PFAS IN EDC/VCM AND PVC MANUFACTURING

Revision 9, 22 September 2023

Executive Summary

PFAS play a crucial role in securing safe and environmentally responsible VCM and PVC manufacturing operations. To provide input into the ECHA consultation on the PFAS restriction proposal, the European Council of Vinyl Manufacturers (ECVM) conducted a survey on the use of PFAS in its members' VCM and PVC plants. This survey was the first of its kind, and whilst it provides a very good overview, it is based on estimations made by companies.

The survey revealed that ca. 65 t/y of low molecular weight PFAS and fluoropolymers are used across 18 use categories in VCM and PVC plants. The biggest yearly volumes used are for refrigerant gases made of low molecular weight PFAS. The F-gas Regulation EU 517/2014 under revision will push to substitute these gases with "natural" alternatives. F-gas are also used to a much lesser extent in air conditioning systems installed in some premises. The 16 other use categories utilise fluoropolymers. The biggest fluoropolymer yearly volumes used are for gaskets, lining in pipes and other equipment, lining in valves, gaskets, O-rings, sealants, hoses and tubing and personnel protection equipment. These uses are not specific to PVC and VCM plants: all the aforementioned equipment can be found in most industrial settings.

Only 2 of the 16 fluoropolymer uses identified in the survey are derogated for 12 years in the current Restriction Proposal. However, for the 14 non-derogated uses in the proposal, there are currently no technically viable and economically affordable alternative materials able to meet the high standards for VCM and PVC plants. In most cases, we understand no alternatives are currently in development.

The Survey results also attempted to identify the destination of the PFAS after use. For the fluoropolymer-containing equipment, steel recycling and chemical incineration are the two most used waste management processes. These processes are run at temperatures far above the thermal decomposition of any PFAS. Some uncontaminated equipment is landfilled.

As no alternatives are available for the fluoropolymers and as the equipment containing the latter is disposed of through low-emission processes after use, ECVM asks for a **time-unlimited derogation** for all fluoropolymer uses in VCM and PVC plants not derogated yet in the Restriction Proposal.

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Table of Content

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The "Universal" PFAS Restriction

The broadest-ever Restriction Proposal under REACH was prepared by five countries (Denmark, Germany, the Netherlands, Norway and Sweden) and published by ECHA in February 2023. The Proposal aims to ban the manufacture, use and future placement on the EU market of >10^3 per- and polyfluoroalkyl substances (PFAS). The ban would not be applied to articles already in use. The use of PFAS in fire-fighting foams is not included in the Proposal, as is the subject of a separate restriction process.

According to the authors of the Proposal, PFAS have adverse effects on environment and human health. Over their lifecycles, PFAS would be either persistent themselves or degrade to other persistent PFAS due to strength of the carbon-fluorine bond. PFAS would remain in environment for decades to centuries. The objective of the ban would be a reduction of >4 million tonnes of PFAS emission over 30 years. If no action is taken, societal costs are claimed to exceed costs associated with a restriction.

The ban would cover the substances on their own or as a constituent, a mixture or an article. In the latter cases, very low concentration limits of PFAS would be allowed:

- 25 ppb for any PFAS as measured with targeted PFAS analysis (polymeric PFAS excluded)
- <250 ppb for the sum of PFASs measured as sum of targeted PFAS analysis (polymeric PFAS excluded)
- <50 ppm for sum of all PFAS (polymeric PFAS included). If total fluorine exceeds 50 ppm in the article, the manufacturer, importer or downstream user needs to provide a proof for the fluorine measured as content of either PFAS or non-PFAS.

PFAS are defined in the Proposal using the very broad OECD definition; any substance that contains at least one -CF2- or -CF3 molecule. Use of this very broad definition was made instead of an exhaustive list, to "avoid regrettable substitutions". According to the authors, polymeric PFAS (fluoropolymers) should also be restricted as they are persistent, contains or degrade into residual low molecular weight PFAS, and can lead to emissions of low molecular weight during their production and end of life lifecycle stages.

The ban would be implemented 18 months after entry into force, with time-limited, use-specific derogations. PFAS for non-derogated uses will be restricted 18 months after being listed on Annex XVII of REACH. There will be no need for an approval by the member states. 11 derogations have been proposed for 6.5 years after entry into force; 33 derogations are proposed for 13.5 years after entry into force. Any derogation will come with reporting requirements and reduction management plans.

Very few of the proposed derogated uses are relevant for the chemical industry. For example, lubricants where the use takes place under harsh conditions, or the use is needed for safe functioning and safety of equipment, will be derogated for 18 months +12 years after entry to force. Industrial uses have not been derogated as a whole since, according to the authors, a delineation with consumer uses would be often impossible. The essential use concept has not been used as it is not a legal concept yet; a revision of REACH is needed for this.

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Provided they are supported by substantiated information, other proposed derogated uses than those described in the Proposal can be added during the Public Consultation launched on 22 March 2023 for six months. ECHA will favor joint submissions from associations, as they are considered as more representative than single company's contributions. The European Council of Vinyl Manufacturers (ECVM) has decided in March 2023 to launch a survey aiming to identify the current uses of PFAS in the European PVC industry. The results of this Survey are summarized in this report, that will serve as basis for a submission from ECVM to the ECHA's consultation.

The PVC Value Chain

PVC is a thermoplastic made of 57% chlorine, derived from industrial grade salt, and 43% carbon (derived predominantly from oil/gas via ethylene). It is less dependent than most other polymers on non-renewable crude oil or natural gas, and hence can be regarded as fossil resource-saving, in contrast to plastics which are totally dependent on oil or gas. The presence of chlorine in the molecule explains PVC's particular versatility because it ensures compatibility with a wide range of other materials. Presence of chlorine also gives to PVC excellent fire resistance.

The specific characteristics of PVC make it a material of choice in many building and construction applications, such as highly insulating, energy-saving profiles, pipes for water and gas, flooring, cable sheathing and roofing. It is also the favoured material for specific medical applications such as blood bags and tubing. Last but not least, PVC can be recycled many times without loss of properties and is increasingly recycled thanks to industry initiatives such as VinylPlus.

PVC is an essential part of the chlor-alkali value chain. Ethylene and chlorine are the major raw materials for PVC, which is therefore affected by, but also impacts, the supply-demand conditions of both ethylene and chlorine. However, PVC represents less than 15% of all ethylene use in Europe whilst it amounts to about 1/3 of all chlorine use. PVC is therefore much more affected by, and has a much bigger impact on, the supply-demand conditions of chlorine than of ethylene. Its impact on chlorine in turn has a determining effect on caustic soda supply and price and thereby on wide sections of the chemical industry at large.

The first step in the PVC manufacturing chain is ethylene dichloride (EDC). EDC is mainly used for the production of vinyl chloride monomer (VCM), which in turn is used exclusively for the manufacture of polyvinyl chloride (PVC) and associated co-polymers. A small portion of EDC is used for manufacturing of ethylenediamine, organic solvents and various pharmaceutical products.

In 2022, 11 companies operated VCM and PVC production plants in the EU27+UK+NO+CH region, for a PVC production volume estimated by Conversio to 3700-3900 kt.

Manufacturing Processes Overview

EDC is synthesised either by the direct chlorination of ethylene or by chlorination using HCl and oxygen (oxychlorination). VCM is then produced through the thermal cracking of dry, pure EDC.

VCM to supply PVC plants can be transported by dedicated pipes when the distance is short. Boats, rail or road trucks are used over longer distances. Most PVC plants have storage and unloading facilities for VCM. VCM storage can either be under pressure or refrigerated at approximately atmospheric pressure.

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The VCM is polymerised into PVC in an aqueous medium, under pressure, through suspension and emulsion processes leading, respectively, to S-PVC and E-PVC grades. This takes place almost exclusively batch-wise in cooled reactors. Residual VCM is stripped from the PVC granules or latex, which are subsequently dried, stored in silos before shipping to compounders or directly to converters who manufacture PVC products.

Detailed information on both steps can be found in Annexes 1 and 2.

Environmental emissions and worker exposure limits

All VCM and PVC manufacturers in Europe need to comply with very strict environmental and worker exposure emissions limits defined at EU and member state level.

Upper values for the environmental emission limits are defined in three EU Best Available Techniques Reference Documents (LVOC, POL and WGC are the relevant ones for VCM and PVC production; they are available on https://eippcb.jrc.ec.europa.eu/reference) issued by the European IPPC Bureau and enforced in the EU Industrial Emission Directive.

Maximum limit values for occupational exposure for EDC (2 ppm) and VCM (1 ppm) are defined in Directive 2004/37/EC.

Since the mid-nineties, the ECVM members have further committed to voluntary abide with lower limits than those in the BREF or in 2004/37/EC and/or comply to the limits earlier than date of implementation after publication. The latest version describing the voluntary commitment is available on https://pvc.org/wp-content/uploads/2023/04/ECVM-charter-pages.pdf.

Uses of PFAS in EDC/VCM and PVC Manufacturing

As outlined above, EDC/VCM manufacturing entails handling multiple highly corrosive and hazardous substances such as chlorine, hydrochloric acid (HCl) and chlorinated hydrocarbons. Compliance with the tight requirements on environmental and worker exposure emissions demands special equipment that can withstand corrosion and ensure tight containment.

Several internal studies from the ECVM members have demonstrated that fluoropolymers (especially the fully fluorinated, most chemically inert PolyTetraFluoroEthylene/PTFE and PerFluoroalkoxy Alkanes/PFA) show the best *set of performances* needed to cope with the harsh process conditions in the EDC/VCM production units:

- Chemical corrosion resistance vs. the great majority of metallic materials used in the chemical industry
- Chemical permeation resistance to provide long term protection
- Temperature resistance (vs other thermoplastics)
- Mechanical strength (vs other thermoplastics)
- Excellent flexibility and sliding properties to secure tightness in rotating equipment (vs metallic materials)
- Good wear resistance when a carbon filler is added to the fluoropolymer

External publications also mention that, for the conditions found in the EDC/VCM plants, the fluoropolymer materials are the first-choice materials for corrosion resistance at high temperature. Volume 2 of the Dechema Corrosion Handbook mentions that fluoropolymers are the first-choice materials for hydrochloric acid equipment at elevated temperatures and concentrations (see extract

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in Annex 3). Fluoropolymers are particularly resistant to hydrochloric acid in presence of chlorinated hydrocarbons.

Less severe conditions are generally experienced in the PVC plants, but various plant sections also require equipment with the outstanding set of performances provided by the fluoropolymers.

Purification of VCM, evacuating the high heat release of VCM polymerisation to produce PVC, and reducing atmospheric emissions in both processes require using refrigerants more effective than cooling water. F-gases are selected by the equipment manufacturers because they are highly effective, energy efficient and non-toxic. Although they are already covered by the F-gas Regulation EU 517/2014 entered into force in 2015 and its Revision proposed in April 2022 by the EU Commission and currently being discussed in trilogues, many F-gases (HFC-125, HFC-134a, HFC-143a, HFC-227ea, HFO-1234yf, HFO-1234ze, HFO-1336mzz, HCFO-1233zd) and their blends (R404A) also fall under the definition of the PFAS Restriction Proposal. In principle, the stricter provision will apply.

A survey has been organised among the seven members of the European Council of Vinyl Manufacturers (ECVM), representing 85% of the European production of PVC, to

- ✓ Identify the use of PFAS in the VCM and PVC plants.
- ✓ Estimate tonnages of PFAS used per year.
- ✓ Assess the process criticality and the feasibility of alternatives to PFAS.
- ✓ Identify end of life destination for each use category.

A very high response rate could be obtained (98% of the EDC/VCM and PVC plants owned by the ECVM members). The respective rates for the 16 EDC/VCM plants, 19 S-PVC plants and 11 E-PVC plants run by the ECVM members are shown below:

	Number of plants in membership	Number of responding plants	Response Rate
EDC/VCM	16	16	100%
sPVC	19	18	95%
ePVC	11	11	100%
Total	**46**	**45**	**98%**

Ca. 65 tonnes of PFAS have been found to be used per year by the ECVM members across 18 use categories. Use of low molecular weight PFAS has been reported only for refrigeration down to -20°C and air conditioning systems installed in some premises. Refrigerants represent 30% of the total use (ca. 20 t/y). All other applications make use of fluoropolymers (ca. 35 t/y). A weight percentage breakdown for each use is shown in the below pie chart.

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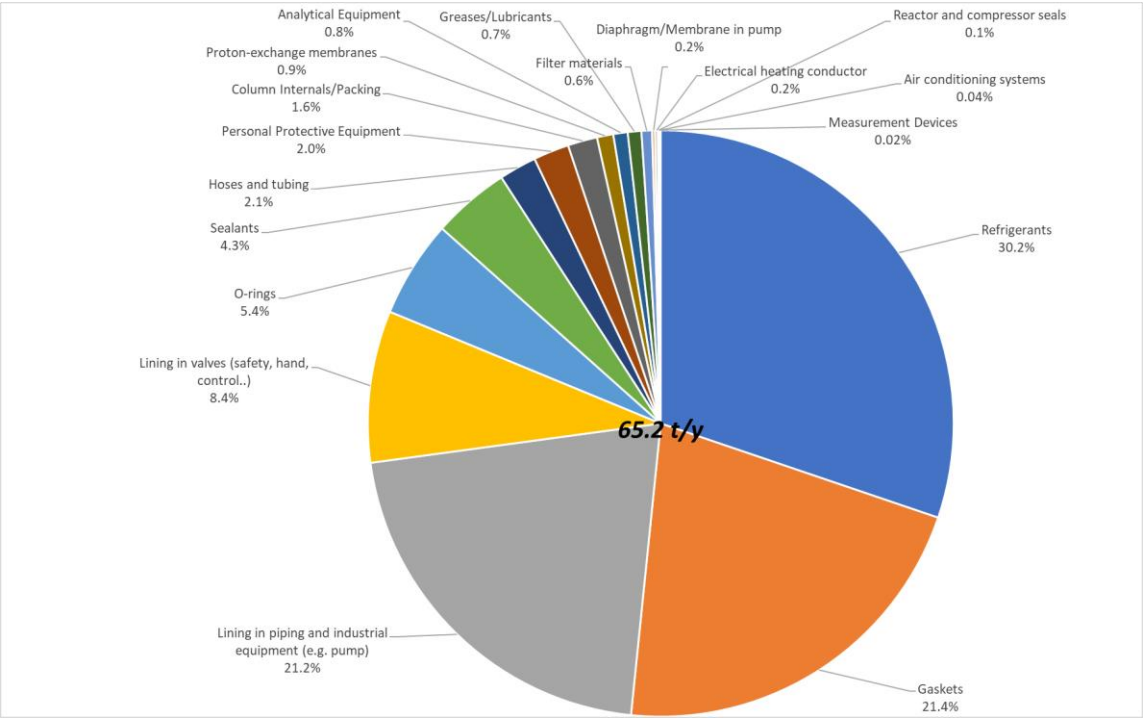

According to the Survey results, the most important uses for the fluoropolymers include gaskets (21.4%), lining in piping and industrial equipment (21.2%), lining in valves (8.4%), O-rings (5.4%), sealants (4.3%), hoses and tubing (2.1%), personal protective equipment (2%).

As shown in the below table, all uses are present in both types of plants, except lining in piping and industrial equipment, lining in valves, column internals/packing and proton-exchange membranes, which are not used in the PVC plants.

The below table also shows that only 3 of the 18 uses in the EDC/VCM and PVC plants are covered by a derogation in the current Restriction Proposal.

Uses	EDC/VCM Plants	PVC Plants	Derogation in Current Restriction Proposal
Refrigerants	YES	YES	NO[a]
Gaskets	YES	YES	NO
Lining in piping and industrial equipment (e.g. pump)	YES	**NO**	NO
Lining in valves (safety, hand, control)	YES	**NO**	NO
O-rings	YES	YES	NO
Sealants	YES	YES	NO
Hoses and tubing	YES	YES	NO

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Personal Protective Equipment	YES	YES	**YES**[b]
Column Internals/Packing	YES	**NO**	NO
Proton-exchange membranes	YES	**NO**	NO
Analytical equipment	YES	YES	NO
Greases/Lubricants	YES	YES	**YES**[c]
Filter materials	YES	YES	NO
Diaphragm/Membrane in Pump	YES	YES	NO
Electrical heating conductor	YES	YES	NO
Reactor and compressor seals	YES	YES	NO
Air Conditioning Systems	YES	YES	**YES**[d]
Measurement Devices	YES	YES	NO

[a] derogation proposed is limited to refrigerants for refrigeration <-50°C, for laboratory tests and measurement equipment, or for refrigerated centrifuges

[b] 12-year derogation for protection against risks of Category III a) from EU 2016/425 (substances and mixtures which are hazardous to health)

[c] 12-year derogation if use takes place under harsh conditions or use is for safe functioning and safety of equipment

[d] 12-year derogation for maintenance and refilling of existing HVCAR without drop-in alternatives, time-unlimited derogation where national safety standards and building codes prohibit alternatives

Uses for which PFAS could be substituted

As mentioned above, **refrigerants** are needed to achieve temperatures below those achievable with water from cooling towers, to reach condensation temperatures of some substances during distillations, or to achieve effective minimisation of gaseous emissions arising from vents or from incinerators. VCM polymerisation is highly exothermic and takes place at relatively moderate temperatures. Polymerisation temperature is an essential process parameter that cannot easily or not at all be ensured by cooling water refrigeration, and hence requires refrigerated water able to reach temperatures down to -20 °C.

The current restriction proposal does not include any derogation for PFAS refrigerants used in industrial refrigeration. It only specifies derogations for low temperature (-50°C) refrigeration, refrigerants for laboratory tests and measurement equipment, and centrifuges. The alternative refrigerants have their own health and environmental risks and require anyway high investments to convert to new industrial refrigerant equipment. Propane and propylene pose a risk of flammability,

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particularly when used in large quantities and in confined spaces; carbon dioxide is hazardous to human health, operates at high pressures and is less efficient at high ambient temperatures; ammonia is highly toxic, resulting in specific requirements for its use. A derogation should be allowed to select environmentally and financially sustainable alternatives.

F gases present in Air Conditioning Systems are subjected to a 12-year derogation for maintenance and refilling of existing HVCAR without drop-in alternatives. A time-unlimited derogation is proposed for refrigerants in HVCAR equipment in buildings where national safety standards and building codes prohibit the use of alternatives.

Uses for which no substitutes have been identified

As mentioned above, the corrosive substances and high temperatures in VCM manufacturing plants require highly mechanically and chemically resistant **piping, valves and other equipment (e.g., pumps) with an inner fluoropolymer lining**. It is very difficult to find suitable alternatives due to the high pressure, high operating temperatures, and types of transported fluids.

As illustrated Annexes 3 and 4, PTFE and PFA can be serviced at temperatures up to 250 °C (without mechanical load). This is much higher than other thermoplastics; PP and C-PVC have a maximum service temperature of 90-95°C; PE and PVC of 60 °C.

A study has been run by one ECVM member on best material to use for an agitated storage vessel containing wastewater from flue gas cleaning of an incinerator for chlorinated hydrocarbons in a VCM plant. The wastewater is alkaline (pH 9.8-11.2) and the working temperature is 100°C. The combination of those two parameters excludes the use of all non-metallic materials. The use of a bisphenol A-based vinyl ester resin, PP and C-PVC is excluded due to their limited maximum operating temperatures (respectively, 85°C and 90-95°C). The use of a VE-NK resin is limited by the pH. As Polyvinylidene fluoride/PVDF is prone to stress corrosion cracking at this high pH, a PTFE-coated carbon steel was recommended as best material.

As another example of the unique properties provided by fluoropolymer linings in corrosive environments, it is interesting to mention the case of a scrubber designed to scrub chlorine and acidic vapors with 22% caustic soda (Annex 5). This scrubber was initially fabricated from fiberglass reinforced plastic (FRP) and installed in 1977. Major repairs began in 1981 and continued at four-year intervals. After exploring several replacement materials, an ethylene-chlorotrifluoroethylene liner was selected for the excellent chemical resistance to caustic soda, chlorine and HCl, and high permeation resistance to chlorine and HCl. Installed in 1987, the scrubber remained in service until the plant shut down in 2001. Examination shortly after plant closing showed the liner to be in excellent condition.

Several other studies have also demonstrated the superiority of PTFE and/or PFA lined pipes compared to conventional metallic materials in terms of chemical resistance.

As stressed in the recent review article of Annex 6, the selection of metallic materials resistant to hydrochloric acid corrosion is a very difficult task, especially under a high flow rate of acid making the material wear and corrode. Very often only titanium grade 7 (most corrosion resistant titanium alloy) or tantalum would be the only acceptable metallic alternatives for the conditions found in the VCM plants. However, these materials cannot meet the required performances in all cases and/or are far costlier than the fluoropolymers.

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One ECVM member has reported that a connecting pipe section made of tantalum suffered from cracks after some years of operations. Other members reported several equipment failures with stainless steel:

- Stress cracking corrosion of the stainless-steel ball and stem of a valve due to HCl et chlorine.
- Stress cracking corrosion on a stainless steel thermowell in presence of HCl
- Corrosion of stainless-steel bolts by HCl
- Corrosion of the stainless-steel outer support layer of bellows under high temperature

Beyond their reduced chemical and temperature resistance, the alternative materials have often a limited commercial availability. For instance, PFA-coated carbon steel is a standard material for pumps, and much more easily available than pumps lined with exotic metallic materials. Plastic material pumps are not (commonly) used. PTFE lining is also a standard solution for pipes.

The current restriction proposal **does not** include any derogation for this PFAS use. A derogation with should be allowed to develop alternatives and implement them.

Gaskets and **O-rings** represent another important use of fluoropolymers in VCM and PVC manufacturing. Only polyfluorinated materials have sufficient resistance to handle EDC, VCM, and the various chlorinated by-products present in EDC and VCM streams. In VCM plants, there exists therefore no real alternative, because of the combination of product type, pressure and temperature. Metal (tantalum, high quality stainless steel) / graphite seals could be used in PVC plants, but they require more space between flanges and hence significant and expensive adjustments as piping will have to be replaced. In a very few cases in the PVC plants, rubber seals could be used.

The current restriction proposal **does not** include any derogation PFAS-containing seals used **in the chemical industry**. A derogation should be allowed to develop alternatives and implement them.

For **sealants**, only polyfluorinated materials have sufficient chemical resistance to handle EDC, VCM, and the various chlorinated by-products present in EDC and VCM streams. PTFE tapes are used between graphite blocks of heat exchangers for HCl stripping during the purification of VCM. In VCM plants, there exists therefore no real alternative, because of the combination of product type, pressure and temperature. In the PVC plants, silicone sealants could be used in sections with no exposure to chlorinated substances.

The current restriction proposal **does not** include any derogation PFAS-containing gaskets. A derogation should be allowed to develop alternatives and implement them.

Flexible **hoses** with an internal PTFE **tubing** and an external braid made of stainless steel, are mostly used in some sections of VCM plants when fixed piping is not the best option (temporary operation, lack of space). They are used for example to drain corrosive fluids such as HCl from condensers of distillation columns. These hoses offer excellent chemical resistance and their structure provides a smooth bore to ensure clean, fast performance, resistant to high pressures and temperatures up to 260°C. PTFE has been proven to outperform rubber, silicone and PVC in these applications. Hoses with an internal PTFE can be used in PVC plants to provide low flow resistance and avoid wear.

The current restriction proposal **does not** include any derogation PFAS-containing hoses and tubing. A derogation should be allowed to develop alternatives and implement them.

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Protective personal equipment (PPE), although representing a relatively low consumption of materials, is obviously essential to ensure workers' health and safety and to allow execution of tasks necessary to protect the environment. Fluorinated substances are commonly used in fire, chemical and corrosion resistant clothing. Despite strenuous efforts by PPE manufacturers to find suitable options affording the same protection level, no commercially available alternatives achieving the performance standards of the VCM and PVC plants exist to date.

The current restriction proposal does include a proposed 12-year derogation for PFAS-containing PPE protecting users against risks of Category III a) (substances and mixtures which are hazardous to health) of EU 2016/425 Annex I. This is indeed the minimum time period necessary to develop, test and implement alternative solutions.

No commercially available substitute to fluoropolymers has been identified for the 9 other use categories with a lower use rate. For 1 of them (Greases/Lubricants), a derogation of 12 years is defined in the current restriction proposal if use takes place under harsh conditions or use is for safe functioning and safety of equipment. No derogations are proposed for the other 8. Due to the absence of substitutes, a derogation should also be granted for each of them.

The below table summarizes assessments made by the ECVM members about the availability, safety, technical feasibility, economic feasibility and viability of the non PFAS alternatives *for an implementation in VCM and PVC plants*. These generic criteria are used by the Committee of Socio-Economic Analysis of ECHA to assess alternatives to substances of concern (see https://echa.europa.eu/documents/10162/17241/scientific_basis_sea_conclusions_en.pdf/c0e85f26-a264-7458-0284-9a1a2579dfd4?t=1631609278955). The table shows that none of the non PFAS alternatives meet all criteria for any use. The development of materials for harsh industrial environment takes meeting all criteria mentioned in the table typically more than 10 year.

Uses	**Development stage of most mature non PFAS alternative (commercially available, in development, no development known)**	**If a non PFAS alternative is available, it would be..**			
		Safer	**Technically feasible**	**Economically feasible**	**Economically viable**
Refrigerants	Commercially available	NO	YES	YES	YES
Gaskets	Commercially available	NO	NO	NO	NO
Lining in piping and industrial equipment (e.g. pump)	Commercially available	NO	NO	NO	NO
Lining in valves (safety, hand, control)	Commercially available	NO	NO	NO	NO
O-rings	Commercially available	NO	NO	NO	NO
Sealants	Commercially available	NO	NO	NO	NO

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Hoses and tubing	Commercially available	NO	NO	NO	NO
Personal Protective Equipment	In development	N/A	N/A	N/A	N/A
Column Internals/Packing	No development known	N/A	N/A	N/A	N/A
Proton-exchange membranes	No development known	N/A	N/A	N/A	N/A
Analytical equipment	No development known	N/A	N/A	N/A	N/A
Greases/Lubricants	No development known	N/A	N/A	N/A	N/A
Filter materials	No development known	N/A	N/A	N/A	N/A
Diaphragm/Membrane in Pump	No development known	N/A	N/A	N/A	N/A
Electrical heating conductor	No development known	N/A	N/A	N/A	N/A
Reactor and compressor seals	No development known	N/A	N/A	N/A	N/A
Air conditioning Systems	Commercially available	NO	YES	YES	YES
Measurement Devices	No development known	N/A	N/A	N/A	N/A

N/A: Not Applicable

PFAS Emission Management

No environmentally significant uncontrolled emission of low molecular weight PFAS should be expected from the fluoropolymers used in the VCM and PVC plants during operation.

Measurements of low molecular PFAS emission to aqueous effluents have been done by some members; none of these measurements show PFAS concentrations above the limit of detection of state of the art analytical methods. In one example, one member has submitted samples of the aqueous effluents from the VCM plant to a lab accredited to use US EPA 537.1 - Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). Results reported were always below the minimum reporting limits: PerFluoroOctanoic Acid (PFOA) <0.0010 µg/l, PerFluoroOctane Sulfonate (PFOS) <0.0010 µg/l**,** PerFluoroOctaneSulfonAmide (PFOSA) <0.0025 µg/l.

Should some forthcoming measurements by its members show detectable levels, ECVM will launch an industry wide measurement campaign to monitor low molecular weight PFAS and define corrective measures.

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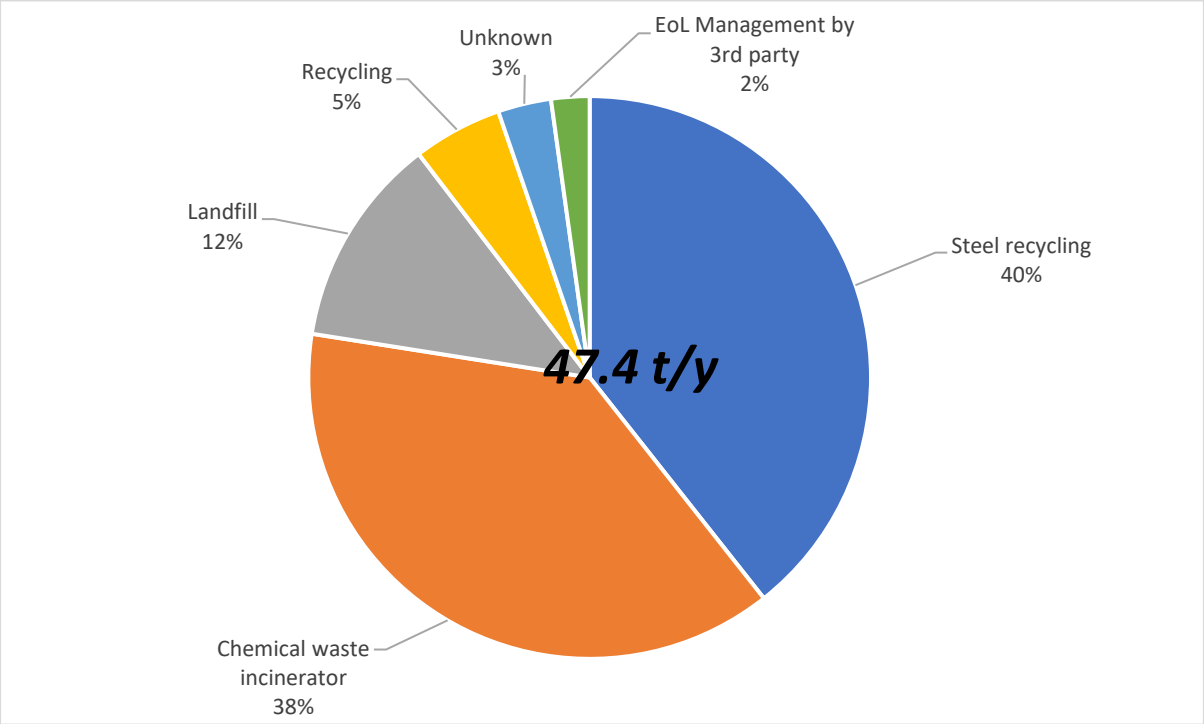
PFAS Waste Management

The Survey results included information on the end-of-life destinations of 17 uses. Accurate information could not be obtained for the 20 t/y refrigerants. The below pie chart shows the destinations aggregated for the other 17 uses.



The below table shows, per use category, the different end of life destinations estimated by the ECVM members. These are **high level estimations** as the ECVM members have not a full overview for all specific waste streams that contain PFAS. Figures are in % weight.

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Use	Recycling	Steel Recycling	Chemical waste incinerator	Landfill	EoL Management by third party	Unknown
Gaskets			**68%**	29%	3%	
Lining in piping and industrial equipment (e.g. pump)		**94%**		6%		
Lining in valves (safety, hand, control..)		**89%**		1%	1%	9%
O-rings			**98%**	1%	1%	
Sealants		27%	**36%**	14%		23%
Hoses and tubing	16%		**79%**	1%	4%	
Personal Protective Equipment	2%		**91%**	1%	1%	6%
Column Internals/Packing	6%		**50%**	30%	14%	
Proton-exchange membranes			**100%**			
Analytical Equipment	7%		**81%**			12%
Greases/Lubricants	**90%**			7%		3%
Filter materials	1%		**56%**	17%	13%	13%
Diaphragm/Membrane in pump	36%			7%	**57%**	
Electrical heating conductor	**100%**					
Reactor and compressor seals		13%				**87%**
Air conditioning systems			**87%**		13%	
Measurement Devices	**100%**					

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Fluoropolymers lined on steel substrates are almost completely treated though steel recycling. PFAS are thermally destructed at the temperatures used (>1500°C) used to melt down the metal scrap. O-rings, sealants, hoses and tubing, PPE, column internals, proton exchange membranes, analytical equipment, filter material, air conditioning systems are almost completely incinerated in a chemical incinerator after use. PFAS are thermally destructed at the temperatures used (>800°C) during the incineration. Primary end products of PFAS combustion are CO, CO2, and HF. Air emissions of HF are strictly controlled by the 2010/75/EU Directive on industrial emissions. Small uncontaminated fractions are landfilled. Grease/lubricants, electrical heating conductor and measurement devices are recycled.

As the end of life of most of the fluoropolymers are managed through low emission processes, we recommend to define **unlimited time** derogations for all fluoropolymer uses in PVC and VCM plants not derogated yet in the current Proposal for which no alternative is currently available or in development. Once alternatives that are safer and technically and economically viable have been developed, such derogations could be revised.

Conclusions/Recommendations

- The only major use of low molecular weight PFAS by the European PVC industry is as refrigerants. All the alternatives having their own challenges and being in any case costly to implement, **a derogation of 12 years** should be allowed to select environmentally and financially sustainable alternatives.
- **Fluoropolymers meet essential uses of the European PVC industry, especially in the VCM plants**. These plants deal with a combined mixture of **acidic** medium including chlorinated hydrocarbons and in use at **higher temperature**.
- There is generally **no economically affordable alternative material available to fluoropolymers** to address these conditions. Less resistant materials can't be used due to the **high risk of failing and product release to atmosphere and potential harm to human life and environment**. For example, rubber lining can't be used in combination of high temperature and the presence of chlorinated hydrocarbons.
- Without use of fluoropolymers, the VCM -and PVC plants- **cannot comply with the high plant safety standards and strict emission limits in place to protect people and environment.**
- At current production level, the few identified alternatives to fluoropolymers will **not be available in large enough volume** to meet the need of the PVC and chemical industry. In most cases there are no concrete substitution projects in place and as such the industry would need more than 10 years to replace fluorinated materials, given the vast use across the companies.
- The vast majority of the fluoropolymer-containing equipment is mainly disposed after use through **low emission processes** (steel recycling, chemical incineration or recycling). A small uncontaminated fraction of the equipment is landfilled.
- In order to ensure that a safe and compliant production of important products can continue to be carried out in the EU in the future, **the use of fluoropolymers in the VCM and PVC plants should be derogated for an unlimited time until technically and economically viable alternatives are found.**

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Annex 1: EDC/VCM Manufacturing Processes

General

The basic process for production of vinyl chloride monomer (VCM) in Europe is by thermal cracking of dry pure 1,2 dichloroethane (EDC), in which EDC is split into VCM and HCl. The cracking products are then separated by distillation. The separated unconverted EDC is purified and recycled for cracking into VCM.

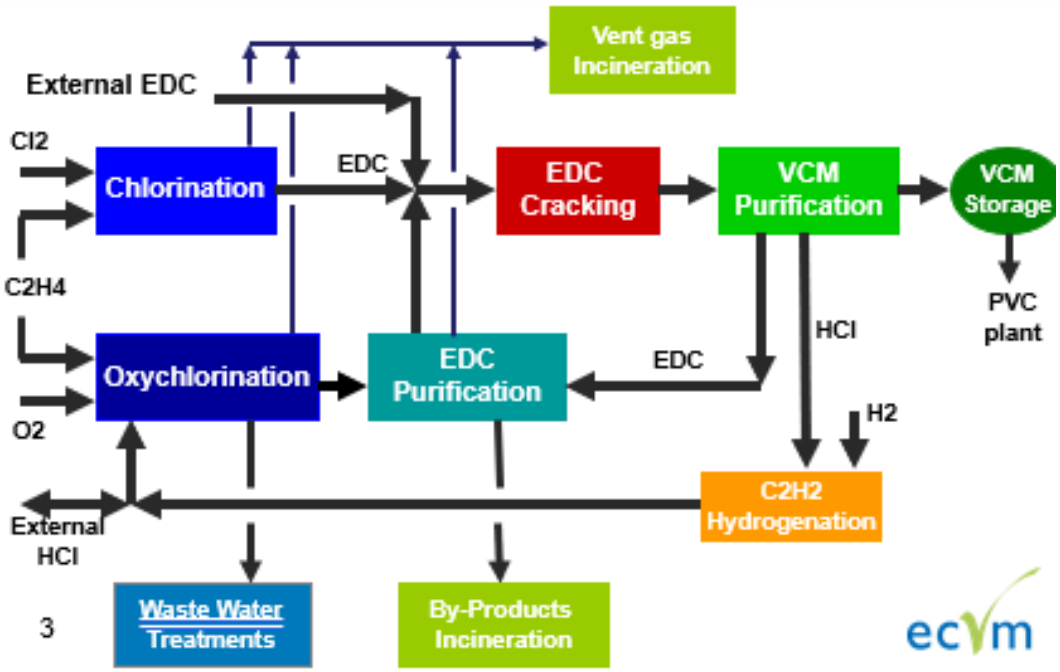
EDC is primarily synthesized by chlorination of ethylene with chlorine (Direct Chlorination). The other route for synthesis of EDC is by chlorination of ethylene with HCl and oxygen (Oxychlorination).

When all the HCl generated in the EDC cracking process is reused on site, and no EDC or HCl is imported or exported, then the EDC/VCM plant is called a "balanced unit". Approximately 90% of the plants in the world operate in this manner. The reactions are represented by the chemical formulae below:

direct chlorination: $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$ (EDC) (-180 kJ/mol);

cracking: $C_2H_4Cl_2 \rightarrow CH_2CHCl$ (VCM) + HCl (+71 kJ/mol);

oxychlorination: $C_2H_4 + ½\ O_2 + 2\ HCl \rightarrow C_2H_4Cl_2$ (EDC) + H_2O (-239 kJ/mol).



Direct chlorination of ethylene

In direct chlorination, EDC is synthesised by the exothermic reaction of ethylene and chlorine, generally in the liquid phase using the EDC product as the reaction medium. The operating temperatures are normally 50 - 120 °C and the pressure range from atmospheric to 5 bar. The reaction product consists of more than 99% EDC and less than 1% other chlorinated hydrocarbons (predominantly 1,1,2 trichloroethane and ethyl chloride).

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Two variants of the direct chlorination reaction are currently used:

- **Low temperature chlorination** in which the reaction is operated below 70°C, i.e. below the EDC boiling point (83.5°C). The liquid EDC leaving the reactor must generally be washed to eliminate the catalyst, thus leading to wet EDC (that requires drying and distillation before cracking), and to a liquid effluent (that requires treatment). This route produces slightly less by-product than high temperature chlorination and allows the use of lower-grade construction materials, but it has high energy requirements because of the EDC distillation.
- **High temperature chlorination** in which the reaction is operated above the EDC boiling point (above 90°C). The EDC leaves the reaction section as a vapour, and it may be possible to send it directly to the EDC cracking unit, thus obviating the need for washing. Energy may also be recovered from the hot vapour stream.

Both processes generate residues (impurities and iron catalyst), and an overhead off-gas vent that needs to be treated prior to emission to the atmosphere.

Oxychlorination of ethylene

This process produces less pure EDC, but it provides a HCl sink, using up all HCl is generated in the cracking step, thereby realising the balanced process.

In oxychlorination, EDC and water are formed by the gaseous phase reaction of HCl, ethylene and oxygen over a copper-salt catalyst at 220–250°C and 2-6 barg. The reaction technology can either be fixed or fluidised-catalyst bed. Fluidised bed reactors have better temperature uniformity and lower operating pressures and temperatures. The reaction is highly exothermic and temperature control is important to minimise the formation of undesirable by-products. The heat of reaction is recovered by surface cooling to generate steam.

The HCl input is recycled from the EDC cracking unit and from VCM purification, but external sources of gaseous, dry HCl with a suitable purity can also be used.

The oxygen source can be ambient air, or oxygen, or a mixture of both.

The reaction products are separated from the inert gas-flow by cooling and condensing at decreasing levels of temperature. Further separation of residual EDC from the inert gas mixture may be appropriate using adsorption or absorption, and this captured EDC can be recovered by stripping.

After quenching and condensation, water and EDC (with other organic chlorinated hydrocarbons) separate naturally into two phases since EDC and most of the other chlorinated hydrocarbons have a low solubility in water. Typical exceptions are chloral or chloro-ethanol, which accumulate in the water-phase.

Dioxin and dioxin related compounds are formed in the oxychlorination reactions as oxygen, chlorine and an organic precursor are all present at high temperatures in the presence of a catalyst. However, these quantities are not emitted into the environment since further control measures allow the emission limits to be achieved.

EDC purification

EDC may arise from direct chlorination, oxychlorination, VCM purification recycle or external sources. All EDC must be to be purified since EDC pyrolysis may be susceptible to inhibition and fouling by trace quantities of impurities.

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Purification may entail:

- washing with water and caustic to remove traces of HCl, chlorine, entrained catalyst and some water-soluble organics. This is often integrated with the direct chlorination, especially if a low temperature chlorination process is used.
- azeotropic drying/light ends distillation in one or two columns, to remove water and chlorinated organic by-products with a boiling point lower than EDC.
- heavy ends distillation, to remove chlorinated organic by-products and tars with a boiling point higher than EDC. Pure, dry EDC is taken overhead the distillation column. Some EDC will be purged with the tars to ensure their mobility.
- further light ends and heavy ends processing to recover more EDC, to remove water from the light ends, or to separate the fractions useful as feedstock for other chlorination processes.
- a chlorination reaction to convert into heavies, those light products that would be difficult to separate from EDC using distillation.

This section generates gaseous vents that require treatment prior to release to atmosphere, and this typically takes place in a catalytic or thermal oxidiser, or in a multi-purpose incinerator where chlorinated hydrocarbons are converted to hydrochloric acid gas (HCl). The HCl is consumed in the oxychlorination section, or converted into an aqueous hydrochloric acid for use in aqueous effluent treatment. There is also a water phase effluent from the EDC azeotropic drying column that is sent to a wastewater stripper section.

EDC cracking

The production of VCM from EDC is achieved by a cracking reaction followed by quenching of the process gas stream. When subjected to thermal cracking at temperatures of approximately 500°C, purified EDC splits into VCM and HCl with conversion rates of 50–65%. Rapid cooling of the pyrolysis gases is of major importance for reducing the formation of tars and heavy by-products. Cold, recycled EDC condensate is often used as the quench medium.

The purity of EDC feed must be greater than 99.5 %w to reduce coke formation and fouling of the reactor. Coke build-up is periodically removed for disposal. The EDC feed must also be dry to prevent equipment corrosion by hydrogen chloride. The furnace is typically gas-fired.

VCM purification

After the cracking reaction, HCl and unconverted EDC are separated from VCM by two-stage distillation. Unconverted EDC is transferred back to EDC purification and recycled to the cracking furnaces. After an optional hydrogenation stage to remove any traces of acetylene, distilled HCl is recycled as feedstock to oxychlorination. Most of the volatile by-products are removed via the HCl flow to oxychlorination.

Liquid VCM product is transferred to storage after an optional step to remove the last traces of HCl. No gaseous emissions are generated in this section and there are only minor quantities of waste (e.g. spent hydrogenation catalyst, and spent alkaline agent for VCM neutralisation).

Storage and loading/unloading

EDC/VCM production operations can include storage facilities for crude and purified EDC, light and heavy by-products, HCl, and VCM. These are designed and maintained to prevent soil, air and groundwater pollution caused by leaks.

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- EDC and chlorinated by-products are stored generally in atmospheric tanks at ambient temperatures and are usually blanketed by an inert gas.
- VCM storage is in spheres or tanks that can either be under pressure at ambient temperature, or refrigerated at approximately atmospheric pressure.
- storage of liquefied dry HCl is generally in closed system pressurised vessels at low temperatures.
- loading and unloading facilities generally have back-balance arrangements, between the storage and the road or rail tank and ship, to reduce emissions. Dedicated VCM liquid lines and return vapour lines remove the need for maintenance by pigging or frequent decontamination. Coupling connections are also purged prior to opening.

Integrated environment protection units

The following abatement units are frequently used on EDC/VCM plants:

- miscellaneous vent condensers/vent absorbers/vent adsorbers, for any vents not connected to the oxidiser.
- gaseous vents thermal or catalytic oxidiser, with HCl absorption system.
- wastewater stripper (using steam or air) with associated hydrolysis of chloral.
- wastewater treatment, with sludge separation.
- acidic effluent neutralisation.

The organic residues are in some cases re-used as feedstock for chlorinated solvents processes. Otherwise, they are incinerated either on the EDC/VCM production site with hydrogen chloride recovery or incinerated off-site.

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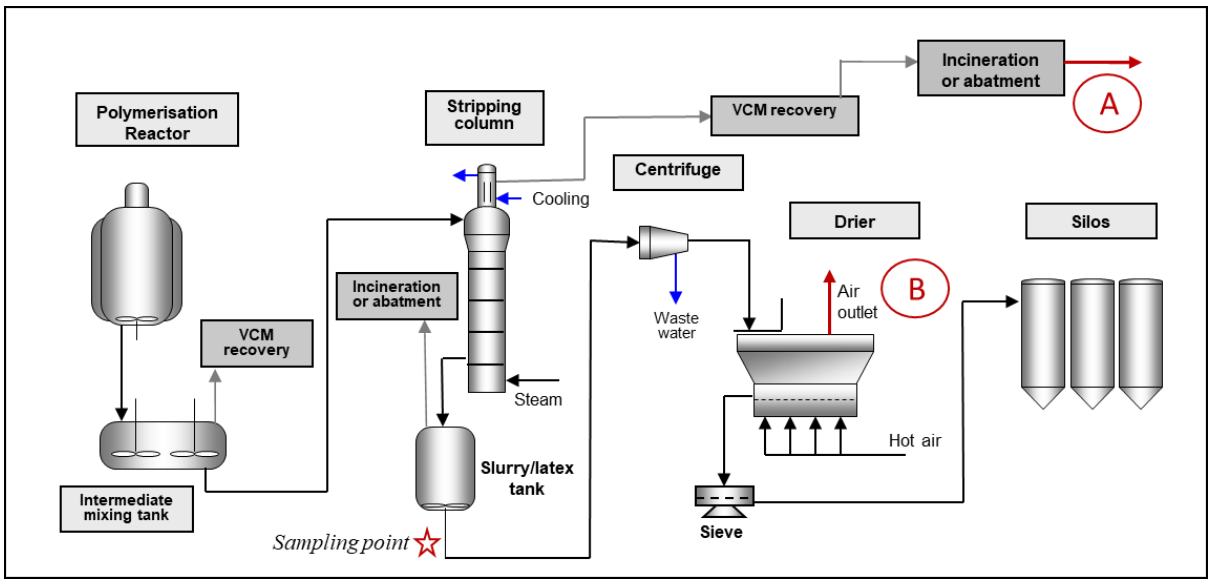
Annex 2: PVC Manufacturing Processes

Common features

At the beginning of any polymerisation, the reactor is charged with water, some other additives and monomer.

The polymerisations are exothermic, thus the reactors must be equipped with cooling facilities. The pressure in the reactor is usually in the range of 4-12 bar and the reaction temperature in the range of 35-70°C. At the end of the reaction 85-95 % of the VCM is converted into PVC. Temperature control is essential, as it determines the length of the polymer chains. Due to the moderate reaction temperatures, effective cooling requires using refrigerated water.

At the end of the reaction, non-converted VCM is vented-off to a gasholder or straight to a VCM recovery unit, before stripping operations. The objective is to reduce the pressure close to atmospheric. This removal of non-converted monomer can be performed either in the polymerisation vessel itself, or in a blow-down tank.



Suspension PVC process

In the suspension PVC process, the aim is to produce a suspension of PVC particles having a mean particle size between 50 and 200 µm. Besides particle size the essential differences between S-PVC grades result from the average length of polymer chains and from the porosity of the particles. Suspension PVC is always produced batch-wise in a stirred reactor.

The monomer is dispersed in demineralised water through the combination of mechanical stirring and surfactants. The polymerisation takes place inside the VCM droplets under the influence of VCM-soluble initiators. A phase of solid PVC primary particles builds up. The PVC particles present at the end of the polymerisation result from the complex aggregation of such primary particles, giving to S-PVC its characteristic cauliflower aspect under an optical microscope.

During polymerisation, some polymer tends also to be formed on the reactor wall. Technological improvements now allow to limit this formation, so that it is no longer necessary to open the reactor after every batch for visual inspection and mechanical cleaning if necessary. In this so-called closed

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reactor technology, the frequency of reactor opening can be reduced to levels below once in 100 batches or even less, depending on the grade.

Emulsion PVC processes

In the emulsion processes, the aim is to produce an aqueous latex with the PVC having a mean particle size (by weight) of between 0.1 and 3 micrometers.

E-PVC is manufactured by essentially three polymerisation processes: batch emulsion, continuous emulsion and microsuspension. E-PVC is typically mixed with plasticisers to a liquid paste known as a plastisol. All these processes are used to produce a range of latex particle size distributions and thus plastisol rheologies. Different paste applications demand different rheology profiles.

In the **batch** emulsion process, the VCM is dispersed using an emulsifier. The polymerisation takes place at the VCM water interface using a water-soluble initiator. This type of process produces a narrow width unimodal latex of small size (approximately 0.2 μm).

In a variation of emulsion polymerisation, the process can be operated **continuously**, in which fresh VCM, emulsifiers and initiator are fed into the reactor and PVC latex is withdrawn continuously. Such processes tend to require greater quantities of emulsifiers than the batch process. They produce latexes with a wide particle size distribution.

An alternative approach for producing a latex with a wide particle size distribution is **microsuspension** polymerisation. In this process, an initiator is used which is highly soluble in the VCM, but is essentially insoluble in water. Polymerisation takes place within the dispersed VCM droplet. The water insolubility of the initiator also helps to stabilise the VCM droplet, and it may be possible to use lower levels of emulsifier compared with the batch emulsion and continuous emulsion processes.

Stripping

Residual VCM is removed by stripping the polymer suspension or latex. This section may include unstripped suspension/latex storage tank(s). The stripping typically uses the effects of steam/nitrogen/vacuum (alone or in combination), and temperature. The process can be performed in different ways:

- **batchwise -** either inside the reactor itself or in a separate vessel.
- **continuously -** outside the reactor.

The stripping must be operated in such a way that the latex remains stable, and neither coagulates nor flocculates. The latex is sensitive to temperature, to agitation and to residence time.

The VCM content of S-PVC after stripping is normally very low. In the case of a latex, the stripping is more difficult and residual VCM content depends on a variety of parameters, for instance: the emulsifier content and type, the latex particle size, the latex stability, recipe and the resin end-properties requirement.

When steam is used for stripping, the overhead steam containing recovered VCM is condensed. The condensate can be returned to the stripping system, or be transferred to the water stripper of the effluent treatment or other sections of the process, in order to recover the contained VCM and thus to prevent VCM emissions from this effluent.

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In all cases, the non-condensed overhead gas containing stripped VCM is collected in a recovery unit.

Before drying, suspension or latexes can be concentrated. For suspension this is usually done through dewatering in a centrifuge. For a latex, it will depend on its stability and concentration on leaving the reactors. Concentration can be achieved by using a membrane or an evaporator.

Drying

Drying is achieved by a combination of temperature and air flow in dryers of various designs. The first drying for S-PVC is often dewatering by centrifugation, yielding a wet cake.

Regarding E-PVC, the small particle sizes of the latex, and the impossibility for most particles to be separated from the water phase, make it necessary to evaporate the water, except in a few special processes where the latexes are coagulated and centrifuged. The latex is usually dried in a spray-drier. During the spray drying, water is evaporated and removed.

Drying conditions have a profound impact on particle morphology and can be used to produce either paste or general emulsion polymers from the same reactor product. In the spray drier, the latex particles of approximately 0.5 µm in size, that stick together into secondary particles of approximately 30 µm mean diameter.

Sieving / Grinding

After drying, S-PVC is usually sieved to remove coarse particles which could cause problems during transformation. E-PVC is classified and ground if required for the end application. Polymers for paste applications normally are ground, those for general emulsion applications are not.

The end product from suspension or emulsion PVC is bagged or transferred to storage silos for bagging or bulk transportation.

VCM recovery

The VCM-containing flows vented from the autoclaves after reaction, released during suspension or latex stripping, vented from unstripped suspension or latex stock tanks and released from the wastewater stripper are transferred to the condensing section of a VCM recovery system. The condensers in the recovery system can be cooled by a multistage combination of normal plant cooling water and refrigeration. The efficiency of VCM recovery is determined by the correct combination of low temperature and increased pressure. In batch polymerisation processes, the gas flow to the VCM recovery plant will fluctuate and a gasholder to buffer these flows is often used.

To limit emissions, vents leaving the recovery plant should pass through a VCM chemical absorption or adsorption unit, a molecular sieve, an incinerator or a catalytic treatment unit.

After recovery, the VCM is held in a holding tank under pressure or refrigeration. The recovered VCM is either returned to the plant from which it arose, or a neighbouring plant, to be used in the polymerisation process together with virgin VCM.

Water treatment

Where manufacturing plants for the polymerisation of E-PVC and S-PVC are located side by side, it is common for them to share the same water treatment facilities.

Any water which may be contaminated with VCM, for example water used for the washing of VCM containing reactors, transfer lines and suspension or latex stock tanks, must be passed through a

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water stripper to remove VCM. The removed VCM is sent to the Recovery Plant, the aqueous effluent to a water treatment facility.

The effluent containing solid PVC is sent to a water treatment plant for solids removal. Such plants are often two step processes. In the first the PVC in the water is flocculated using proprietary coagulating agents. The clear water either goes to drain or for reuse on the plant, the coagulated solids are removed either by thickening and sedimentation in the second chamber, or by dissolved air flotation. The clear water leaving the second chamber is frequently returned to the first chamber for additional treatment. Such processes also have the effect of reducing the overall organic content (COD) of the effluent.

Alternatively large sedimentation pits or lagoons may be used. These must be sufficiently large and the percentage flow rate of water sufficiently low, to ensure that adequate sedimentation and separation does occur.

Annex 3: Dechema Corrosion Handbook (hydrochloric acid)

Hydrochloric acid.pdf

Annex 4: Chemical and Temperature Resistance of Fluoropolymers vs. Other Plastic Materials.

AUSIMONT.pdf

Annex 5: Fluoropolymer Lining for a Chlorine Scrubber

Fluoropolymers for chlorine scrubbers.pd

Annex 6: Metal Material Resistant to Hydrochloric Acid

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