down to 1 ppm, the final mass resin must be stripped for fairly long times at high temperature in the post-polymerizer. Getting heat into a powder is not a simple task.

Eventually, direct steam injection was used to heat the resin in the post-polymerizer and then often a nitrogen sweep was required to remove the VCM and dry the resin. Introducing an inert gas such as nitrogen into the VCM recovery system becomes problematic, because it is very difficult to remove VCM from the nitrogen to levels that allow the nitrogen to be safely emitted to the environment. Also, the clean reactor coatings for the suspension polymerization process seem to work much better than anything available for the mass process. Mass polymerizations cannot, at this time, be operated in closed-polymerizer mode to the extent that suspension polymerizations can. All of these developments have had an adverse effect on the relative viability of the mass process. As of 2024, there are no mass PVC process plants in operation in North America.

3.5 Special Considerations

3.5.1 Polymerization Kinetics

In an earlier section, it was described how PVC polymerizations are auto-accelerating reactions, because the rate of reaction inside the swollen PVC particles is substantially faster than the polymerization in the liquid VCM. With a long half-life initiator, this results in a reaction rate that is proportional to the conversion. Long half-life initiators are generally not used, so the acceleration tends to drop off as the active initiator is consumed. A typical reaction rate curve of heat versus conversion is shown in Figure 3.6.

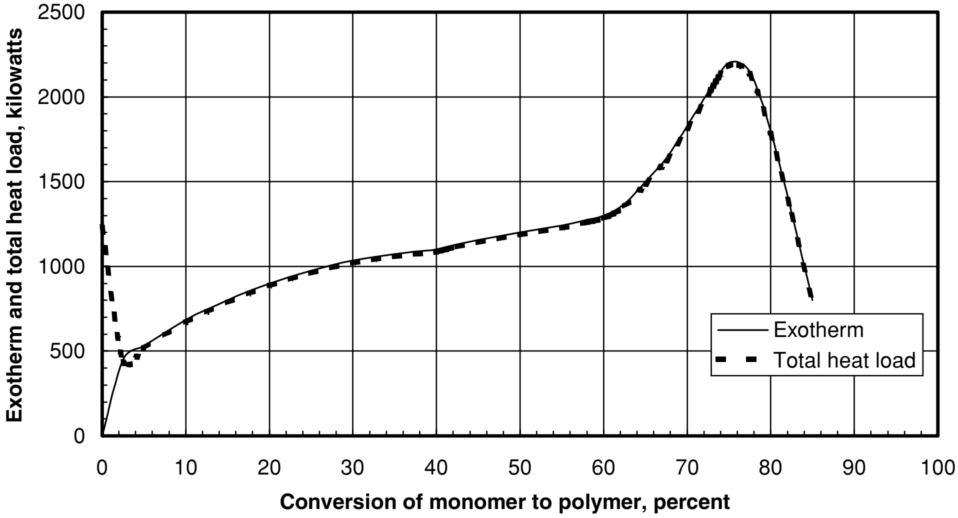


Figure 3.6 Plot of heat load versus conversion predicted by a computer polymerization model for an isothermal polymerization as described in the text