Imaging and Printing Association

I & P Europe

Contents

The non-confidential version has 30 pages
The confidential version has 32 pages

Introduction

To Introduce I&P Europe

I&P Europe – Imaging and Printing Association is a European association of product manufacturers and technology providers for the imaging and printing industry. I&P Europe members' products include conventional and digital materials and their processing solutions. The product portfolio of the membership includes in particular consumables such as inks for digital printing applications, toners, pressroom chemicals, printing plates, photographic mixtures and films as well as equipment products such as printers, printing machines etc..

I&P Europe strives for working together with competent authorities in Europe and at the supranational level in the Stockholm Convention.

I&P Europe wishes to emphasize that from an environmental and health perspective, our organization is fully committed to the replacement of PFAS in imaging and printing products.

I&P Europe - Imaging and Printing Association e.V. is pleased to participate in the public consultation on the PFAS Annex XV dossier.

The present submission is addressing the use of PFAS in photosensitive materials.

Background information

Introductory background information that situates I&P Europe in the context of the PFAS dossier.

I&P Europe has a long history of involvement in the regulatory PFOS/PFOA dossiers and in the subsequent related dossiers including PFBS / C4-C7 short chain PFAS / PFHxS / C9-C14 long chain PFCAs / PFHxA and the current comprehensive PFAS dossier, dating back to the early days of the initial PFOS dossier.

Throughout this period, I&P Europe has been striving to cooperate with competent authorities in Europe and at the supranational level in the Stockholm Convention and continues to do so.

Also member companies of I&P Europe actively and consistently pursue further elimination of these substances where possible, thereby demonstrating their commitment to act as a responsible industry, a fact we think adds to the credibility of the I&P Europe trade association.

- The PFOS dossier provides an excellent example because also in the past years when PFOS, listed in Annex B of the Stockholm Convention, still had photo imaging specified as an acceptable purpose, further elimination of its use in remaining photographic applications was successfully pursued to the point that it has been reduced to below regulatory limits in photographic materials and is planned to be fully eliminated by 2024.
- Also in the PFOA dossier I&P Europe at the POPRC-14 meeting (Persistent Organic Pollutant Review Committee of the Stockholm Convention) voluntarily narrowed down its request for a specific exemption to include only photographic coatings applied to films, which was reflected in the decision on PFOA by the Conference Of the Parties on its COP-9 meeting in May 2019. In turn the derogation for photographic coatings as foreseen in the "draft Commission delegated Regulation (EU) amending Annex I to Regulation (EU) 2019/1021 of the European Parliament and of the Council as regards the listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds" is therefore also limited to "photographic coatings applied to films, until 4 July 2025". I.e. the reduced scope of the derogation for photographic coatings in the draft EU Regulation stems from a voluntary call by I&P Europe to narrow down the scope of this specific exemption, made possible as a result of sustained commitment and research by its member companies.

Once again we were able to reach out to the member companies of I&P Europe Imaging and Printing Association in preparation of the current public consultation on the proposed restriction of PFAS and can therefore herewith provide a contribution based on newly updated feedback from member companies.

The last survey of our member companies in relation to PFHxA showed that the materials where PFHxA-related substances are currently used not only include some remaining photographic films but also some printing plates for which in the process of looking for alternatives for C8-related substances (i.e. PFOS or PFOA related) until now only PFHxA-related substances proved to be acceptable.

In addition, this has now also been reported in the context of the current comprehensive PFAS dossier under consideration.

The search towards alternatives for perfluorinated C8 substances or fluorinated telomer based C8 substances in photographic coatings applied to films and in printing plates typically involves a "hierarchy of preferred substitutes" with non-fluorinated hydrocarbon alternatives being preferred, followed by non-perfluorinated substances, further followed by perfluorinated substances with ultra-short chain lengths (C3 or C4), then by perfluorinated short chain alternatives (C5-C7) and only if no other alternatives have been found, the use of C8 is continued until applicable transition times expire in order to then discontinue them completely.

Sustained research did result for some applications in finding combinations of two or more hydrocarbon substances demonstrating a super-additive effect that resulted in performance characteristics comparable to PFOS/PFOA.
There are also some critical photographic materials and some printing plates for which extensive research to find alternatives for PFOS or PFOA related substances resulted in so called "regrettable substitution" including the use of PFHxA related substances, shorter perfluoroalkyl substances or other PFASs.

PFOS/PFOA's – and replacement PFASs that have been used to substitute C8 PFASs – are essential for the application of coating layers during the manufacture of some remaining conventional photographic products, i.e. products in which the image formation is based on silver halide technology: they have multiple functions, serving (1) as surfactants, (2) as static control agents, (3) as dirt repellents during coating operations, (4) as friction control agents, (5) and to provide adhesion control of coated layers. At the customers' site, PFASs (1) ensure uniform interaction between the photoprocessing chemicals and the film and (2) prevent customer dissatisfaction, such as water stains and dust on film surfaces after photoprocessing.

PFASs used are unique in that they provide the combination of all these properties in one molecule, without any adverse effects on the colloidal stability of the photographic emulsion or on the photographic performance of the end product.

It should be noted that these findings resulted from sustained elaborate and often product specific research the results of which are clearly in the domain of confidential business information and are as such not shared between member companies of I&P Europe.

This process has required extensive resources over a period of more than 10 years to find – on a case by case basis for many different photosensitive materials – suitable alternatives, do the prototyping and ultimately the development to commercial products and introduction on the market.

Given the specific challenge of achieving the combination of all the necessary properties in photosensitive materials without the use of fluorinated compounds, the complete removal of PFASs is certain to require a long development time. To replace all PFASs in these photographic coatings on film and in printing plates will require further sustained research and in order to do so a derogation allowing an extended transition time of 5 years will still be needed when imposing restrictions on PFAS.

Problem analysis

Specific applications in photosensitive materials for which the use of PFAS compounds is essential and for which the knowledge around the underlying functional requirements is only available at the manufacturer of the photosensitive materials, not at the PFAS producer.

There are certain specific instances of PFAS use that are unique to photosensitive materials and for which the knowledge and know-how concerning the underlying functional requirements is limited to the manufacturers of the photosensitive materials

Certain PFAS compounds are necessary and even essential in photosensitive materials because they possess the right combination of properties to meet functional requirements that are very specific to photosensitive materials.

In a number of cases, it is anticipated that PFAS-free alternatives can be found and deployed in a timely manner within the projected timeline of the PFAS restriction proposal.

However, for some applications in photosensitive materials, this is not the case and a longer transition period of 5 years is indispensable to safeguard the production of state-of-the-art photosensitive materials.

The manufacturers of the PFAS ingredient or the PFAS-containing component do not have the information as to why that PFAS is suitable or state-of-the-art for certain specific applications in photosensitive materials and have no knowledge as to which non-PFAS alternative may or may not work as a substitute and for what fundamental underlying technical reason.

For this reason, I&P Europe developed the present contribution addressing the use of PFAS in specific applications in photosensitive materials and submits it to the the public consultation on the PFAS Annex XV dossier.

Scope

Photosensitive materials for which the use of PFAS compounds is essential and for which PFAS free alternatives are not (yet) available.

The use of PFAS in remaining critical applications in the imaging sector is very specific and it is difficult to classify these into one of the use sectors included in the Annex XV dossier for PFAS.

I&P Europe therefore proposes to add an additional use sector "photosensitive materials" to include as sub-uses photographic AgX technology based coatings on film and plates on the one hand and coatings for offset pre-press applications on the other hand.

A very brief description of the proposed use sector "photosensitive materials" and its sub-uses is given immediately below. In separate "supporting information" sections later in this document and in the confidential appendices to this document, the technical function of PFAS is described in detail and detailed information is provided on (the lack of) alternatives, the time required for substitution with non-PFAS compounds, the cost of substitution, the CASNr and tonnages of the PFAS used, emissions to the environment and measures to minimize release into the environment.

1. Examples of photosensitive imaging materials based on conventional silver halide (AgX) technology include e.g. photographic films (such as color negative films, color reversal films, instant photo films and black/white films), graphical films, films for aerial photography (including military applications), medical imaging films (X-ray films), mammographic film for breast cancer diagnosis, films for non-destructive testing (NDT).

   Remaining uses of PFAS compounds are necessary - and even essential - in photosensitive materials because the PFAS compounds used possess the right combination of properties to meet functional requirements that are very specific to photosensitive materials.

   PFASs used have multiple functions, serving (1) as surfactants, (2) as static control agents, (3) as dirt repellents during coating operations, (4) as friction control agents, (5) and to provide adhesion control of coated layers. PFOS/PFOA's are unique in that they provide the combination of all these properties in one molecule, without any adverse effects on the colloidal stability of the photographic emulsion or on the photographic performance of the end product. At the customers' site, PFASs (1) ensure uniform interaction between the photoprocessing chemicals and the film and (2) prevent customer dissatisfaction, such as water stains and dust on film surfaces after photoprocessing.

   In some instances, it is anticipated that PFAS-free alternatives can be found and deployed in a timely manner within the projected timeline of the PFAS restriction proposal.

   However, for a number of photosensitive materials, this is not the case and a longer transition period of 5 years is indispensable to safeguard the production of state-of-the-art photosensitive materials.

2. With coatings for offset pre-press applications we refer to the lithographic printing plates (offset plates), where we can make a distinction between, on the one hand, the long-established printing plates that are developed after exposure (various forms of wet processing are possible here, ranging from conventional chemical processing over "low-chem" processing to "chem-free" processing) and, on the other hand, completely process-free, i.e. processless printing plates that became available relatively recently

   Process-free or processless lithographic printing plates have been developed with the intention of reducing the environmental impact of printers. Progress has been made in converting wet process customers as the plate features of the processless technologies are improved to be comparable to the existing wet process plates. Comparable performance of the key feature of machine readability has only been achieved using a PFAS material, more specifically a trifluoromethylsulphonate-group based colour former, a specific dye type incorporating a triflate group ($-SO_2-CF_3$) .PFAS-free alternate colour systems with comparable performance are not yet available and require additional R&D necessitating a transition period of 5 additional years.

The demand

A transitional period that is extended to 5 years after entry into force of the restriction for the use of PFAS in photosensitive materials.

In some cases, it is anticipated that PFAS-free alternatives for uses in photosensitive materials can be found and deployed in a timely manner within the projected timeline of the PFAS restriction proposal.

However, for some specific applications in photosensitive materials, this is not the case. Moreover, for certain specific applications the development (R&D) and implementation of PFAS-free alternatives cannot be achieved within a 5 year additional derogation period. Therefore a longer transition period of an additional 5 years is indispensable to safeguard the production of state of the art photosensitive materials.

PFAS can currently not be replaced in photosensitive materials including remaining photographic AgX technology based coatings on film, paper and plates on the one hand and coatings for offset pre-press applications on the other hand.

The following text is proposed for specific derogations:

By way of derogation, paragraphs 1 and 2 shall not apply to:
a. fluorinated compounds in photographic AgX technology based coatings on film, paper and plates until 6.5 years after EIF. **b. fluorinated compounds in offset pre-press applications until 6.5 years after EIF.**

Supporting information

With respect to the use of PFAS in critical applications in remaining photosensitive materials requiring a transitional period of 5 years after entry into force, in the following dedicated "supporting information" sections as well as in the confidential appendices to this document, detailed information is provided on: - technical function of the PFAS - information on (lack of) alternatives - required timing on replacement - cost of substitution - CASNR or chemical name of the PFAS substances used - tonnages of PFASs used - emissions to the environment - measures to minimize release into the environment

For remaining PFAS uses in photosensitive materials including photographic AgX technology based coatings on film, paper and plates and coatings for offset pre-press applications, the above mentioned information items are provided in separate sections on the next pages.

Whenever information was flagged as CBI by submitting I&P Europe member companies that contributed to this document, it has been provided in one of the confidential appendices enclosed. For a specific item it is hence possible that some information is presented in more than one confidential appendix.

1. Photographic AgX technology based coatings on film, paper and plates

technical function of the PFAS

PFAS used in photographic film products have at least four functions (1) modifying surface tension to allow coating and manufacturability; (2) mitigate electrostatic build-up during transport in both manufacturing and in customer handling; (3) allow photoprocessing chemicals to uniformly interact with the film; and (4) avoiding customer dissatisfiers such as water marks and dust on film surfaces after photoprocessing.

Photosensitive materials contain gelatin as their main matrix. Gelatin is a unique protective colloid for silver halide (AgX) grains and plays an important role in multilayer coating, which is why it has been used for photosensitive materials for more than 100 years. Because of its triboelectric series characteristic, gelatin charges positively during film manufacturing, during transport in cameras or in photofinishing equipment. Once the charge has exceeded a certain degree, it sparks accompanied with emission of light, so called static light.
Silver halide (AgX) grains are very photo- or light-sensitive. Because of its photosensitivity, even weak light emission caused by static exposure can create several fogging issues on the materials. The static electric charge effect is a bigger problem for plastic substrates such as PET than for paper substrates. Immediately following this section, some images are given to illustrate fogging damage to photosensitive films caused by static exposure.
Electrostatic charge also causes dust contamination on the film, which harms the image quality of photosensitive materials.

Photographic films are most basically defined by a flexible support structure, typically acetate or polyester, with multiple imaging layers on one or both sides of the flexible support. The multiple imaging layers are composed of an aqueous/gelatin matrix comprised of light capturing silver halide microcrystals and many other chemical substances including chemicals that are involved in the creation of permanent images. The number of layers can vary depending on the photographic product but is typically between 5 and 14 layers – some having as many as 18 thin individual layers containing up to 200 chemicals. During the coating process the chemicals in the individual layers may not mix or mingle. All this is what makes state of the art photographic films truly “high-chem” products in which PFAS – with its inherent combination of properties in a single chemical molecule – plays an essential role. The PFAS materials reside in the upper most overcoat (OC) layer that defines the air-liquid interface during the manufacturing coating operation.

Multi-layer films are created by delivering individual layer solutions through a series of slide slot-hoppers that flow off the hopper as a curtain and onto a moving support web. Combinations of surfactants, such as PFASs, are employed to modify, control, and maintain both the dynamic and static surface tension of the top-most layer during this curtain-coating operation. PFAS materials are uniquely capable of providing a significant reduction in surface tension while utilizing a relatively low quantity of material. A reduced surface tension is required to ensure layers wet the surface and spread evenly to avoid repellencies in the film layer and to promote layer thickness uniformity. This property stems from the presence of fluorine instead of hydrogen atoms in long aliphatic portion of the surfactant molecule making it less soluble in water and preferentially aggregating at the air-water interface. These PFASs stabilize the air-liquid interface during several physical transitions the film layers experience during manufacture. As the curtain initially drops toward the web, layer thinning occurs. As the curtain engages with the fast-moving web, shear thinning occurs. PFAS also reduces the propensity for edges of the coating to withdrawal by enhancing the ability of layers to spread. As the moving web enters both chilled temperature regions that set the gelatin and drying areas, with low-humidity, along the web path the physical characteristics of the film change as water is slowly removed and a dry film is formed. Throughout these transitions, the presence of PFAS assures layer integrity by avoiding repellencies or other physical breaks in the layer's construction.

The moving polymeric support can generate electrostatic build-up on the surface of the web due to contact with rollers, camera conveyance, and other machine elements. Photographic materials are highly susceptible to damage from light-exposure if there is a discharge of any electrostatic build-up. PFAS materials in the top-most surface are able to mitigate the electrostatic build-up as the film is conveyed through manufacturing operations and customer equipment.

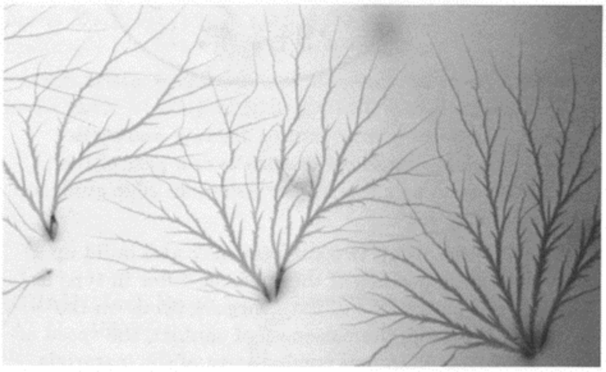
Once the photographic products have been exposed per the customer's application, the product is then photoprocessed to create a final image. Photoprocessing is composed of a series of aqueous chemical baths that swell the dried gelatin matrix, introduce a chemical developer, and finally wash away development by-products. PFAS is a key element of successful developer activity as it influences the developer spread characteristic and is related to how uniformly the developer solution wets and penetrates the surface of the film and diffuses through the film.

Lastly, during photoprocessing, PFAS materials provide surfaces that improve product performance and customer satisfaction. PFAS helps sheet away any residual chemicals or water adhering to the surface after the washing and drying of the processed film. Water marks are a customer dissatisfier and the surfactant properties of PFAS assist in reducing this issue. Lastly, the ability of PFAS to mitigate electrostatic build-up assists in reducing dust attraction to the surface.

Below are some images illustrating fogging damage to photosensitive films resulting from static exposure:

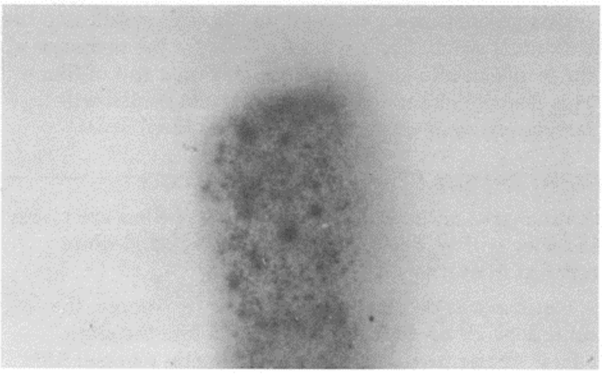
Branch Static

These branch-like markings are the best-known form of static. They occur under low-humidity conditions, such as inside heated buildings or outdoors in very cold weather. For instance, they might be produced inside a camera when a charge builds up on moving film and then jumps to the camera body. The tips of the branches point in the direction the film was traveling when the discharge occurred. This form of static is sometimes described as "forked lightning."



Moisture Static

This shows up as a fogged area on the film. Unlike other kinds of static, moisture static occurs in *moist* conditions, usually when you unwind a roll of film that has a high moisture content. The moisture encourages closer contact between film surfaces, which encourages static buildup. This type of mark is also called "blotch static."



Spot Static

Spot static shows up as small, isolated spots on the film—sometimes with a cloud around each spot. These spots occur when film is handled excessively or too rapidly during preparation for processing in low-humidity conditions, or when static builds up on a camera and then jumps to the film. Bar static is similar to spot static; it looks like a row of spots, often surrounded by fogged areas, running across the film from edge to edge. It can form when you unwind a tightly rolled roll of film.

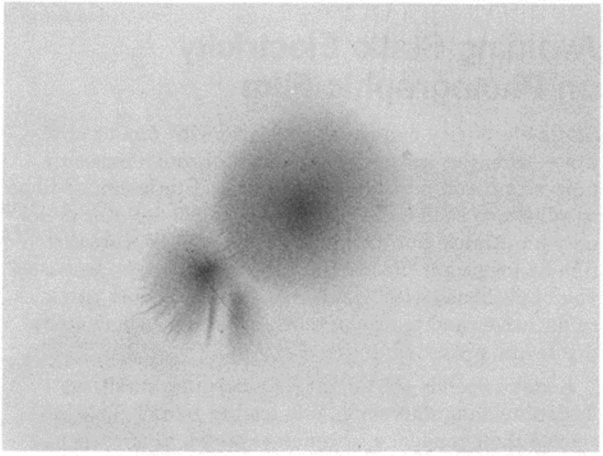


Figure. Fogging damages for photosensitive film caused by static exposure

Reference: Avoiding Static Electricity on Photographic Film, Kodak publication

Information from KODAK reference K-3, 1986

information on (lack of) alternatives

In order for alternatives to PFAS substances used in photographic coatings to meet the technical specifications for use in photographic coatings of photosensitive materials, they must provide the equivalent combination of properties referred to in the previous section “technical function of the PFAS”.

Most importantly any alternatives to PFAS substances used in photographic coatings must provide the equivalent combination of surface-active properties that include (a) static and dynamic surface tension characteristics to allow coating and manufacturability; (b) uniformity of photoprocessing results by controlling surface wetting; (c) lack photoactivity and thus do not interfere with the imaging process; (d) compatible with photo-retouching materials; (e) control splicing tape adhesion properties; (f) improve camera, projector, and printer transport to eliminate unwanted photographic effects and (g) prevent the build-up of particles that can clog magnetic strip readers.

The ability to control surface tension in imaging materials is a critical aspect of the use of PFAS substances as coating aids. In order to function, imaging materials may be coated with up to 18 layers of light sensitive materials at high speed to prevent drying of materials as they are applied. PFASs used play a key role in minimizing manufacturing waste by contributing to the technology for creating coatings of high complexity in a highly consistent manner. The coating aid must allow the rapid uniform spreading of the layers so that irregularities in the coatings are avoided. Any irregularity in coating thickness makes imaging materials useless and increases manufacturing waste significantly. Coating aids must not be photoactive; otherwise, unacceptable fogging or speed effects may occur in the coatings.

Perfluorinated coating aids also have special properties at low concentrations for controlling static charge during the manufacture and use of imaging materials. This is particularly important for imaging materials that have a high sensitivity to light, including light produced by static discharge during transport of imaging materials. Excessive friction during the transport of imaging materials and contamination of imaging materials by dirt or clogging of magnetic strip readers with debris can lead to significant waste of imaging materials during manufacturing and use.

PFAS substances used control the adhesion of various tapes used to attach imaging materials to spools and to each other during processing. The strength of the bond between the tape and the imaging materials must be controlled so that imaging devices (e.g., cameras, photoprocessors) and imaging materials are not damaged during transport.

To illustrate the difficulty of further introducing alternatives into the materials in which PFASs are still used, information provided by a particular I&P Europe member company is given below.
It is emphasized that the variety of necessary properties from PFASs combined with over 70 different film formulations greatly complicates the identification of an alternative formulation. The challenge is additionally difficult as currently they use 7 different PFAS materials in combinations with non-PFAS surfactants to provide the performance features. As it is typical to use 2-3 surfactants to achieve performance, there is an additional difficulty in screening likely candidates. They report that in the last two years, 15 non-PFAS materials have been evaluated without identifying replacement materials.

The surfactant categories for these materials are below:

Polyether polyol
Diethyl hexyl sulfosuccinate
Alpha olefin sulfonate
Alcohol phosphate
Acetylenic based formulated surfactant
Siloxane based
Polyether siloxane copolymer
Ethoxylated polydimethyl siloxane
Polysiloxane block polymer
Alcohol ethoxylate
Cocoamine ethoxylate
Decanol ethoxylate
Silicone copolymer
Quaternary silicone surfactant

No candidate has successfully passed the second phase of evaluation in the five-step process they use in evaluating likely candidates, which is described in the next section as supporting information regarding required timing for replacement of PFASs used.

required timing on replacement

Where alternatives have been validated for the manufacturing of photographic products, they are already in use by the photo imaging industry. The alternative products are unique to each company and are proprietary. Research into alternatives to PFASs still in use is continuing for the remaining uses, however at potentially high cost ratio and with limited chances for success, as only the difficult applications and the smaller niche applications remain.

The example given in the previous section to illustrate the difficulty of further introducing alternatives into the materials in which PFASs are still used, as made available by one of I&P Europe's member companies, can also be used to justify and substantiate the requested necessary replacement time.

They use a five-step process in evaluating likely candidates – which is a situation that is typical or comparable for most, if not all, other member companies:

1. Investigation and searching of literature and manufacturer’s catalogs etc. Physical properties, hazard ratings, compatibility with other photographic materials (aqueous, gelatin etc.).
2. Determine the static and dynamic surface tension properties. This requires determining quantity and concentration to achieve successful laboratory melt properties.
3. Experimental coating and testing. Varying the laydown quantity and combining blend percentages, simple machine coatings in a gelatin matrix are generated for analytical tests
    a. Impact charge – electrostatic measurements of coated materials determining the propensity of charge transfer in various geometries (front to back of film, front to nearby metal, etc.).
    b. Developer Spread Testing – evaluating the surface wetting behavior of developer solutions on coated materials.

   c. Ancillary properties that impact photographic films (friction, formation of repellencies, elasticity, susceptibility to air currents, formation of streaks, etc.).
4. Pilot coating of full film formulations. Evaluate practical performance and internal testing of actual film. Ultimately this will be required for all films in the portfolio.
5. Trial production coating. Product will be coated under full manufacturing conditions and will be finished to trade dress and submitted for external customer testing. This will provide material for variety of customer photoprocessing conditions.

The member company states that materials chosen thus far have all been in chemical categories thought to have good surfactant characteristics as a starting property. It is the secondary properties of electrostatics and surface wetting that have been challenging. The discovery process includes a long lead time to evaluate and test. They further state that currently, an estimate of required time is not available, however based on the lack of success in the last two years a minimum of a five year derogation is needed.

Speaking generally for the I&P Europe member companies that manufacture photosensitive materials, where alternatives have been validated for the manufacturing of photographic products, they are already in use by the photo imaging industry. The alternative products are unique to each company and are proprietary. This process has required extensive resources over a period of more than 10 years to find – on a case by case basis for many different photosensitive materials – suitable alternatives, do the prototyping and ultimately the development to commercial products and introduction on the market.
Given the specific challenge of achieving the combination of all the necessary properties in photosensitive materials without the use of fluorinated compounds, the complete removal of PFASs is certain to require a long development time. To replace all PFASs in these photographic coatings on film and in printing plates will require further significant sustained research and in order to do so a derogation allowing an extended transition time of 5 years will still be needed when imposing restrictions on PFAS.

cost of substitution

It is not possible for the industry as a whole to estimate the costs to replace the remaining critical uses of PFAS substances. Since the formulae for imaging coatings are proprietary and differ from company-to-company and product-to-product, the product development teams from each manufacturer must evaluate replacement materials for their own specific formulations and each company will experience difference costs to undertake reformulation.
Each formulation change may take several years of effort by research and development teams. Developing alternatives to PFAS substances involves laboratory scale research evaluations of many different candidate chemicals or formulations, interaction studies to define chemical and imaging interferences, film coating experiments to assess the feasibility of machine coating, studies to understand how coatings will behave during high-speed film transport during manufacturing and processing, internal trials using full scale processes and equipment, and trade trial evaluations to learn how a product will behave during customer use. In evaluating alternatives, imaging companies consider not only the performance of the substance, but also the environmental, health, and safety attributes.

However, if an average estimate is requested, we can state that costs to substitute PFASs typically amount to 500-1000 kEuro for a single photographic material.

The primary barrier to complete elimination of the use of PFASs at this time remains technical. However, the cost of research and development is also a relevant consideration, since this investment represents a significant financial burden during a time when the imaging industry is focused on the creation of innovative new digital imaging technologies. As a matter of fact the economic costs associated with substitution of PFOA's in the remaining critical photographic uses have in some cases become prohibitive, where it concerns small remaining critical uses being niche products in markets that I&P Europe members anticipate to further decline.

In confidential appendix 1 an estimation of costs of substitution is provided for the particular member company selected to incorporate the illustrative example that was chosen to substantiate the above sections "information on (lack) of alternatives" and "required timing on replacement".

CASNR or chemical name of the PFAS substances used

See confidential appendix 1.
See confidential appendix 2.

tonnages of PFASs used

See confidential appendix 1.
See confidential appendix 2.

emissions to the environment

Potential for Environmental Release of PFAS during Manufacturing.

Environmental releases from the manufacturing of conventional photographic products are estimated to be extremely low for a number of reasons including:

1. the small amounts of PFAS materials added during the coating stage of the photographic product (0.1-0.8 µg/cm2) have beneficial effects throughout the life of the product. Therefore the PFAS must predominantly remain in the product for the product to perform adequately;
2. manufacturing facilities for photographic materials either have incineration capability on-site or use incineration facilities available through off-site contracts. Wastes containing PFASs may arise from a variety of sources. In all cases, these waste streams are managed appropriately to minimize the potential for exposure and release to the environment.

<u>Wastes from Coating Operations</u>

Wastes from coating are disposed of through high temperature incineration. This waste category has been estimated as 1-3% of the total PFAS material in analogy with former data for PFOS developed in the course of the former regulatory process for PFOS. Unused but excess coating materials are sent for silver recovery by high temperature incineration This category of waste may account for 5-28% of the total amount of PFAS used, again in analogy with former PFOS data.

Some companies may use PFAS related substances in the overcoat layer. Whereas the overcoat does not contain silver (as opposed to photographic emulsion layers), any excess is not sent for silver recovery by incineration but rather treated in a large STP. This quantity of PFAS is estimated to be well below 1 kg per year and is further declining because of market trends.

<u>Wastes from Finishing Operations</u>
The finishing stage involves slitting the rolls of film that are up to several meters wide into sizes appropriate for the product type. The wastes from this process are all solid and are either incinerated directly or incinerated after recovery of silver and PET (polyethylene terephthalate) film base and other materials. Ultimately, all waste from finishing is incinerated, accounting for an estimated 5-25% of the total of PFAS chemicals.

<u>Wastes from Photo-processing Operations</u>
I&P Europe member companies no longer use PFAS in their photo-processing solutions.
During the wet processing of any photographic film or paper containing PFASs, we would anticipate very little PFAS chemical being released.

This is confirmed by analytical data yielding a PEC/PNEC of 0.000 24 << 1 in the wash section of a wet film processor for medical film, which constitutes a worst case example, and a PEC/PNEC = 0. 000 000 010 << 1 at the emission point of that processor in a typical hospital setting in Germany**.

**: reference "Use of PFOA in critical photographic applications" – presentation at the Workshop on PFOA and its Ammonium salt. Production, use, risk – 4 May 2010, slide 10

Potential for Environmental Release of PFAS during Product Use.
Environmental releases originating from photographic products are estimated to be very low.

The imaging industry recycles hundreds of millions of kilogrammes of manufacturing and post-customer waste annually, including solvents, PET, and silver. Because of the high value of silver, I&P Europe members have developed highly effective processes to recover as much used and waste photographic material as possible in order to recover the precious metal.

Consumer film and paper (except for small amounts of materials returned by photofinishers) are usually not returned to the manufacturer. Consumers typically store their film and printed images indefinitely and usually across generations. Materials that are discarded are usually disposed of in municipal solid waste systems. The proportion of municipal waste that is incinerated will vary considerably on a national and local level.

Recycling of commercial film may be carried out with several goals in mind: recovery of silver; recovery of film base material (PET); and protection of intellectual property or sensitive information. For film that is constructed on a PET base, the emulsion layers are separated using enzymes or chemicals, the PET base is separated and sent for recovery, and the emulsion solutions are either biologically treated or chemically treated with a flocculant, precipitated, dried and are in both cases subsequently incinerated at high temperature to produce an ash that is used for recovery of silver. Film that is not on a PET base is incinerated directly at high temperature to recover the silver. For commercial (e.g., entertainment, industrial x-ray, graphics arts, and printing) and medical imaging industries, film materials are collected by a small number of registered organizations who are responsible for the secure destruction of the film in order to ensure data protection of sensitive private information or intellectual property. The materials are incinerated and the silver and other raw materials are recycled as described above.

Any waste solvents are incinerated in hazardous waste incinerators. To treat wastewaters, most recyclers have primary treatment facilities on-site so as to maximize silver recovery; sludges from primary treatment facilities are collected and used for silver recovery. Recycling operations located at manufacturing sites also have secondary wastewater treatment systems where sludges are collected and incinerated at high temperatures.

Conclusion

The total amount of PFAS materials required for continued uses in the remaining critical applications in the photographic industry is very low and estimated to account for less than 0.0054% of the total use in the EU, in analogy with former data in this case developed by the German and Norwegian authorities in the course of the former regulatory process for PFOA.

In addition, the occupational exposure to and environmental releases of PFAS related materials associated with continued uses in photographic products are controlled and pose no unacceptable risk to human health or the environment.

measures to minimize release into the environment

In the last three decades there has been an ongoing effort to assess the function of PFAS materials in the production of photosensitive materials and to reduce use of these substances.

Social cultural value of photosensitive materials

One of the member companies of I&P Europe submitted a contribution on the social cultural value and importance of photosensitive materials, which is presented in appendix 1.

2. Coatings for offset pre-press applications

When we talk about lithographic printing plates (offset plates), we can make a distinction between, (i) conventional plates that are developed after exposure (various forms of wet processing are possible here, ranging from conventional chemical processing using an alkaline developer over "low-chem" processing to "chem-free" processing) and (ii) process-free, i.e. processless printing plates which are automatically developed during the start-up process of the printing press without using a developer.

In both types of offset plates it is necessary to uniformly apply the photosensitive component onto the printing plate and to increase the affinity of the surface of the photosensitive component with the inks. This is often achieved by using specifically designed side-chain per-fluoro polymers.

Processless lithographic printing plates have been developed with the intention of reducing the environmental impact of print shops. Progress has been made in converting wet process customers as the plate features of the processless technologies are improved to be comparable to the existing wet process plates. Comparable performance of the key feature of machine readability has only been achieved using a PFAS material, more specifically a trifluoromethylsulphonate-group based colour former, a specific dye type incorporating a triflate group ($-SO_2-CF_3$).
PFAS-free alternate colour systems with comparable performance are not yet available and require additional R&D necessitating a transition period of 5 additional years.

technical function of the PFAS

In order to fulfill essential requirements (a) in the production of offset plates and (b) in the applicability of processless plates, PFAS is used: (a) as wetting agents (surfactants) with perfluoroalkyl side chains and (b) as specific colour formers containing a triflate group ($-SO_2-CF_3$).

(a) Specifically designed side-chain per-fluoro polymers are often used to uniformly apply the photosensitive component onto the printing plate and to increase the affinity of the surface of the photosensitive component with the inks.

(b) A trifluoromethylsulphonate-group based colour former is used in process-free printing plates to generate a read-out contrast after printing plate exposure without the need for chemical development steps or any wet processing.

The proprietary colour former – a cyanine dye infrared absorber modified to incorporate a triflate group ($-SO_2-CF_3$) and therefore a PFAS compound – is essential to generate exceptional colour formation with exceptional stability upon irradiation with thermal laser wavelengths used for imaging printing plates. Unique features of such plates include efficient use at low exposure energy, stable colour generation for process-free printing plates and a performance of the key feature of machine readability that is comparable to the existing wet processed plates.

information on (lack of) alternatives

When a trifluoromethylsulphonate-group based colour former is used in process-free printing plates, irreversible colour formation occurs upon interaction with a NIR laser. Alternatives (leuco dyes) show

a reversible colour formation and are not directly addressed by the used laser sources. Alternatives are thus significantly less efficient or performant, requiring higher dosages which lead to unacceptable drop in printing plate robustness and end product performance (extra cost, chemical waste, energy consumption).
One member company of I&P Europe member reported that >50 new PFAS-free structures were synthesized and evaluated and that no replacement was found with comparable characteristics in process-free printing plates.

Another aspect has to do with the fact that many print shops use optical plate readers for measurement of plates both in pre-press and on the press as an essential part of their quality processes to ensure accurate print reproducibility and for compatibility with their automation processes. Many of these plate readers use a light source typically between 600 – 650nm. Readability has been achieved with wet process plates for many years but has been far more difficult to achieve in a process-free plate. Without this performance there is a significant barrier to conversion to process-free. The only processless plate which has provided the necessary performance with respect to machine readability, together with image stability, uses a PFAS: the trifluoromethylsulphonate-group based colour former. See also confidential appendix 3.

required timing on replacement

(a) Although we have been researching alternatives to PFAS free surfactants, it is very difficult to accurately estimate the time frame and cost for transition because of the many different types of pre-press products. Generally, it takes more than 2 years to develop materials, 2 years to prototype and scale up, more than 2 years to be evaluated by customers, 3 to 5 years for proper safety evaluation and certification, and several years for supply responsibility. This means that replacement would take more than 12 years and transition costs would exceed 5 million euros. Member companies are committed to making maximum effort to transition to PFAS free wetting agents, but an additional 5-year transition period remains a requirement to achieve success (i.e. 6.5 years after EIF).

(b) A transitional period that is extended to 6.5 years after entry into force of the restriction for the use of a trifluoromethylsulphonate-group (-SO2-CF3) based dye in contrast systems of process-free plates is equally needed to allow time to continue research efforts for the development of PFAS-free processless plates.
There are a series of development challenges in securing a PFAS-free processless litho plate and due to the nature of the work these may require several years to complete:

- Synthesis of new, novel compounds (Design)
- Screening and then optimisation in the formulation (Design)
- Scale-up of new material and testing for manufacturability on the coating lines (Cost)
- Field testing (Design)

A litho plate coating has many unique design requirements and constraints and as a result it is almost impossible to find off-the-shelf materials that could be used in a litho plate. It is also difficult to find commercial partners for designing new materials for this application as the total worldwide volume is low. As a result, synthesis is provided primarily by the plate supplier’s limited R&D resources.

The processless litho coating is a highly complex, highly optimised mixture of more than 10 components (including resins, oligomers, IR dyes, initiators, colour dyes, stabilisers, and surfactants) which is matched to a unique aluminium support surface to complete the printing plate. Changes to a single component cannot be fully understood without a full optimisation and multiple tests, including press testing and shelf-life testing. The individual experimental cycle is lengthy, and the full development cycle is extensive as a result.

These unique materials do not typically find uses in other industries and the volumes are in litho plate use is low (see also confidential appendix 3). This limits manufacturing scale and does not allow any dilution of scale-up costs, all of which leads to an expensive raw material cost. Litho plates do not command large margins in the industry and are very sensitive to coating raw material costs. It is a critical requirement that new raw material be produced at a competitive cost. If it is not possible to identify a cost-effective synthetic route to achieve target costs, a new material may be necessary, starting the whole design / scale-up process again.

Manufacturability on the coating lines is a critical process which requires high yield and good uptime to meet cost requirements for the finished plate. Small-molecule components in litho plate coatings can lead to problems on line from crystallisation to filtration issues to light and dark spots. Often these issues cannot be predicted in the lab and only come to light after a significant amount of manufacturing experience, which is only possible after the design work and raw material scale-up but can result in “starting over”. These issues have significantly increased development cycle times in past litho plate developments.

Finally, significant field testing is required which can take up to a year. Litho printers cover many print applications with many significant differences in equipment, consumables and substrates: runlengths from fewer than 1000 to +1 million impression runs; supports from metal to cardboard to high gloss paper; from oil-based inks to glossy UV-cured inks; from 20 year old, poorly maintained presses to modern, fully automated production machines. While the plate companies do have some printing equipment it is simply not possible to test internally across all the applications that the processless plate must work in. To confirm the necessary robust plate performance for commercial success a wide range of applications must be tested in commercial printers. This can only be done with line produced plates and so is at the end of the development cycle but can still fail!

At any point in the development journey a failure can mean moving back to an earlier step in the process adding months and sometimes years to a project. The 5 year extension is requested for sufficient time to secure a PFAS-free alternate.

CASNR or chemical name of the PFAS substances used

See confidential appendix 3.
See confidential appendix 4.
See confidential appendix 5.

tonnages of PFASs used

See confidential appendix 3.
See confidential appendix 4.
See confidential appendix 5.

emissions to the environment and measures to minimise release

(a) emission of PFAS to the environment at the end of the use of the printing plate is very limited.

(i) conventional processable offset plates using alkaline developers, plates are developed in automatic processors, and waste liquid materials are collected in waste tanks installed in each automatic processor. Waste alkaline liquids containing PFAS are properly treated by specialized disposal companies, minimising exposure to the environment.

(ii) for process-free plates, the development process is conducted automatically during the start-up process in the processor and coating components are removed by tacky inks. The ink containing the removed coating components is transferred to paper in the first printing and becomes a preparatory waste material. PFAS can be thermally decomposed during the recycling or incineration process.

For both types of printing plates, the aluminum plates after printing are removed from the press and sent to metal recycling to recover the raw aluminum. PFAS is thermally decomposed during the recycling process.

(b) For processless plates, it can be argued that the amount of PFAS dye ending up in the environment at the end of the plate use is essentially zero. From plate manufacturing to customer use, essentially all the PFAS will be thermally degraded.

During the plate manufacturing process, all dye packaging and filter debris (powders and solutions), and waste solvent mixtures are collected and incinerated with zero environmental emissions. Coated aluminium waste is collected and sent for aluminium recycling which involves heating to > 650^{o}C to melt the aluminium which degrades the PFAS dye.

At the customer the processlesss plate is imagewise exposed to a thermal laser to create an image for printing, during which the exposed areas undergo a hardening reaction. This press-ready plate is loaded on the press and developed automatically during the press start-up process. The non-imaged, i.e. non-hardened, areas are removed from the plate by the tacky ink. The ink containing the removed coating is transferred to the printed paper in the first few prints, the so-called make-ready waste.

This make-ready waste is generated while the operator optimises the printing conditions to achieve the necessary print quality, for example, setting color levels and ensuring the different colors are registered pefectly. These waste sheets contain the removed portion of the coating, including PFAS, which is trapped in the dried ink within the matrix of the paper. Waste sheets are sent to recyling during which the paper will be washed out and foamed. The PFAS will be removed from the paper fibres with the ink and will be incorporated in the foam and mud which is skimmed, dried (squeezed) and utilized for energy production, thermally degrading the PFAS.

After the print job is completed the used plate carrying the exposed areas of the coating, is removed from the press and sent for metal recycling to recover the aluminium. Again any PFAS will be thermally degraded in this process.

Furthermore, the total annual usage of the dye is very low in comparison to many of the materials and uses that have highlighted the concerns of these PFAS materials. A litho plate comprises a very thin coating on an aluminium support. The coatings are typically 1 micron thick and 1 mg/m^2, and the PFAS dye is only a minor component of the coating at around 5%. Additional information regarding annual usage numbers is given in confidential appendix 3.

Finally, in this case for process-free plates we are specifically dealing with a single functional group of $-SO_2-CF_3$, with one group per dye molecule. This is not an example of a polymer containing repeating fluorinated side chains, and the total F content of these dyes is only a low proportion, typically less than 5% by mass.

APPENDIX 1

Social cultural value of photosensitive materials

We would like to explain the importance of photosensitive materials from cultural perspective. Photosensitive materials such as microfilms, instant photo films, and film archive film are used routinely by the European industry and community. We think these materials still play an important role in many ways.

1) Microfilms have been used as data storage media with very long-term reliability for valuable cultural information in national museums and research institutes in Europe (e.g. the British Library).

   The German State Archives Microfilm programme:
   https://youtu.be/zRJBbNz0-44

   Long-term storage of records relating to radioactive material disposal in the UK:
   https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/876817/NDA_WPS_870_03_-_GD_-_Long-term_Management_of_Information_and_Records_-_Explanatory_Material_and_Guidance.pdf

   UK Long-term Archiving guidance:
   https://www.gov.uk/guidance/archiving-your-trade-documents

   https://www.gov.uk/guidance/aviation-turbine-fuel-excise-notice-179a

   https://www.gov.uk/government/publications/2010-to-2015-government-policy-library-services/2010-to-2015-government-policy-library-services

   https://www.legislation.gov.uk/ukpga/1969/59/part/II/enacted?view=plain

2) Photographic films, including instant films, contribute to human relationships. When COVID19 was spread all over the world and everyone was obliged to wear masks, some trials were reported in which railroad clerks showed their real faces by taking picture by instant photo films. It improved the communication with the customer.

   https://www.kanaloco.jp/news/life/entry-430150.html

   https://www.tokyo-np.co.jp/article/111479

   Similar attempts were reported at hospitals across Europe. Doctors and nurses had difficulty connecting with their patient because their personal protective equipment covered their faces. They took their own photos using instant film and attached them in front of their hospital gowns. Their patient can see the person behind the mask, which helps their communication.

   https://petapixel.com/2020/06/04/fujifilm-is-donating-instant-cameras-to-hospitals-across-europe-to-help-doctors-connect-with-patients/

   https://www.standard.co.uk/tech/fujifilm-instax-cameras-healthcare-workers-patients-covid19-a4459666.html https://www.expresshealthcare.in/covid19-updates/ppe-clad-covid-warriors-now-need-not-be-faceless-to-their-patients-thanks-to-fujifilm-india/424464/

3) The photo-rescue project demonstrates the importance of visible photographic images. The silver halide photographic system was originally wet processed to produce non-diffusing images in a gelatin binder. Even when photographs were submerged in muddy water, some could be saved after being properly treated. On the other hand, electronic media are often beyond saving in this situation.
For example, many people and homes were lost in the massive earthquake and tsunami disasters in Japan and New Zealand. What those left behind were looking for were photographs. We would like to point out that the photo rescue project, which saves people's precious memories, was not only carried out in Japan, but also in New Zealand. We believe that photography has an aspect of common value as a global cultural asset.

Photo rescue in New Zealand: Special team brings flood-damaged photos back to life
https://www.1news.co.nz/2023/03/31/special-team-brings-flood-damaged-photos-back-to-life/
Photo rescue in Japan:
https://holdings.fujifilm.com/en/sustainability/activity/other-activities/social-contribution-activities/photo-rescue

https://photo-rescue.fujifilm.com/en/

4) Photographic film is also used as recording media for archiving (e.g. film archiving film RDS from Fujifilm). In principle, digital data itself does not deteriorate. However, the digital recording media, data format, recording and reading application, software, etc. cannot be guaranteed for more than 10 years. There is a risk that data may be destroyed or disappear in a short period of time such as 10 years because of various causes. Updating data to avoid risks is quite expensive (the so-called digital dilemma). Disney movies, TV programs and important research data from international institutions are archived by this type of film. The Smithsonian Museum in the United States is archiving and preserving historical data on film. From the viewpoint of archiving, photographic recording media which store images are better than digital recording media that electronically convert and store the data.

References:
https://www.oscars.org/science-technology/sci-tech-projects/digital-dilemma

CONFIDENTIAL APPENDIX 1

This section contains confidential business information and is added as a separate confidential attachment.

CONFIDENTIAL APPENDIX 2

This section contains confidential business information and is added as a separate confidential attachment.

email: [redacted]@ip-europe.com
www.ip-europe.com
Mainzer Landstrasse 55
60329 Frankfurt am Main
Germany

CONFIDENTIAL APPENDIX 3

This section contains confidential business information and is added as a separate confidential attachment.

email: [redacted]@ip-europe.com
www.ip-europe.com
Mainzer Landstrasse 55
60329 Frankfurt am Main
Germany

CONFIDENTIAL APPENDIX 4

This section contains confidential business information and is added as a separate confidential attachment.

email: [redacted]@ip-europe.com
www.ip-europe.com
Mainzer Landstrasse 55
60329 Frankfurt am Main
Germany

CONFIDENTIAL APPENDIX 5

This section contains confidential business information and is added as a separate confidential attachment.

email: [redacted]@ip-europe.com
www.ip-europe.com

Mainzer Landstrasse 55
60329 Frankfurt am Main
Germany