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To:

European Chemicals Agency (ECHA)

Subject:

Derogation request for exemption of "ultrashort-chain fluorocarbon C3F6 in low pressure plasma coating processes" from the PFAS restriction proposal

24th of August 2023

Dear Sir/Madam,

I am writing to submit a derogation request on behalf of NW BV to the European Chemicals Agency (ECHA) concerning the use of a ultrashort-chain fluorocarbon C3F6, in combination with low pressure plasma coating processes. We kindly request the exemption of this specific application from the PFAS restriction proposal as stated under the ANNEX XV RESTRICTION REPORT.

NW BV, commercially active under the name nanoWatt, is a prominent player in the development and manufacturing of low-pressure plasma coating equipment, committed to environmental sustainability and adhering to all relevant regulations and directives set forth by the European Union. Our research and development team has worked extensively to identify viable and eco-friendly alternatives to hazardous chemicals often used in the industry.

In certain applications however, the use of fluorocarbons remains an essential and irreplaceable component for achieving the desired performance and product quality, especially when it comes to depositing coatings possessing oleophobic properties.

In low-pressure PACVD (Plasma-assisted Chemical Vapor Deposition) processes, the material or substrate to be treated/coated is placed in a vacuum chamber. After the air has been evacuated from that chamber, a precursor gas or vapor is introduced into it. Subsequently, this gas or vapor is brought into an ionized state (=plasma) by applying an electro-magnetic field to it. These ionized species polymerize on the surface of the material to be treated, thus forming a nano-coating. These plasma-polymers are generally highly branched and highly cross-linked, and adhere well to solid surfaces. giving less chance to delaminate during application.

Using these processes, it is possible to deposit a very thin nano-coating on substrates, where the properties of the coatings are determined by the used precursor (source material which can be a liquid or a gas), the system's design and the defined parameter settings for plasma generation.

Low-pressure PACVD systems and processes are used in many sectors, such as filtration, technical mesh and membranes, consumer textiles (apparel), medical plastics, industrial and consumer electronics.

Some of the applications in the beforementioned sectors, as well as other applications in other sectors which are currently not using low-pressure PACVD, require an **oleophobic** behavior.

Following the restriction on PFOA/PFOS containing substances and the subsequent restriction on PFHxA containing substances and longer chain C9-C14 PFCAs, nanoWatt invested substantially in the development of mainly halogen-free alternatives, but also in the use of the ultrashort-chained fluorocarbon C3F6, the latter for those applications having the expressed need for **oleophobicity, indispensable to the application** (and for instance not for use as DWR treatment).

Although the achieved level of oleophobicity, using this gas as a precursor, is in general lower than when applying long-chain fluorocarbon precursors, it has shown to be sufficient for targeted applications, using the low-pressure PACVD technology.

The grounds for our derogation request are as follows:

1. Scope or restriction options analyses

The use of fluorinated species is indispensable in certain coating applications requiring explicit oleophobic functionalities. Some of these applications have already been listed in the restriction proposal Annex XV as proposed exemptions.

Derogation for C3F6-based PACVD processes

NW requests an exemption for the use of C3F6 as precursor in combination with a low-pressure plasma-assisted chemical vapor deposition process for all applications where **oleophobicity** is an explicit property for the application.

This is the case for, among others, following materials:

- Technical woven mesh
- Non-woven filter material and electrets
- High-performance membranes
- Textiles

Used in, among others, following applications or products:

- Filtration material for graphics, medical, automotive, food, pharma, aerospace, mining & refining, architecture (acoustic vents, ventilation filters, room ventilation,...) and electronics
- PPE apparel
- Medical textiles (including in-situ used materials) like wound dressings, protective masks, surgical coats,...
- Medical devices (intravenous filter sets, pipets,...)
- Electronic devices: mobile phones, portable media players, high fidelity equipment, tablets, laptops, portable devices and televisions.
- Liquid filtration (fuel filtration, water separation, pressure filtration equipment,...)
- Packaging
- Venting (matrasses, beddings, venting barrier media for industrial applications)

The use of this specific coating method to form fluoropolymer nanocoatings is very environment-friendly for several reasons:

- The processes are dry, the precursor material is used in the gas phase in order to apply the coating.
- The process gases are fully contained in a vacuum vessel, the only emission of such system is through the outlet of the vacuum pump, where point-of-use abatement systems can be employed in order to treat/catch potential unwanted species.
- Only a very small amount (flow) of pure precursor is needed in order to apply the ultrathin coating and generate the required properties.
- Seen the absence of air or pollutants in general, the deposited coating is very pure and will not only be applied superficial, but also towards the core of the material, this way creating functionality with only a few tens of nanometers coating thickness.
- No need for post-processing of plasma coating is required: drying, sintering, compounding, postreaction, crosslinking etc.

Limitation of the proposed exemptions

Some of the applications already listed in the restriction proposal Annex XV as proposed exemptions, are already using ultra-short chain fluorocarbons in combination with low pressure plasma assisted chemical vapor deposition processes to obtain nano-coatings having **oleophobic surface functionalities**.

NW requests a limitation for those exemptions to the use of C3F6-based low-pressure PACVD for the cases where it offers a working solution.

Other methods to deposit fluoropolymer coatings often require not only fluorine containing monomers but also fluorinated production aids, such as polymerization catalysts, surfactants, emulsifiers, additives and dispersion aids. In contrast to PECVD processes, wet-chemical processes require a thicker coating to ensure the coating uniformity and functionality (micron to mm thick). These wet chemical processes produce a significant amount of PFAS containing liquid waste.

2. Hazard or exposure

The likelihood of exposure to C₃F₆, and any possible hazard related to this, is very limited when being used in low-pressure plasma-assisted chemical vapor deposition processes. The gas is used under vacuum as a precursor material in the manufacturing of fluoropolymer nano-coatings. The gas is fully contained in the vacuum chamber and is lead over the vacuum pump to a well-positioned exhaust point, thus avoiding any possible interaction with people. The amounts of gas used are very limited. If 100% of the injected gas would be exhausted (which is obviously not the case, though no exact figures exists, the purpose of the process is to polymerize the gas onto the substrate as a plasma fluoropolymer), this would be 0,012m³/h for a typical machine. The exhaust stream can also be perfectly abated with efficiencies reported over 99%, in order to further limit exposure to the exhausted species.

See attachment 1: document about abatement example.

The resulting plasma-polymer coating is extremely thin, highly branched and cross-linked and adheres very well to the substrate, this way limiting exposure throughout the lifetime of the product by release of species.

The species contained in the coating are in line with the Oeko-Tex® 100 standard, see attachment 2: analysis report (confidential).

In contrast, the wet finishing methods are environmentally unfriendly multi-steps processing, that consume large amounts of chemical substances, generating hazardous chemical wastes and toxic emissions in air/water/soil with high chemical oxygen demand (COD), imposing expensive purification treatments and government permissions to eliminate or neutralize noxious residues by multiple cleanings with consequently large quantities of water and energy consumed.

Development of a dry resource-efficient process that dramatically reduces or eliminates the use of water (up to 100%) and consequently, energy consumption and CO₂ emission of at least 20% along the overall value chain.

3. Environmental emissions

During the last few years environmental legislation forced the textile industry to address concerns about the possibility to change current textile manufacturing methods to processes with greater efficiency and a lower environmental impact. At this respect, the main issues of the textile industry are the high consumption of chemicals, water and energy, the generation of huge amounts of toxic effluents and greenhouse gases.

Chemical finishes by conventional methods (padding & subsequent thermal fixation) are not environmentally friendly since a huge amount of water and chemical products are used, and a lot of energy is required for thermal curing and to evaporate the water.

The most important issue related to long chain fluorocarbons ($\geq C_6$) used in traditional finishing is their environmental and health threat. The presence of PFOS and PFOA, combined with their persistence, toxicity, and bio-accumulative potential, makes these chemicals a particular concern.

The energy consumed in traditional wet chemical processes for hydro- or oleophobic textiles is almost triple in comparison with physical methods such as plasma treatment. According to data provided by FP7 ACTECO project, the energy used to obtain oleophobic materials by wet chemical process is around 25.7 MJ/functional unit while by plasma process the consumption is only 7 MJ/functional unit. Important quantity of wastes and consequent emission of ecologic unfriendly effluents are generated during these wet-chemical treatments contributing to the global warming (Table 1). As the developed plasma deposition process is very similar to that of plasma deposition process used in the ACTECO project, we expect similar results for C_3F_6 process.

Table 1. Environmental burden generated by oleophobic/hydrophobic textiles treatments (http://www.acteco.org/Acteco/public/results/LCA_oleophobic_PET_public.pdf)

Treatment type	GWP (kg CO ₂)	AP (g eq SO ₂)	POPC (g C ₂ H ₄)	EU (g PO ₄ ³⁻)
Plasma oleophobic PET	0.40	1.22	0.19	0.26
Traditional oleophobic PET	1.67	2.36	2.81	0.76

GWP = Greenhouse effect (global warming); **AP** = Acidification; **POPC** = Photochemical ozone formation (Photo-smog); **EU** = Eutrophication

Low-pressure PACVD processes are known for their minimal use of precursor material. Calculation example for a C_3F_6 -based process : a machine, capable of treating material on roll having a width of 1 meter, operates at a speed of 2m/min, using a precursor flow of 200ml/min C_3F_6 . So, in order to treat 1m² of this material, 100ml C_3F_6 gas is used. This represents 0.004 mol or 0.6g of C_3F_6 .

A part of this amount polymerizes on the substrate, forming a plasma-fluoropolymer nanocoating. Another part does not polymerize and is exhausted. So far, the percentages have not been identified yet.



Emission factor to soil/water=0 for fluorinated gases, as stated on p228 AnnexB, so mainly emissions in the atmosphere could be of concern. Half-life threshold of C3F6 is 3.5 days and it's determined not to be bio-accumulative.

See attachment 3: "Environmental risk evaluation report: Hexafluoropropene [HFP]" and attachment4 "ECETOC JACC No. 48".

The quantities deposited on the substrate are minimal, almost negligible, and their impact on the environment is limited throughout the lifecycle of coated customer's products.

The usual recycling techniques, as already existing for untreated material, can be employed for treated material.

4. Baseline

5. Information on alternatives

Fluoro-compounds are widely used in all global industries, especially for water, oil and stain repellency, for example in the textile and machine industry. A replacement did not seem to be possible until now. Most of the effective fluoro-compounds are based on the fluorocarbons which contain chains of more than 6, 8 carbons. When applied via classical “wet-chemistry” these long-chain fluorinated polymers often contain residual raw materials and trace levels of long-chain perfluoroalkyl acids (PFAAs), such as significant amounts of perfluorooctanoic acid (PFOA), which is a hazardous substance of concern in Swiss and European chemistry restrictions.

Despite substantial efforts invested in research and development, suitable alternatives that comply with the proposed restriction have not yet been identified for specific applications requiring oleophobicity.

The unique characteristics of ultrashort-chain C3F6 fluorocarbon makes it exceptionally effective for the intended purposes, and we have not identified any substitutes capable of replicating the same performance and properties.

However, C3F6-based low-pressure PACVD processes do offer an environmental-friendly alternative to wet-chemical fluoropolymer processes

6. Information on costs

Advanced manufacturing system is the key success factor to being competitive for the manufacturing sector in Europe. C3F6 solution leads to flexible manufacturing, clean processes, and improved production processes with high throughput rates, reduced costs, to increase the competitiveness in a sustainable and energy-efficient way.

NW invests substantially in the development of low-pressure plasma deposition processes, with the aim to offer environment-friendly alternatives to wet-chemical processes. Therefore, it's essential to distinguish between the low-pressure PACVD process and other processes, in order to enable this technology to gain market share and see the benefits fully reflected in the environment.

The low-pressure plasma technology requires a higher capital expenditure compared to other technologies, but gains this back during use by the much lower consumption of base material, lower energy consumption and the absence of high waste volumes.

In case this distinguishment is not made when defining derogations for certain applications, it will lead eventually to a stop in further development and a possible disappearance of the low-pressure PACVD technology for these purposes, thus limiting further development of environment-friendly deposition techniques.

7. Information on benefits

As company driven by development of environmental friendly technologies, we are supporting new legislation aiming to reduce the use of and exposure to harmful substances. We believe that technologies limiting the amount of needed source material and the amount of waste should get special attention though, as they can be key enablers to get polluting technologies replaced.

The scaling potential is extremely large, as the C₃F₆ solution addressed cross-KET (key enabling technologies):

- Nanotechnologies: by creating materials and devices on nanoscale with the involvement of plasma deposition processes for the manufacture of filtering materials.
- Advanced materials: introduce new functionalities and improved properties in filtering materials, while adding value to existing products and processes, in a sustainable approach.
- Advanced manufacturing systems: overcome the problems of the currently available technology for achieving repellence on textiles, such as: water-based methods/toxic resources, poor adhesion of the thick coating/excessive amount of deposited chemicals and, consequently, high environmental impact, high cost due to the extensive thermal energy consumption in the curing step.

The new solution will overall lead to new products and services, capable of enhancing human health, while conserving resources, energy and protecting the environment:

- No air pollutants such as HF/NO_x, thanks to vacuum closed reactor and use of a dry scrubber installed in the exhaust line. Traditional processes involve high emission of pollutants contributing to the total global warming.
- Low raw material consumption (about 60%), thanks to high density nanoscaled coatings.
- Reduction of energy and chemical consumption by replacing the traditional wet chemical padding process.
- 100% elimination of water and soil pollutants.
- Contribution to circular economy, since the coated polyester fabrics can be recycled.

8. Other Socio-Economic Analysis (SEA) issues

Low-pressure PACVD equipment and its associated processes require a high initial capital expenditure, which often forms a hurdle to implement this environment-friendly technology.

Although the advantages compared to wet chemical processing (much smaller amount of base material (precursor) usage, low energy consumption, low waste volume) result over time in an -at least- equal cost, it's nowadays mainly implemented only by the so-called early adopters.

Next to reasons of keeping the status-quo or shorter term visions or objectives, also the high tech aspect of this technology and the possible impact on needed (technical) profiles to operate and maintain the equipment is a, mainly psychological, hurdle.

Exempting this technology as requested, would give the opportunity to convince companies about its potential and enable a further roll-out to other (non-PFAS) processes, where the same advantages apply as well:

9. Transitional period/deferred entry into force

It's very unlikely that in the projected derogation periods of 5 or 12 years for certain applications, a solution will be found to totally avoid the use of PFASs in applications where oleophobicity is needed. Therefore we ask for an exemption unlimited in time for low-pressure chemical vapor deposition using C3F6, in order to be able to provide the best available solution for those applications in need.

10. Exemptions

Exemption is asked for:

The use of C3F6 gas as a precursor in low-pressure plasma-assisted chemical vapour deposition, in order to produce plasma fluoropolymer nanocoatings on products where an oleophobic property is indispensable for the product.

In light of the reasons stated above, we earnestly request the ECHA to grant a derogation for the use of ultrashort-chain fluorocarbon gas C3F6 in combination with low pressure plasma assisted chemical vapor deposition coating processes, specifically for applications needing oleophobic properties.

We assure that we remain fully committed to continuous research and development aimed at identifying sustainable alternatives that comply with all relevant regulations.

We appreciate the ECHA's dedication to promoting the safe and responsible use of chemicals within the European Union.

Granting this derogation will allow us to maintain our competitive edge while we continue to explore environmentally friendly solutions for our industry.

Thank you for considering our request. We are open to any further discussions or providing additional information as required.

Please feel free to contact us at [REDACTED] [@nanowatt.eu](mailto:[REDACTED]@nanowatt.eu) or +32476494905.

Sincerely,

Marc Sercu
General Manager
NW BV (nanoWatt)