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Number 5

EMISSION SCENARIO DOCUMENT ON PHOTOGRAPHIC INDUSTRY

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Series on Emission Scenario Documents No.5

EMISSION SCENARIO DOCUMENT ON PHOTOGRAPHIC INDUSTRY

Environment Directorate

Organisation for Economic Co-operation and Development

June 2004

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The Inter-Organization Programme for the Sound Management of Chemicals (IOMC) was established in 1995 by UNEP, ILO, FAO, WHO, UNIDO and the OECD (the Participating Organizations), following recommendations made by the 1992 UN Conference on Environment and Development to strengthen co-operation and increase international co-ordination in the field of chemical safety. UNITAR joined the IOMC in 1997 to become the seventh Participating Organization. The purpose of the IOMC is to promote co-ordination of the policies and activities pursued by the Participating Organizations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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Explanatory notes

Purpose and background

This OECD Emission Scenario Document (ESD) is intended to provide information on the sources, use patterns and release pathways of chemicals used in photographic industry to assist in the estimation of releases of chemicals to the environment.

This ESD should be seen as a 'living' document, which provides the most updated information available. As such, an ESD can be updated to take account of changes and new information, and extended to cover the industry area in countries other that the lead (Germany). Users of the document are encouraged to submit comments, corrections, updates and new information to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org). The comments received will be forwarded to the OECD Task Force on Environmental Exposure Assessment, which will review the comments every two years so that the lead country can update the document. The submitted information will also be made available to users within the OECD web-site (www.oecd.org/env/riskassessment).

How to use this document

The user of this ESD needs to consider how the information contained in the document covers the situation for which they wish to estimate releases of chemicals. The document could be used as a framework to identify the information needed, or the approaches in the document could be used together with the suggested default values to provide estimates. Where specific information is available it should be used in preference to the defaults. At all times, the values inputted and the results should be critically reviewed to assure their validity and appropriateness.

For the estimation of the emissions of chemicals used in photographic industry, the following data and information should be preferably known:

- photographic processes
- intended use (e. g. bleaching agent, antifogging agent)
- component for which bath or for emulsion
- concentration in bath or in area of photo material
- removing rates

It should be taken into consideration that the photographic industry is a very dynamic branch. For example, the digital photography will become more important in the near future.

Coverage

This ESD covers Industry Category 10 – photographic industry. It describes the processes of the life cycle stage "industrial/professional use" and the emission estimations to local surface waters. The emission estimations for the life stages "production" and "formulation" and for other compartments other than surface water are described in the Technical Guidance Document on Risk Assessment Part II Appendix I, A & B Tables for IC 010 (EU, 2003).

How this document was developed

The original document is based on the ESD for Industry Category (IC-010) "Photographic Industry" published in the "Technical Guidance Document (TGD) on risk assessment in support of

Commission Directive 93/67/EEC on risk assessment for new notified substances and Commission Regulation (EC) No 1488/94 on risk assessment for existing substances”, Part IV Chapter 7 (EU, 1996).

In 1999, Umweltbundesamt (UBA Germany) commissioned the amendment of the ESD at the Institute for Environmental Research, University of Dortmund (INFU) (contract no 360 01 027). During the years 1999 to 2001 Umweltbundesamt, the Institute for Environmental Research University Dortmund (INFU), the European Photographic Chemical Industry Association (EPCI) and the Rethmann Photo Recycling GmbH jointly revised this document, defined generic point sources for the various processes and incorporated the life cycle stage “disposal”. In the year 2001, Umweltbundesamt submitted this draft to the European Union for inclusion into the amended Technical Guidance Document on risk assessment [EU, 2003 Part IV, Chapter 7].

Germany as the lead country submitted this draft to OECD, and the draft was circulated to the member countries in February 2002. Comments were received from the following organizations and institutions: UK (Environment Agency and Health and Safety Executive), US EPA and US industries (OECD, 2002). In 2002, Umweltbundesamt and the European Photographic Chemical Industry Association (EPCI) jointly incorporated the comments and revised the draft. The following revisions were made:

- correction and completion of the description of processes in photographic industry
- revision of units and symbols, if possible, according proposals of RIVM (17 May 2000)
- incorporation of information provided by German photographic industry and the European industry associations.

Releases to the air and releases to landfill from used film and paper need be to considered the next version.

Contents

1 INTRODUCTION

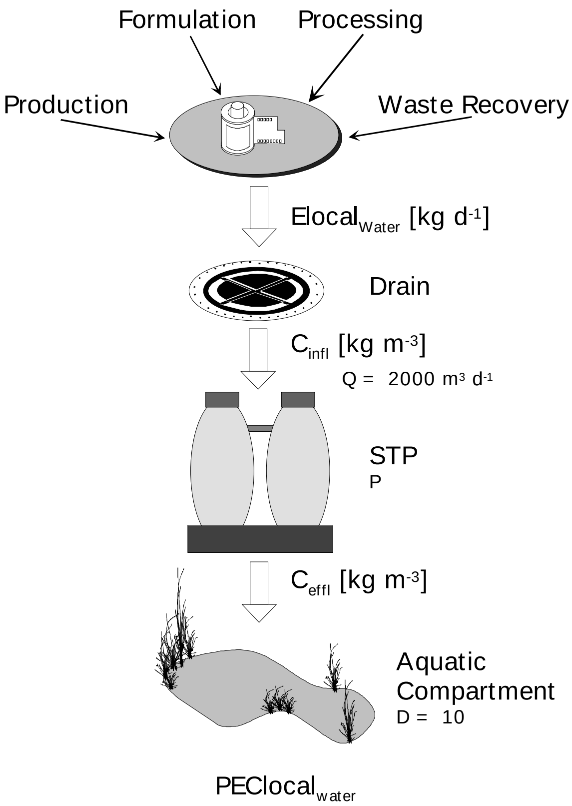
1. This document presents a methodology to estimate the emission rates (releases) $Elocal_{water}$ of photo chemicals (IC-10; UC-42) into the water compartment. The estimation is given under realistic worst case conditions. The surface water concentration $PEClocal_{water}$ is calculated from the emission rate $Elocal_{water}$ (emission in $kg.d^{-1}$) by using the standard model of the wastewater treatment plant.

2. There are two main applications for photo chemicals:

- ingredient in a processing solution (developer, fixer, bleach, bleach-fixer),

- ingredient in photographic material (film, paper).

3. The relevant photographic processes, the X-ray-process and the reprographic process are part of this emission scenario document. The chemicals used in the photographic processes may enter the environment via the product, unused material or wastes. In photographic processing emissions occur from the use and waste disposal of photographic products because most substances except for silver are discharged into the water compartment. Representative emission scenarios for each process are considered.



C_{infl}: influent concentration
C_{effl}: effluent concentration
Q: $EFFLUENT_{stp}$
effluent discharge rate of STP
P: elimination in STP
D: dilution factor

Figure 1 Scenario for the determination of the $PEClocal_{water}$

2 LIFE CYCLE OF PHOTO CHEMICALS

4. Emissions into the water compartment may occur at any phase of the life cycle of a photochemical. The life cycle starts with production and formulation. The next step is the processing. It ends with either recovery or emissions to wastewater or waste (Figure 2). The release of chemicals into the environment from private sources is not environmentally relevant. Therefore only the industrial use (processing) is considered.

5. The use of the chemical within the relevant process is considered as well as the consumption and the emissions into the water compartment. The water compartment is also contaminated by waste, waste disposal procedures and recovery. These emissions are also described.

6. For releases during syntheses of chemicals used in the photographic industry, see the specific scenario for production. For releases during their formulation, see section 4.1 and for calculations the IC-10 in the A- and B-Tables of the TGD (TGD 2002). For releases to the environmental compartments of 'air' and 'soil', at all stages of the life cycle, the reader is again referred to in the A- and B-Tables, in TGD.

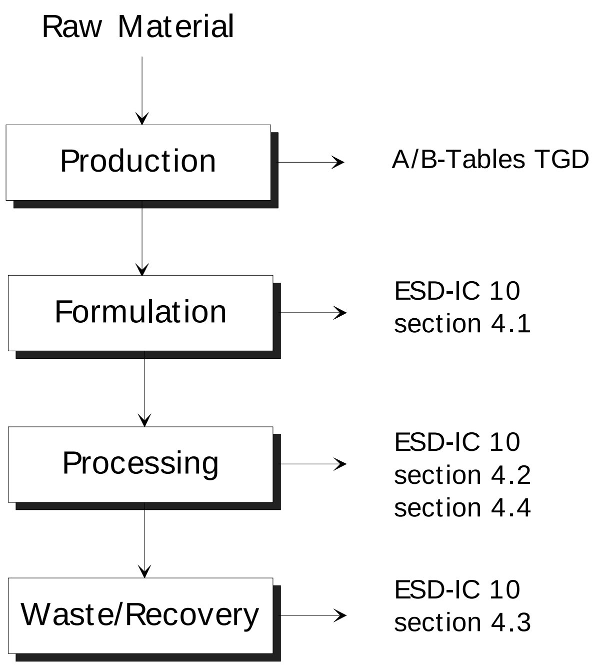


Figure 2 Stages in the life cycle of photo chemicals in which emissions to the water compartment may occur

3 PHOTOGRAPHIC PROCESSES

7. Generally exposed film material contains image information transmitted through the light effect to the silver halide crystals finely dispersed in the emulsion layer. The two main types of photo processing, by which the majority of photographic material is developed, are:

- negative/positive processes
- reversal processes.

8. These processes are used in black-and-white (monochrome) and in colour (polychrome) photography. The processes are categorized by a classification code system according to Kodak abbreviations or, in the case of monochrome photography, to the author.

9. Figure 3 shows the market shares of the standard processes in the EU.

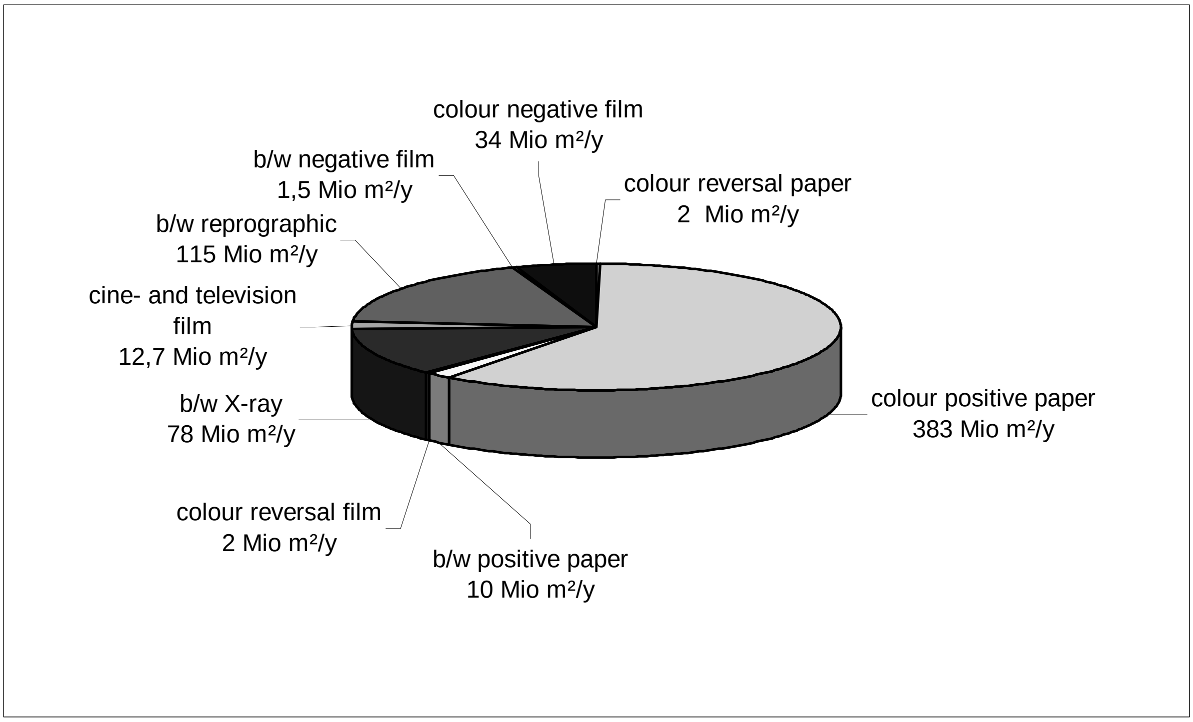


Figure 3 Market shares of photographic processes in the European Union [EPCI 2001], [INFU 2001]

10. Figure 4 shows the quantity of processed photographic material in European countries.

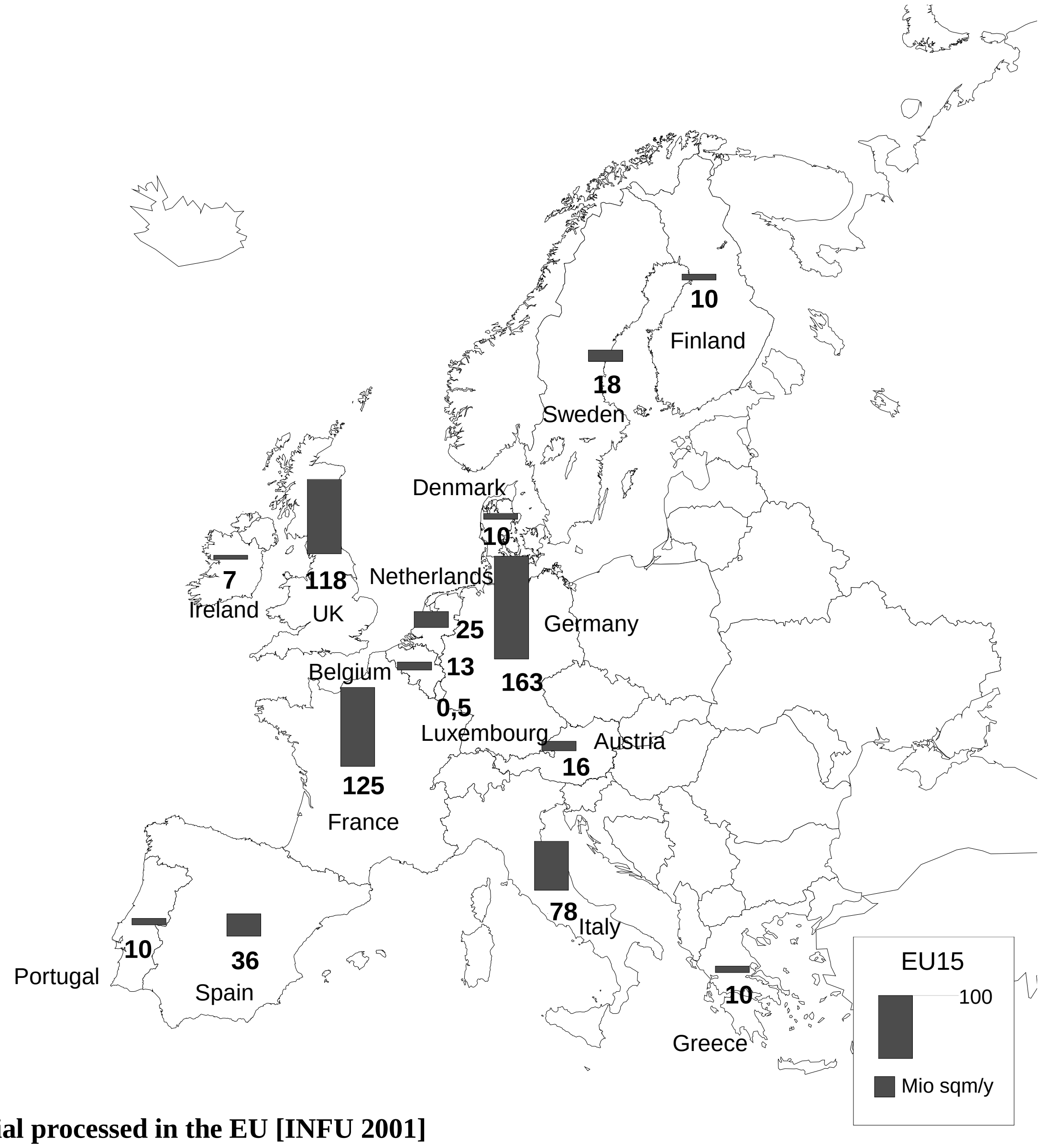


Figure 4 Material processed in the EU [INFU 2001]

11. In the following chapters (3.1 – 3.5) examples of various processing configurations are shown. Not all of them are used worldwide but can be considered as most common variations of the European Photographic Industry.

3.1 Negative/positive processes for film and paper

12. Negative/positive processes first provide the negative. Afterwards it is copied onto a positive material (paper or film) thereby reproducing the original image. The silver halide that had been exposed to light, is reduced to metallic silver, the primary silver image, in a developing solution. The non-exposed silver is removed from the emulsion layer by a subsequent fixing process. The remaining negative image is then transferred via light exposure to the positive material (film or paper).

Developing:

$$\textit{developer} + \textit{exposed silver halide} \rightarrow \textit{oxidized developer} + \textit{metallic silver}$$

Fixing:

$$\textit{non-exposed silver halide} + \textit{complexing agent} \rightarrow \textit{silver complex}$$

As in the black-white process the exposed silver halide crystals are reduced to elementary silver by the developer to provide the primary silver image.

Chromagenic developing:

In contrast however to the black-white process, the oxidized form of the developer forms the colour in a chromagenic process together with the colour coupler, which is also located in the emulsion layer.

$$\textit{oxidized developer} + \textit{colour coupler} \rightarrow \textit{colour}$$

Bleaching:

The silver image is removed in a bleaching bath, because it reduces the brilliance of the colour. In the bleaching solution, oxidizers like ammonium ferric (III)-EDTA are used to reoxidize the elementary silver to the ion, which is then transferred into the silver halide. In this form it is washed out together with the unexposed silver halide in the following fixing step.

$$\textit{elemental silver} + \textit{Fe(III) complex} \rightarrow \textit{silver ion} + \textit{Fe(II) complex}$$

$$\textit{silver ion} + \textit{complexing agent} \rightarrow \textit{silver complex}$$

Negative/positive processes provide a colour negative image and after exposure of this negative on a positive material (paper, film) a reproduction of the colours which is true to the original.

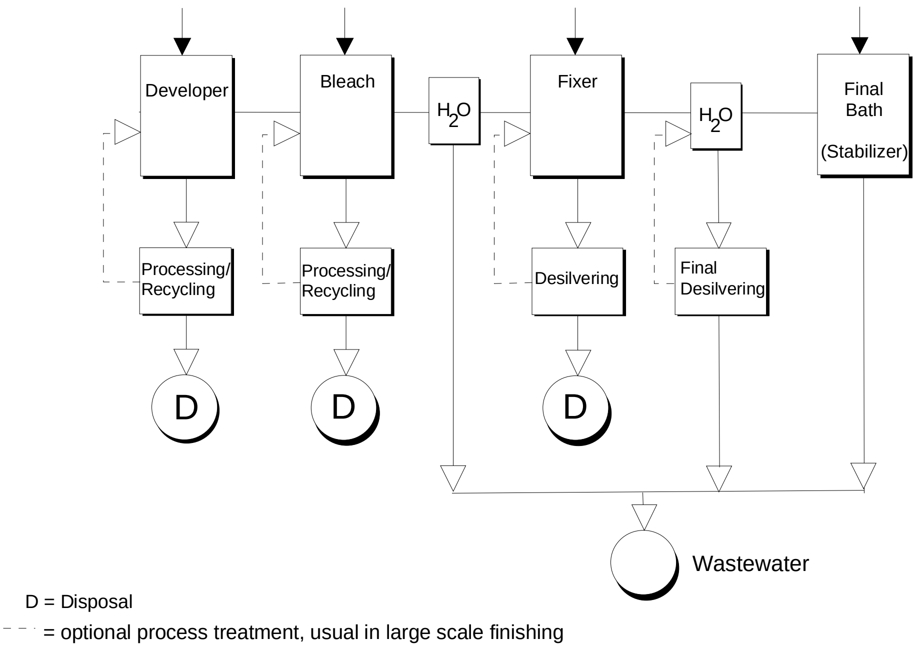


Fig. 5: Colour negative film process (C-41)

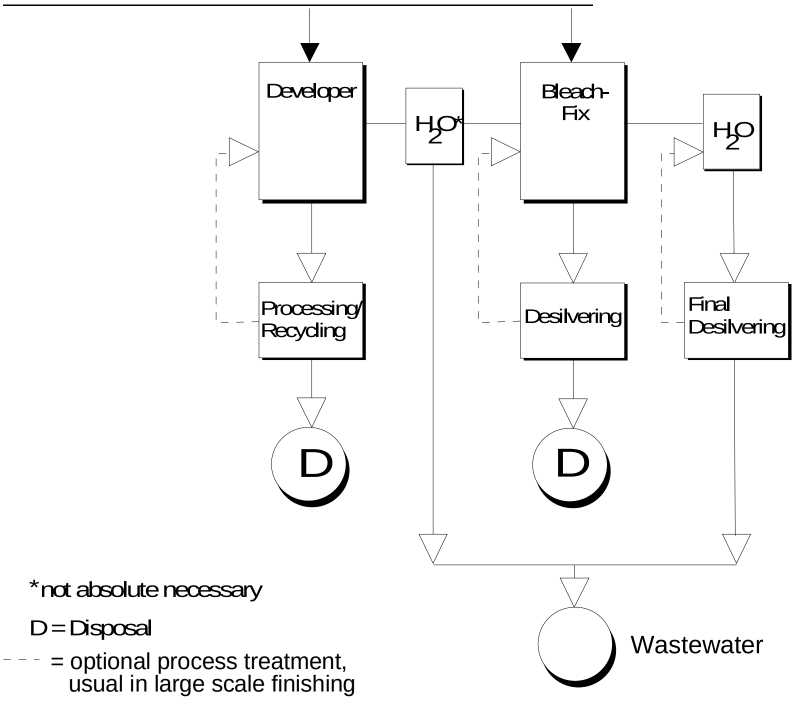


Fig. 6: Colour positive paper process (RA-4 with a combined bleach-fix-bath)

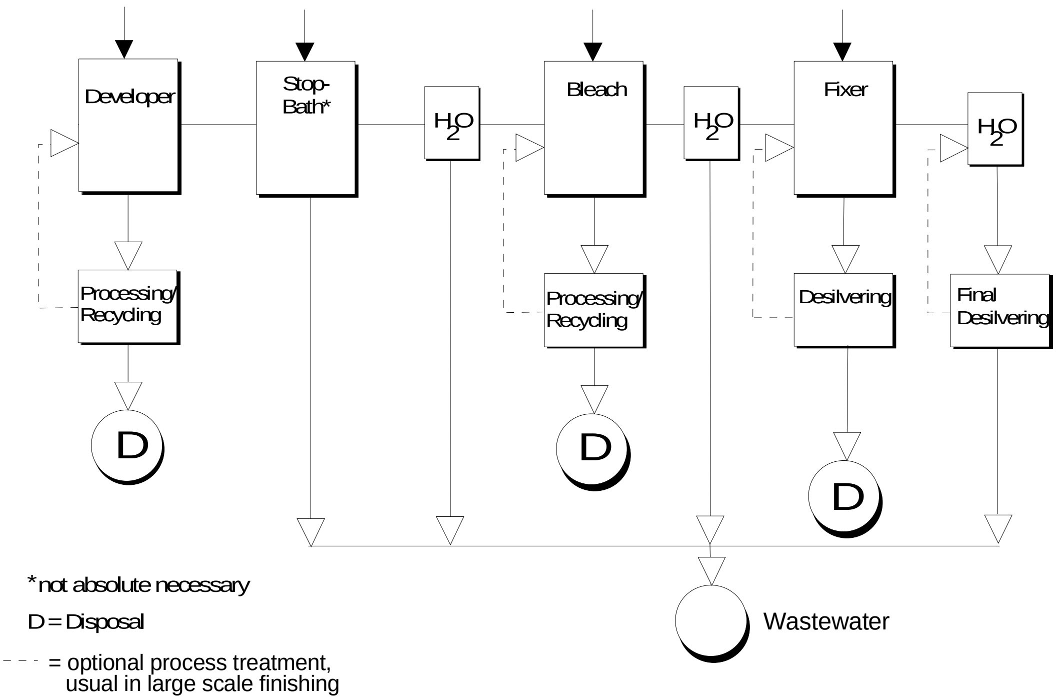


Fig. 7: Colour positive paper process (RA-4 with bleach- and fixer-bath)

3.2 Reversal processes

13. The reversal processes provide the positive image in a direct manner. In the case of the colour reverse process a conventional black-white development is performed first, resulting in a silver negative image. The silver halide, which is unexposed during first exposure, is then either subjected to a reversal second exposure or a chemical treatment in a reversal bath. Thus, in the same material the subsequent colour developing process provides a colour-positive. Finally the silver is removed in the bleaching and fixing solutions.

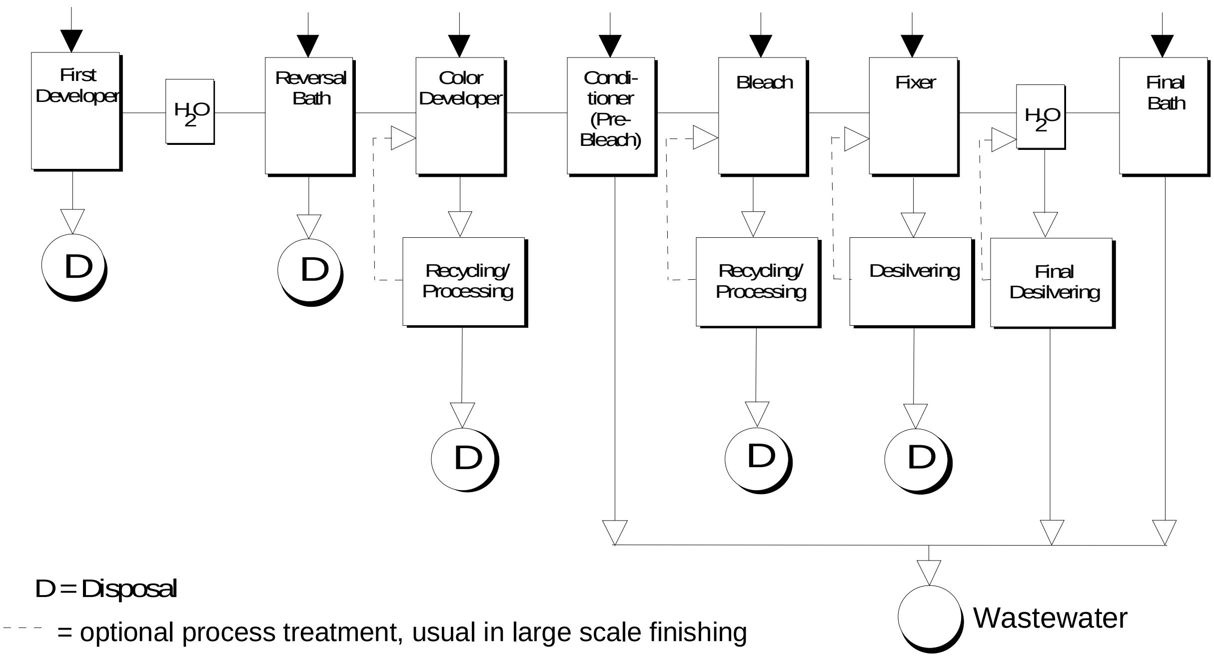
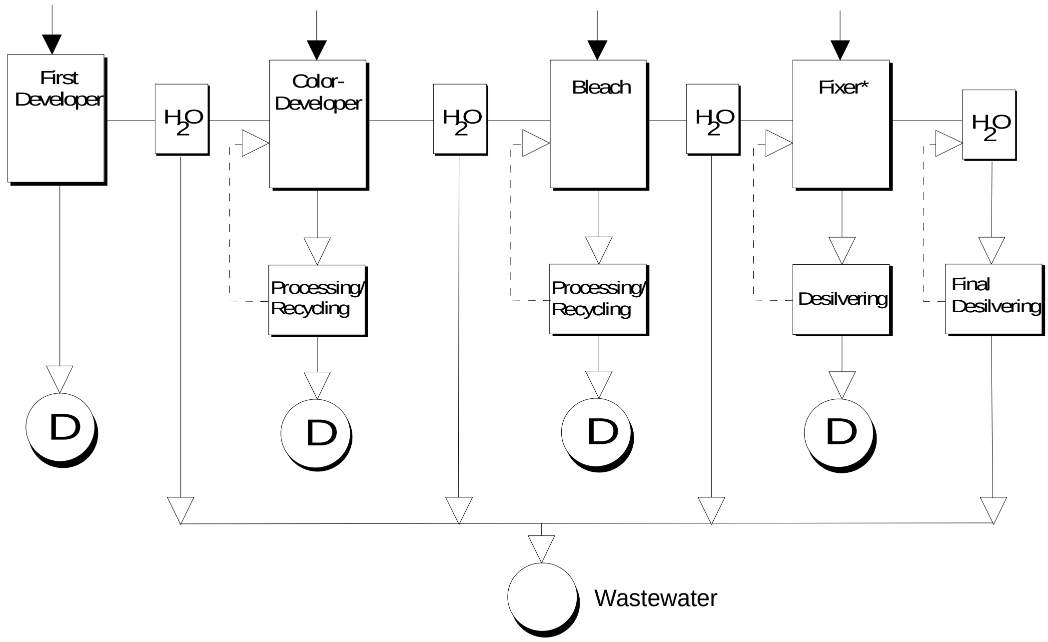


Fig. 8: Color reversal film process (E-6)



*Partly bleach-fix bath

D = Disposal

- - - = optional process treatment, usual in large scale finishing

Fig. 9: Color reversal paper process (R-3)

3.3 X-ray processes

14. The X-ray processes provide the negative image. Basically the process is a conventional black/white negative process. Since X-ray images require a strong contrast and quick availability of the pictures, the chemicals used in the processing solutions are present a higher concentration.

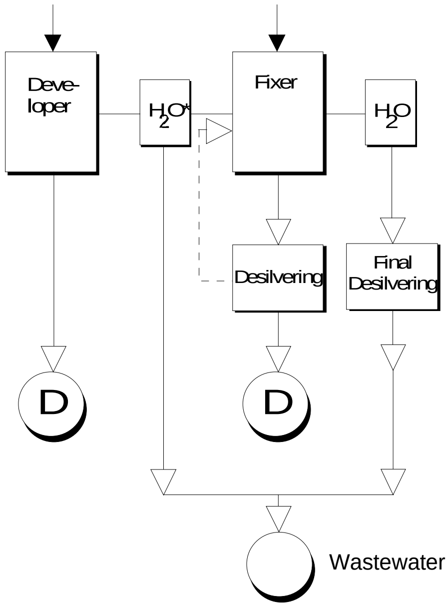
15. The basic reasons for this high consumption of chemicals are the double-sided film emulsion layer, high blackening and necessity for a fast availability of the pictures.

16. The digital technology, which is expected to see increased use in the X-ray field in the next years, will decrease these emissions. This is a distinct advantage of this new process. Nevertheless, the classical X-ray technology will never be completely replaced, since the quality of the images in the new process is not as good as with the classical method, and the high cost of the conversion to the new technology also poses an obstacle.

3.4 Reprographic processes

17. The classic layout and reproduction techniques use photographic methods. In photo setting, black/white films are created, which are used to produce copies for the printing process. In reproduction techniques, black/white copies are used as well as colour copies. Depending on the printing process used later, line-, screen- or half-tone reproductions can be created here. When working with coloured pictures, colour filters are used to create a colour separation for each of the basic colours. During this process, the coloured original is photographed onto a black/white film through this filter. The resulting colour

separations yellow, cyan and magenta as well as black are then developed into separate printing copies. With the development of modern computer technology, it is now possible, to process text and image information digitally, and print it directly onto photosensitive material using laser technology.



*unusual in reprographic- and X-ray processes
D = Disposal
- - = optional process treatment, usual in large scale finishing

Fig. 10: X-ray-, black and white-, reprographic film and paper processes

Cine and TV-films process

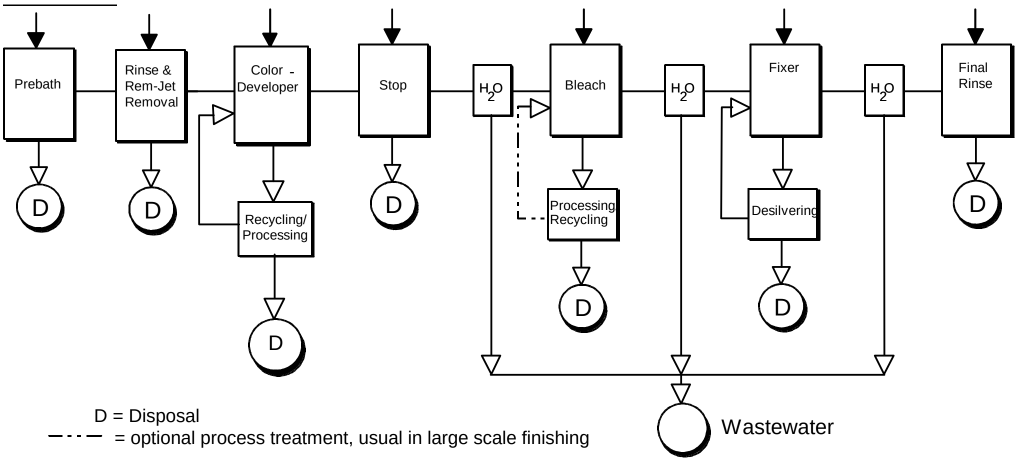


Fig. 11: Cine and TV-film negative process (ECN-2)

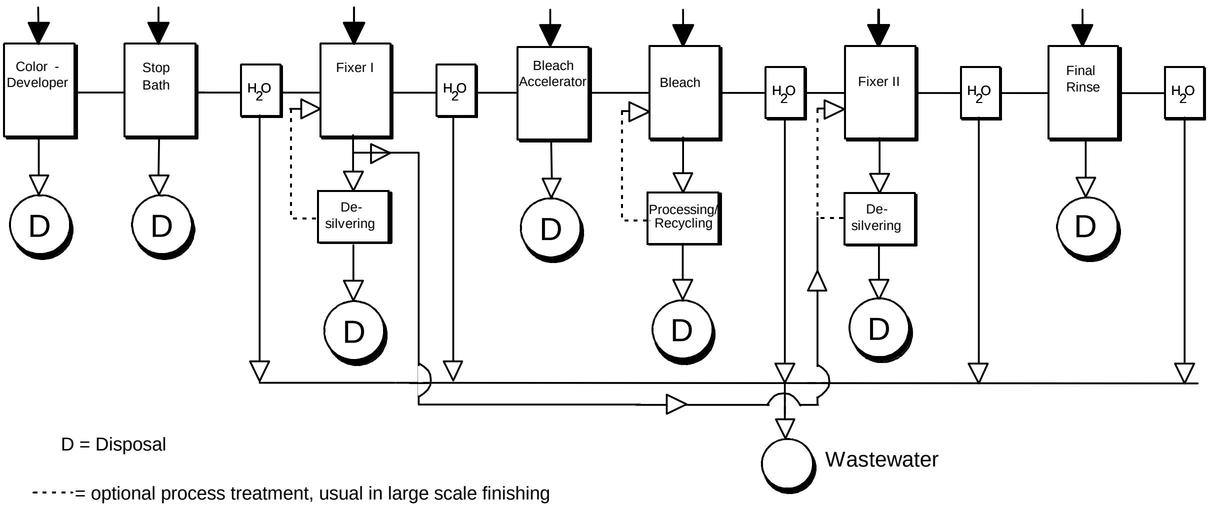


Fig. 12: Cine and TV-film positive process (ECP-2D)

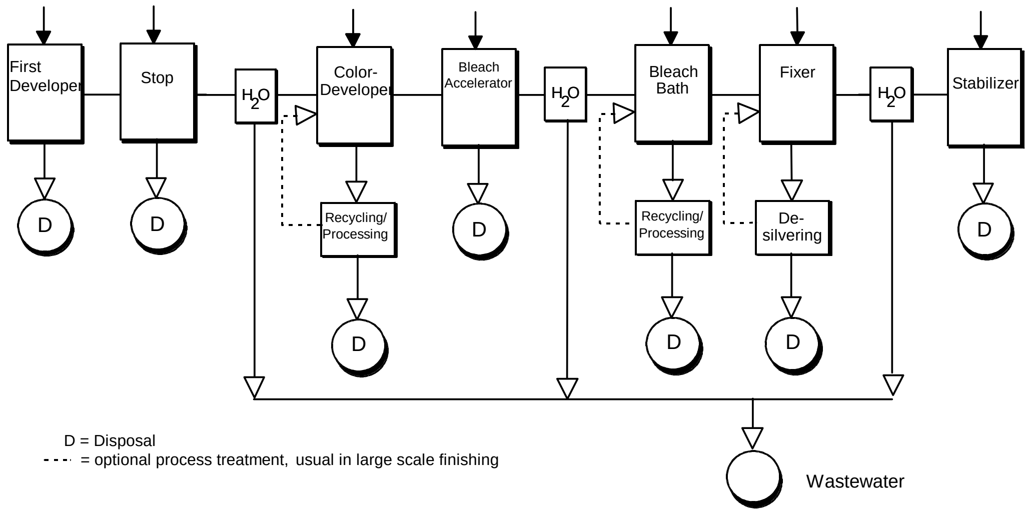


Fig. 13: Cine and TV-film reversal process (VNF-1)

4 EMISSION SCENARIOS

18. The various emission sources of the photographic industry and the generic scenarios are described below. The following emissions have been taken into account for the water compartment:

- Emissions during formulation of processing chemicals as concentrated liquids (formulation in life cycle)
- Emissions from the processes used in the photographic industry (processing in life cycle)
- Emissions during waste disposal of used processing baths by specialized waste processing companies (waste disposal in life cycle)

4.1 Formulation of processing chemicals as concentrated liquids

19. Concentrated solutions of photo chemicals are made by dissolving and mixing the individual substance with other ingredients in water or in a highly water soluble solvent. Emissions may occur:

- to the drain: a small amount of the substance enters the drain when the mixing equipment is cleaned with water.
- as liquid waste: defective batches or batches out of specification.

20. When specific industrial data are not available, the emissions of the formulation stage should be estimated according to the A and B-Tables IC 10 in the TGD.

4.2 Emission by processing solutions

21. As main components or small dosage additives, photo chemicals fulfill definite functions in the various photographic processes. Table 2 describes the most important baths and the substance classes (functions) included in them.

Table 1 Processing steps depending on the material to be processed

processing bath	Description	function groups of ingredients
developing	In order to obtain a visible image from the exposed emulsion, all silver ions of those crystals, which constitute the latent image, must be reduced to metallic silver. To do this, the exposed silver halide is reduced by means of a developer solution, resulting in a primary silver image and the oxidized developer. In colour photography dyestuffs are formed in a subsequent step by reaction of the oxidized form of the developer and colour couplers in the emulsion layer.	developer antioxidant pH-regulating agent antifogging agent auxiliary solvent other

processing bath	**Description**	**function groups of ingredients**
bleaching	In the bleaching solution the metallic silver is oxidized to silver ion in the emulsion layer. Oxidizing agents are employed for converting the metallic silver into a silver salt, which can easily be removed by the following fixing step.	bleaching agent bleach accelerator rehalogenizing agent antifogging agent other
Fixing	Unexposed silver halide as well as silver salt formed in the bleaching baths of colour photographic material is removed from the emulsion layer leaving only the silver or colour image. The fixing agent forms water-soluble silver complexes with silver salts.	fixing agent pH-regulating agent hardening agent antioxidant other
bleach-fixing	Bleaching and fixing baths are combined in one bath (processing photographic paper).	fixing agent bleaching agent hardening agent antioxidant other
reversing	The formation of silver latent image specks in unexposed areas of the film is caused by chemical substances of the reversal bath (Only for reversing photographic film).	reversing agent pH-regulating agent other
stopping	To stop development at a specific time, the photographic material is transferred from the developer bath to an acidic solution, the pH of which is usually between 3 and 5. Alternatively cold water is used in some processes.	pH-regulating agent other
conditioning	Conditioning baths are used to accelerate the subsequent bleaching process. Only for reversal photographic material.	antioxidant antifogging agent bleach accelerator other
clearing/hypo elimination	In order to remove traces of the bleaching substances from the emulsion layer, a clearing bath containing mainly sulphites can be applied as an addition in the reversal process. This step can also be used for hypo elimination following fixing.	clarifying agent pH-regulating agent other
stabilizing	Binding of unused color coupling agents.	stabilizer interlacing agent other
washing	In the final washing step traces of bath components are removed from the emulsion layer as far as possible. Intermediate rinsing water *or counter current tanks are* necessary to minimize carry-over effects from one bath to another.	lime resisting agent other
Pre-bath	Softens remjet backing for removal.	pH adjustment, salt

4.2.1 Definition of the generic point source

22. It is necessary to define the generic point source for the various processes in order to determine the emission during the life cycle step of processing.

a) A typical point source for the photographic processes **E-6, R-3, C-41, RA-4, BW-P and BW-N** would be a **wholesale finisher** with a paper throughput of 2 000 000 m² y^{-1} and continuous processing machines This particular company processes films on paper and slides exclusively but on a large scale. The film and paper throughput in this company is made up of 2 % E-6, 1 % R-3, 11 % C-41, 81 % RA-4, 4 % BW-P and 1 % BW-N. Assuming 6 working days in 52 weeks per year, **6410 m² film/paper** are developed per day. The film and paper amount produced is estimated over the market share and size of the C-41/RA-4 finishers.

b) A **large x-ray division** in a hospital typically has a developed area of 40 000 m² film per year. Assuming 365 working days, the area developed per day is **110 m².d^{-1}**.

c) For reprography a **large printing office** is used as a point source. This company develops about **80 m² film per day** (25 000 m² per year).

d) A **copying facility** as the point source for the processes **ECN-2, ECP-2 and VNF-1** develops about **420 m² film per day**. Of these 46 m².d^{-1} are developed with ECN-2, 366 m².d^{-1} with ECP-2D and 8 m².d^{-1} with VNF-1.

In the following table these data are summarized.

Table 2 Defined generic point source for the life cycle step of processing

point source	photographic processes			produced film and paper [m².d^{-1}]
wholesale finisher	total		100 %	**6410**
		C-41	11 %	**700**
		RA-4	81 %	**5200**
		E-6	2 %	**130**
		R-3	1 %	**60**
		BW-N	1 %	**60**
		BW-P	4 %	**260**
X-ray division	total		100 %	**110**
		BW-X		
printing office	total		100 %	**80**
reprographic		BW-R		
copying facility	total		100 %	**420**
		ECN-2	11 %	**46**
		ECP-2D	87 %	**366**
		VNF-1	2 %	**8**

4.2.2 Release estimation

23. Usually the photographic industry employs continuing processes. Different technologies, like continuous processing machines, leader belt processors and in professional labs dipping machines are

available. Adding regenerating solutions constantly regenerates the photochemical process bath. The consumption of photo chemicals is made up of the desired photochemical transformation, the undesired chemical reaction and the transport of the substance into later baths with the film material.

24. This part of the emission scenario deals with the entry of photochemical substances into the water compartment as a result from the different processes. Solely the intermediate and final rinsing creates the emission. An estimation of the release is therefore made through the carry-over rate "CO".

25. The overflow of a photochemical process is collected in special tanks and turned over as waste to a waste disposal specialist.

26. The amount of rinsing water used is not relevant, since this is an input/output-analysis referring to the photo chemicals used. The real amount of wash water is very much depending on the applied technologies and equipments and can vary from 1 to 5 $L.m^{-2}$ (for the described point of source; wholesale finisher) and even more. The photographic material (film and paper) surface area processed per day "$Area_{mat}$" represents the defined point sources a), b), c), d).

27. To calculate the emission rate, the concentration of the substance in the fresh working solution C_{bath} is required. The applicant or industry should provide this value, or if not known, process- and bath-relevant formulas can be found in Tables 4 and 5.

28. If information regarding the process and bath are not given, the highest concentration is chosen as a default value. This principle is applied to all other emission estimation parameters as well.

29. The emission is estimated as follows:

$$Elocal_{water} = C_{bath} \cdot Area_{mat} \cdot CO \cdot (1 - F_R) \qquad (1)$$

Symbols:

symbol	Explanation	unit[1]	default	remarks
$Elocal_{water}$	local emission to waste water per day	[$kg.d^{-1}$]		
C_{bath}	content of the substance in fresh working strength solution or after establishment of balance	[$kg.m^{-3}$]		from applicant or industry see Tables 4 and 5
$Area_{mat}$	Surface area of photo material processed per day	[$m^2.d^{-1}$]		see Table 3
RR	replenishment rate	[$L.m^{-2}$]		see Table 3: parameter depends on process and bath
CO	carry-over rate	[$L.m^{-2}$]		see Table 3: parameter depends on process
F_R	fraction removed or converted during processing	[-]	0	from applicant or industry

[1] A factor of 10^{-3} has to be considered, when converting liters into cubic meters.

Comment: Reverse baths in the R-3 and conditioning baths in the R-3 and E-6 process are sometimes introduced directly into wastewater. This also applies to rinsing- and stop- baths (these contain small amounts of surfactant and strongly diluted acetic acid). In these cases the emission is calculated without the carry-over rate in the following manner:

$$Elocal_{water} = C_{bath} \cdot Area_{mat} \cdot RR \cdot (1 - F_R) \qquad (2)$$

30. In the case of the minilab, a washing step does not take place. Therefore no introduction into the water compartment has been considered. In this case the emission takes place in the waste stage of the life cycle.

31. In some cases the applicant may announce a substance, which is exclusively used in a bath that is followed by a second bath, which is no washing step. In those cases $C_{1/2}$ the concentration of substance 1, used in bath 1) and carried over in bath 2), should be modified to:

$$C_{bath1/2} = C_{bath1/1} \cdot CO \cdot (CO + RR_2)^{-1}$$

In those cases:

$$Elocal_{water} = C_{bath1/2} \cdot Area_{mat} \cdot CO \cdot (1 - F_R) \qquad (1a)$$

Symbols:

symbol	Explanation	Unit[1]	default	remarks
$Elocal_{water}$	local emission to waste water per day	[kg.d^{-1}]		
$C_{bath1/2}$	content of the substance from bath 1 in bath 2 after establishment of balance	[kg.m^{-3}]		
$C_{bath1/1}$	content of the substance in fresh working strength solution or content of the substance after establishment of balance in bath 1	[kg.m^{-3}]		from applicant or industry see Tables 4 and 5
$Area_{mat}$	surface of photo material processed per day	[m².d^{-1}]		see Table 3
RR_2	replenishment rate of bath 2	[L.m^{-2}]		see Table 3: parameter depends on process and bath
CO	carry-over rate	[L.m^{-2}]		see Table 3: parameter depends on process
F_R	fraction removed or converted during processing	[-]	0	from applicant or industry (0 %-at content of the substance)

Table 3 Release estimation parameter[2]: RR: replenishment rate by the listed process and process stage, CO: carry over rate by the listed process, $Area_{mat}$: surface area processed per day for the listed process, [Agfa 98], [Fuji 2001], [Kod 98], [Tet 2001], [INFU 2001], [EPCI 2001]

process[3]	**bath**	**RR[4] [L.m^{-2}]**	**CO [L.m^{-2}]**	**$Area_{mat}$ [m^2.d^{-1}]**
C-41 colour negative	developing	0.30–0.60	0.080	700
	bleaching	0.10–0.90		
	fixing	0.40–0.90		
	stabilizing	0.90		
RA-4 colour paper	developing	0.06–0.12	0.040	5200
	bleach fixing	0.07–0.14		
RA-4 devided bleaching and fixing	developing	0.06–0.12		
	stopping	0.15–0.20		
	bleaching	0.05–0.10		
	fixing	0.055–0.100		
	stabilizing			
E-6 colour reversal film	primary developing	0.9–1.8	0.080	130
	reversing	1.0–1.1		
	colour developing	1.0–2.0		
	conditioning	0.9–1.1		
	bleaching	0.2		
	fixing	0.4–1.0		
	stabilizing	1.0		
R-3 colour reversal paper	primary developing	0.17–0.33	0.050	60
	colour developing	0.05–0.50		
	bleach fixing	0.07–0.20		
	stabilizing			
R-3 devided bleaching and	primary developing	0.17–0.33		
	colour developing	0.05-0.50		
	bleaching	0.07–0.14		
	fixing	0.055-0.100		

[2] fraction removed or converted during processing F_R = 0 (default) fraction of waste-reduction F_{RW} = 0 (default)

[3] values of C-41, RA-4, E6, R-3, BW-P and BW-N are related to point source (a) -wholesale finisher
values of BW-X are related to point source (b) -hospital
values of BW-R are related to point source (c) -printing office
values of ECN-2, ECP-2 and VNF-1 are related to point source (d) –copying facility

[4] recycling processes of bath-solutions for point source (a) –wholesale finisher- are considered

process[3]	**bath**	**RR**[4] **[L.m⁻²]**	**CO [L.m⁻²]**	**Area$_{mat}$ [m².d⁻¹]**
fixing	stabilizing			
BW-N	developing	0.5-0.6	0.180	60
	fixing	0.4-0.9		
BW-P	developing	0.2-0.3	0.070	260
	fixing	0.055-0.30		
BW-X med.	developing	0.35-0.40	0.040	110
	fixing	0.4-0.6		
BW-X tech.	developing	0.5-0.6	0.040	
	fixing	0.8-1.2		
BW-R Film	developing	0.2-0.3	0.040	80
	fixing	0.15-0.30		
ECN-2 cine- and television-film negative	prebath rinse	0.375	0.180	46
	colour developing	0.845		
	stopping	0.560		
	bleaching	0.180		
	fixing	0.560		
	final rinse	0.375		
ECP-2D cine- and television positive	color developing	0.646	0.180	366
	stopping	0.721		
	primary fixing	0.187		
	bleach accelerating	0.187		
	bleaching	0.187		
	SECONDARY FIXING	0.187		
	final rinse	0.374		
VNF-1 cine- and television-film reversal	primary developing	0.348	0.180	8
	primary stopping	2.254		
	color developing	1.639		
	bleach accelerating	0.410		
	bleaching	0.410		
	fixing	1.281		
	stabilizing	0.615		

Remark:
The carry-over rates of professional labs differ from wholesale finishers in some processes as follows:

Process	CO [L.m^{-2}]
C-41	0.170
RA-4	0.070
E-6	0.170

Table 4 Release estimation parameter: C_{bath}: content of substance in processing solutions

process	processing solution	function of ingredient	[kg.m^{-3}]
C-41	Developing	Developer	5 - 8
		pH-regulating agent	20- 50
		Antioxidant	3- 6
		antifogging agent	1- 2
	Bleaching	bleaching agent	50- 120
		pH-regulating agent	10- 20
		rehalogenating agent	50- 120
	fixing	fixing agent	120- 150
		pH-regulating agent	10- 20
	stabilizing	stabilizing agent	<2
RA-4	developing	developing agent	6- 8
		pH-regulating agent	20- 40
		Antioxidant	3- 8
	bleaching	bleaching agent	30- 50
		pH-regulating agent	5- 10
		rehalogenating agent	10.5-52.5
	fixing	fixing agent	50- 90
		Antioxidant	6- 10
		sequestering agent	1- 3
	bleach-fixing	fixing agent	50- 100
		bleaching agent	30- 60
		pH-regulating agent	10- 20
		Antioxidant	5- 10
E-6	primary developing	Developer	15- 30
		pH-regulating agent	20- 35
		antifogging agent	1- 2
	reversing	reversing agent	1- 2
	colour developing	Developer	6- 10
		pH-regulating agent	20- 50
		Antioxidant	3- 6
	conditioning	pH-regulating agent	10- 20
	bleaching	bleaching agent	100- 150
		rehalogenating agent	50- 80
	fixing	fixing agent	120- 180
	stabilizing	stabilizing agent	1- 2
R-3	primary developing	Developer	15- 20
		pH-regulating agent	15- 30
		antifogging agent	1- 2
	colour developing	developing agent	5- 7
	bleach-fixing	fixing agent	50- 100

process	**processing solution**	**function of ingredient**	**[kg.m^{-3}]**
		bleaching agent	30- 60
		PH-regulating agent	10- 20
		Antioxidant	5- 10
BW	developing	Developer	5- 15
		pH-regulating agent	20- 70
		antifogging agent	0- 10
	fixing	fixing agent	50- 150
		pH-regulating agent	5- 20
		Antioxidant	5- 20
BW-X (med.)	developing	Developer	10- 20
		pH-regulating agent	20- 60
		hardening agent	1- 5
	fixing	fixing agent	100- 150
		pH-regulating agent	5- 20
		Antioxidant	5- 20
BW-X (tech.)	developing	Developer	10- 25
		pH-regulating agent	40- 80
		hardening agent	1- 5
	fixing	fixing agent	100- 200
		Antioxidant	8- 20
		pH-regulating agent	5- 15
BW-R	developing	Developer	10- 25
		pH-regulating agent	2- 20
		Antioxidant	2- 8
	fixing	fixing agent	70- 120
		pH-regulating agent	5- 15
		Antioxidant	5- 15
ECN-2	prebath	Salt	100
		pH-regulating agent	20
	colour developing	Antioxidant	1.4
		antifogging agent	0.43
		pH-regulating agent	13.5
		Developer	3
	stopping	pH-regulating agent	26.3
	bleaching	bleaching agent	
		antifogging agent	30.4
		pH-regulating agent	8.5
	fixing	fixing agent	68.2
		Antioxidant	12.9
	final rinse	Surfactant	0.1
ECP-2D	colour developing	Antioxidant	2.4
		pH-regulating agent	9.5
		antifogging agent	0.8
		developer	2,5
	stopping	pH-regulating agent	26.3
	primary fixing	fixing agent	54.8
		Antioxidant	8.9
	bleach accelerating	Antioxidant	2.9
		pH-regulating agent	3.7
	bleaching	bleaching agent	13.7

process	processing solution	function of ingredient	[kg.m^{-3}]
	secondary fixing	fixing agent	54.8
		Antioxidant	8.9
	final rinse	Surfactant	0.1
VNF-1	first developing	developer	0.2
		Antioxidant	1.6
		pH-regulating agent	16.1
		fixing agent	0.8
		Stabilizer	0.1
		antifogging agent	0.004
	primary stopping	pH-regulating agent	16.7
	colour developing	Developer	6.7
		Stabilizer	0.06
		antifogging agent	0.02
		pH-regulating agent	2.6
		Antioxidant	4.3
	secondary stopping	pH-regulating agent	16.7
	bleach accelerating	Antioxidant	5.6
		pH-regulating agent	4.4
	bleaching	bleaching agent	47.2
	fixing	fixing agent	93.9
		Antioxidant	5.2
	stabilizing	stabilizing agent	1.9

32. The following additional table provides an overview of the amounts of photo chemicals used in certain process baths. No distinction is made according to processes, but other ingredients of photographic baths are listed as well.

Table 5 Release estimation parameter: C_{bath}: content of substance in processing solutions -overview-

Processing solution	Function of ingredient	C_{bath} Contents in colour processing baths [g.L^{-1}]	C_{bath} Contents in black/white processing baths [g.L^{-1}]
developer	developing agent	4.0-11.5	11-15
	antioxidant	0.5-6.5	5-20
	alkali buffering agent	11-30	5-20
	complexing agent	0.1-4.0	2-5 1-10
	antifogging agent	0.4-1.6	17
	auxiliary solvent	12-19	
bleach	bleaching agent	50-80	
	bleach accelerator	0.2-0.4	-
	rehalogenizing agent	65-120	-
fix	fixing agent	70-120	110-140
	acid buffering agent	-	5-9
	hardening agent	-	ca. 5
	antioxidant	5-8	2-11
bleach fix	fixing agent	40-90	
	bleaching agent	30-70	
	hardening agent	-	
	antioxidant	5-10	

Processing solution	Function of ingredient	C_{bath} Contents in colour processing baths [g.L^{-1}]	C_{bath} Contents in black/white processing baths [g.L^{-1}]
reverse	reverse agent pH-regulating agent		
stabilizer	stabilizing agent	0.5-2	
conditioner	antioxidant antifogging agent bleach accelerator	7-12	
stop	hardening agent pH-regulating agent		
water	pH-regulating agent lime resisting agent		

4.3 Emission during waste disposal of used processing baths by special disposal companies

33. In some EU-countries (e.g. the Netherlands) the return rate of used photo baths is high with a volume of about 90 %. In other EU countries these rates are extremely low, what indicates, that sometimes more than 80 % of the used baths are emitted directly or indirectly to the environment. Such diffuse sources are not considered in this ESD.

34. In this ESD the release of the main emission sources is used to determine the $Elocal_{water}$. In some areas (for example the X-ray film development) a more economical use of chemicals will probably come due to lack of funds in most of Europe. There will always be companies that work significantly better (with smaller amounts of waste) as well as those that work much worse. Therefore, for the calculation of the emission the realistic worst-case is assumed.

35. Silver is removed from the waste in greater amounts. About 95% of the collected silver-containing baths are desilvered. In some countries desilvering and the injection in flue gas cleaning is used, in others the desilvered baths are incinerated or evaporated. There are some more recycling or disposal technologies available on the market, but their significance is not very high at the moment.

36. A detailed differentiation between the development processes is not possible and makes no sense in the context of the disposal practice.

4.3.1 Definition of the generic point source

37. A disposal company treats 600 – 14000 m³ photochemical baths per year. A typical company treats a volume of about 2000 m³ per year. Assuming 250 working days, **8 m³ d^{-1}** are treated per day. This volume is divided according to the shares of the used process baths (see Fig. 14).

38. Specific information of the disposal volume of used photochemical baths in the EU is not clearly indicated. An estimate of the disposal volume of used photographic baths for Germany is one L.y^{-1}, per one inhabitant.

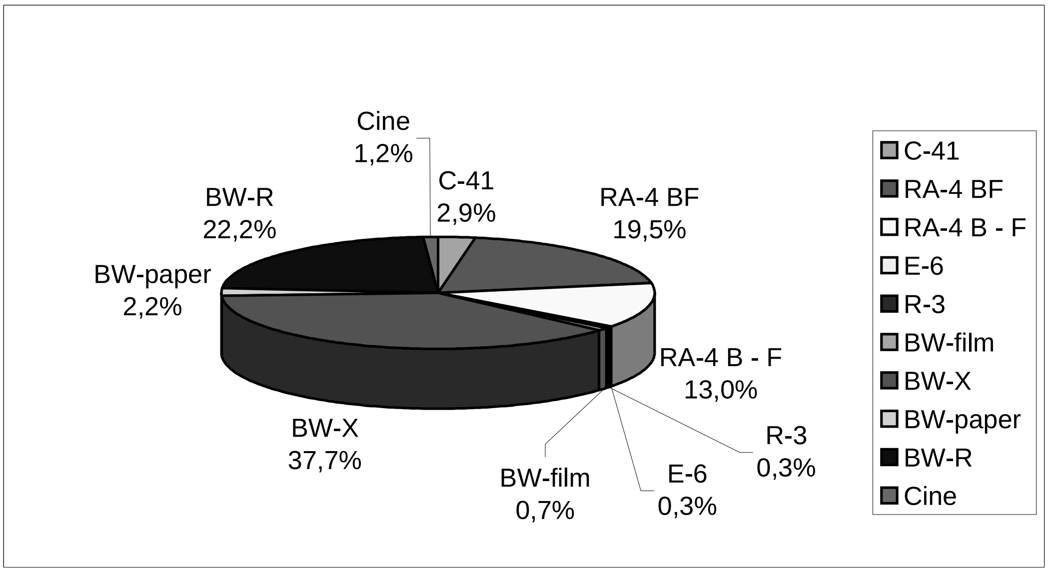


Fig. 14: Photographic processes by the size of their used baths shares [Bau98] [INFU 2001]

4.3.2 Release Estimation

39. The calculation of the emission is made accounting the volume at the disposal company as appropriate for the process:

$$Elocal_{water} = C_{bath} \cdot Vtreat \cdot (1 - F_R) \cdot (1 - F_{RW}) \qquad (3)$$

40. Since it is not possible to determine the disposal structure of a substance, when it is first introduced, the default value assumes that 100 % of the substance used enters the environment. A reduction of the waste can only be assumed, if the applicant can guarantee the disposal of the substance. Therefore, to calculate the emission, the waste reduction "F_{RW}" is included. A possible example scenario could be: a new chemical substance for a minilab is introduced, and acquiring the substance includes a service contract with the producer.

Symbols:

symbol	explanation	unit[1]	default	remarks
$Elocal_{water}$	local emission to waste water per day	[$kg.d^{-1}$]		
C_{bath}	content of the substance in processing solutions	[$kg.m^{-3}$]		from applicant or industry see Tables 4 and 5
$Vtreat$	treated volume per day	[$m^3.d^{-1}$]		see Table 6: parameter depend on process and bath
F_R	fraction removed or converted during processing	[-]	0	from applicant or industry
F_{RW}	fraction of the substance removed from solution by waste treatment	[-]	0	from applicant or industry

41. Table 6 shows the values of treated volume per day (Vtreat) for the defined generic point source by the size of the used baths' shares according Figure 14. In part I the colour and black/white photographic processes are differentiated. In part II the specific photographic processes are differentiated.

Table 6 Release Estimation Parameter: Treated volume [INFU 2001. EPCI 2001]

point source	photographic processes		Vtreat [m³.d⁻¹]
disposal company	**total**	**100 [%]**	**8**
	Part I: Used for calculation, if specific process is unknown		
	colour process	**37.0**	**3.0**
	Developing	32	1.0
	Bleaching	11	0.3
	Fixing	18	0.5
	Bleach fixing	39	1.2
	black/white process	**63.0**	**5.0**
	Developing	46	2.3
	Fixing	54	2.7
	Part II: Used for calculation, if specific process is known		
C-41	**colour negative film**	**2.9**	**0.2**
	developing	40	0.08
	bleaching	40	0.08
	fixing	20	0.04
RA-4	**colour positive paper**	**32.5**	**2.6**
	developing	30	0.78
	bleaching	8	0.21
	fixing	18	0.47
	bleach fixing	44	1.14
E-6	**colour reversal film**	**0.3**	**0.03**
	primary developing	44	0.013
	colour developing	44	0.013
	bleaching	10	0.003
	fixing	2	0.001
R-3	**colour reversal paper**	**0.3**	**0.03**
	primary developing	62	0.019
	colour developing	25	0.007
	bleach fixing	5	0.002
	bleaching	5	0.002
	fixing	3	0.001
BW-N	**black/white negative film**	**0.7**	**0.06**
	developing	85	0.05
	fixing	15	0.01
BW-P	**black/white positive paper**	**2.2**	**0.18**
	developing	90	0.16
	fixing	10	0.02
BW-X	**black/white X-ray**	**37.7**	**3**
	developing	40	1.2
	fixing	60	1.8
BW-R	**black/white reprographic**	**22.2**	**1.8**
	developing	52	0.9
	fixing	47	0.9
	activator	1	
Cine	**cine- and television film**	**1.2**	**0.1**
	developing		
	bleaching		
	fixing		

4.4 Ingredients in photographic material

42. Emissions from photographic materials can take place during the life cycle steps

- production of the photographic material (coating of the basic plastic layer with emulsions, production of the bath concentrates)
- processing of the photographic material in the developing processes (see chapter 4.2)
- disposal of the used photographic material (baths, film, photographic paper (see chapter 4.3).

43. No data are available for possible emissions during the production process of photographic material.

44. The positive silver halide crystals, color couplers and numerous adjuvants are incorporated in gelatine based emulsion layers. Emissions occur, when:

- small amounts go to the drain when the coating equipment is cleaned with water
- waste or defective batches or coating solutions are removed for destruction or collected for silver recovery.

45. The emulsion layers contains different functional groups of ingredients [Bau94], these are listed in Table 7.

Table 7 Function of substances in the emulsion layer

functional groups	Description
light sensitive agents	silver halide crystals of different grain size
colour couplers	form image dyes together with oxidized developer
Sensitizers	increase the sensitiveness
correction dyes	protect light-sensitive films from undesired spectral regions
spectral sensitizers	give particular sensitivity to a spectral region
antifogging agents	prevent the production of non-image silver

Table 8 Silver release in emulsion layers [DIBt 1999]

Process	content Ag [g.m^{-2}] in unused material	release Ag [%] from material	content Ag [g.m^{-2}] in developed material
BW-X (med.) (traditional film)	5	60	2
BW-X (med.) (laser film)	3	60	1.8
BW-X (tech.)	12	50	6
BW-R (black/white reprographic. paper)	2	50	1
BW-R (black/white reprographic. film)	6	80	1.2
BW-film	7	50	3.5
BW-paper	2	50	1

4.4.1 Release estimation for substances from photographic materials at processing

46. During processing, those substances, which are soluble in water, are partially dissolved from the photographic material and enter the processing and cleaning solutions.

47. The release by dissolving from the emulsion layer to the intermediate or final rinsing water may be estimated as:

$$Elocal_{water} = C_{mat} \cdot Area_{mat} \cdot F_{dis} \cdot (1 - F_R) \qquad \textbf{(4)}$$

Symbols:

symbol	explanation	unit[1]	default	remarks
$Elocal_{water}$	Local emission to waste water per day	[kg.d^{-1}]		
C_{mat}	content of the substance in photographic material	[kg.m^{-2}]		from applicant or industry see Table 9: worst case value for the used bath is given, depends not on process
$Area_{mat}$	surface of photo material processed per day	[m².d^{-1}]		see Table 3
F_{dis}	fraction which dissolves during processing from emulsion layer to the rinsing water	[-]	1	from applicant or industry
F_R	fraction removed or converted during processing	[-]	0	from applicant or industry

48. Unfortunately detailed information about the different process specific materials (ingredients in emulsion layers for colour film, for b/w-film, for x-ray-film etc.) is not available. Therefore it is not possible to differentiate in the following Table 9.

Table 9 Release parameter: C_{mat}: content of substance in photographic material

Ingredient	**content C_{mat} [mg.m^{-2}] paper**	**content C_{mat} [mg.m^{-2}] film**
Sensitizers	1	25
photographic stabilizers	5	100
Fungicide	30	150
silver as Ag	500	12,000
halides (Cl-. Br-. I-)	300	7,000
split of products		
· masking compounds in colour negative films	40	80
· remaining groups of colour couplers	80	800
· stabilizers	0	80
wetting agents	10	300
filter dyestuffs	50	250

5 DISPOSAL OF USED PHOTOGRAPHIC MATERIAL

49. Although emulsion constituents may be changed during processing, most of them remain on the film and paper, which are returned to the customer after processing. Waste prints and negatives are disposed of in municipal waste streams, ending up in landfills or incinerators.

50. Manufacturers and companies that deal with waste of photographic film and paper are concerned to extract the silver efficiently. Silver recovery from solid waste material (incineration, wet oxidizing) and wastewater can be assumed.

6 EXAMPLES

A Calculation of the emission rate of a sequestering agent of the RA-4 fixing bath (processing stage) (equation 1).

Input Data

C_{bath}	=	3	$kg.m^{-3}$
$Area_{mat}$	=	5200	$m^2.d^{-1}$
CO	=	0.04	$L.m^{-2}$
F_R	=	0	-

Output Data

$Elocal_{water}$	=	0.624	$kg.d^{-1}$

Calculation:

$$Elocal_{water} = C_{bath} * Area_{mat} *CO*(1- F_R)$$
$$= 3\ kg.m^{-3}*5200\ m^2.d^{-1}*0.04*10^{-3}\ m^3.m^{-2}$$
$$= 0.624\ kg.d^{-1}$$

B Calculation of the emission rate of a developing agent of the RA-4 developing bath during waste disposal (equation 3).

Input Data

C_{bath}	=	8	$kg.m^{-3}$
Vtreat	=	0.78	$m^3.d^{-1}$
F_{RW}	=	0	-
F_R	=	0	-

Output Data

$Elocal_{water}$	=	6.24	$kg.d^{-1}$

Calculation:

$$Elocal_{water} = C_{bath} * \text{Vtreat} *(1- F_R)\ (1- F_{RW})$$
$$= 8\ kg.m^{-3}*0.78\ m^3.d^{-1}$$
$$= 6.24\ kg.d^{-1}$$

C Calculation of the emission rate of a substance for an X-ray (med.) developer during waste disposal (equation 3).

Input Data

C_{bath}	=	25	$kg.m^{-3}$
Vtreat	=	1.2	$m^3.d^{-1}$
F_{RW}	=	0	-
F_R	=	0	-

Output Data

$Elocal_{water}$	=	30.0	$kg.d^{-1}$

Calculation:
$Elocal_{water}$ = C_{bath} * Vtreat *(1- F_R) (1- F_{RW})
= 25 $kg.m^{-3}$*1.2 $m^3.d^{-1}$
= 30 $kg.d^{-1}$

D Calculation of the emission rate of a pH-regulating agent for developing bath during a reprographic process (BW-R) (equation 1)

Input Data

C_{bath}	=	20	$kg.m^{-3}$
$Area_{mat}$	=	80	$m^2.d^{-1}$
CO	=	0.04	$L.m^{-2}$
F_R	=	0	-

Output Data

$Elocal_{water}$	=	0.064	$kg.d^{-1}$

Calculation:
$Elocal_{water}$ = C_{bath} * $Area_{mat}$ *CO*(1- F_R)
= 20 $kg.m^{-3}$*80 $m^2.d^{-1}$*0.04*10^{-3} $m^3.m^{-2}$
= 0.064 $kg.d^{-1}$

E Calculation of the emission rate of a sensitizer in the emulsion layer of a photographic colour paper (RA-4) (equation 4).

Input Data

C_{mat}	=	$1*10^{-6}$	$kg.m^{-2}$
$Area_{mat}$	=	5200	$m^2.d^{-1}$
F_{dis}	=	1	-
F_R	=	0	-

Output Data

$Elocal_{water}$	=	0.0052	$kg.d^{-1}$

Calculation:
$Elocal_{water}$ = C_{mat} * $Area_{mat}$ * F_{dis} *(1- F_R)
= $1*10^{-6}$ kg*m^{-2}*5200 m^2*d^{-1}*1
= 0.0052 kg* d^{-1}

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8 ABBREVIATIONS

BW-N	black/white negative film process
BW-P	black/white positive film process
BW-R	black/white reprographic process
BW-X	black/white X-ray process (medical and technical)
C-41	colour negative film process
E-6	colour reversal film process
ECN-2	cine- and television film negative process
ECP-2D	cine- and television film positive process
EP-2	colour negative film process
EU	European Union
IC	industrial category
P3-X-N	colour negative film process
P3-X-P	colour negative film process
$PEClocal_{water}$	Predicted Environmental Concentration (at the local stage)
R-3	colour reversal paper process
RA-4	colour positive paper process
STP	Sewage Treatment Plant
TGD	Technical Guidance Document of the European Union
VNF-1	cine- and television film reversal process