Standard Operating Procedure

TU/e

SOP details

Title	OrmoMould Fabrication for Polymer Imprinting
Description	This SOP describes how to fabricate an OrmoMould using OrmoStamp® to produce a hard mould with various topographies to imprint polymers via hot embossing
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Version number	1

	Name	Date	Signature
Prepared	Mehmet Tas	29-03-2021	
Reviewed	Burcu Gumuscu	24-5-2021	Revised.
Reviewed			
Authorized	Jan de Boer	18-4-23	

Version changes

Version	Name	Date	Changes made
1	Mehmet Tas	30-03-2021	First full version
2	Mehmet Tas	12-05-2021	Burcu's comments are addressed.
3	Burcu Gumuscu	24-5-2021	Revised, final.
4			
5			

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1 Purpose

This SOP describes how to fabricate an OrmoMould from a negative PDMS mould using a hybrid polymer called OrmoStamp® to realise the positive of the topographical features of a PDMS mould. This step is needed since the hot embossing process requires a hard mould to imprint polymer surfaces via hot embossing (SOP 1.6).

2 Principle

OrmoStamp® is an inorganic-organic hybrid polymer for the easy fabrication of transparent working stamps used in nanoimprint lithography (NIL) as a cost-effective alternative to quartz or electroplated stamps. OrmoStamp® can be applied in thermal NIL and/or UV-based NIL. Stamp copies can also be fabricated using OrmoStamp® hybrid polymer. It works well with the hot embossing procedure since it has excellent mechanical properties, stability and sub-micron resolution capabilities, can accommodate imprinting temperatures up to 160 °C and has a long stamp lifetime, i.e. (can be used many times for hot embossing).

3 Before You Start

You must complete PDMS mould production (SOP 1.4) before you start this protocol. It is not possible to make an OrmoMould from a silane treated Si wafer. Once the PDMS mould is produced, it should be cleaned with the nitrogen spray gun to make sure the surface is clean. This SOP can be used to make any type of OrmoMoulds on a glass or silicon dioxide substrate from a 4-inch PDMS negative mould, regardless of the sizes of the topographies. Before using this SOP, get an introduction to the microfabrication lab for the cleanroom (Feynman lab) and the equipment needed for this process from the super users.

OrmoStamp® is a UV sensitive hybrid polymer so it should be processed under yellow light in cleanroom environment with controlled ambient temperature and humidity. Best results are achieved at temperatures of 20–25 °C and relative humidity of 40–46 %.

4 Required materials

4.1 Workplace

This SOP should be performed in the microfabrication lab (Gemini- Noord, Feynman lab). Follow the safety protocols instructed by the lab managers and perform the experiment accordingly in allocated locations in the lab.

4.2 Equipment and disposables

- 4" Glass (BF) 33 Wafers (Supplier: Pi-Kem, Double-side Polished, Surface Roughness R_a = 2 nm)
- Spin coater
- Programmable hot plate

- UV-LED Light Source Machine (Brand: Idonus)
- N_2 (Nitrogen) spray gun
- Fumehood
- Plastic pipette (2ml) (LP Italiana, supplier VWR)

4.3 Chemicals

- OrmoPrime®08 (Micro Resist Technology GmbH, located in the chemical cupboard)
- OrmoStamp® (Micro Resist Technology GmbH, the bottle is located in the chemical cupboard)

5 Procedure

OrmoMould is fabricated in two steps; first OrmoPrime®08 processing to improve adhesion and then OrmoStamp® mould fabrication.

5.1 Working procedure

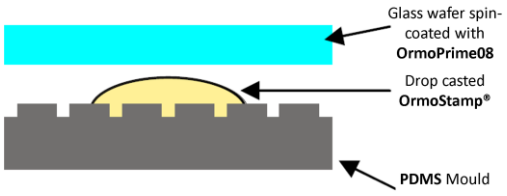
5.1.1 OrmoPrime®08 processing

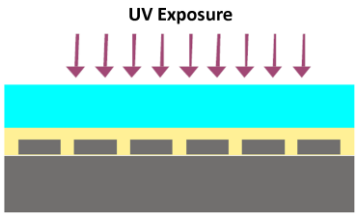
In order to achieve an optimized adhesion of OrmoStamp® to glass or quartz substrates, it is highly advisable to use an adhesion promoter such as OrmoPrime®08. This will prevent damaging your OrmoMould during hot embossing and will extend its lifetime.

Substrate preparation (Optional)	1. The glass substrate has to be free of impurities and moisture prior to OrmoStamp® coating. It should be spin-cleaned with acetone/ 2-propanol, baked at 200 °C for 5 min and cooled to room temperature immediately before coating. Alternatively, short oxygen or ozone plasma cleaning is recommended. 2. Pre-cleaning with a gentle etching agent (e.g. acetic acid) will also improve the adhesion. If you are using clean, new wafers out of the box, this is not necessary.
Spin Coating 	3. Cover the inner walls of the spin coater with aluminium foil as explained in the operating manual located next to the spin coater. 4. Place your clean glass wafer on the vacuum chuck in the centre. 5. Take 1 ml of OrmoPrime®08 using a plastic pipette.

	6. Spin coat OrmoPrime®08 resist @3000 rpm (acceleration 1000 rpm) for 30 s.
Hard bake 	7. Hard bake on a hotplate @ 150°C for 5 min.
Note: The film thickness is around 150 nm after baking. Make sure you let the substrate cool down to room temperature (~10 min) before you move on to the next step. A primed glass wafer can be stored up to 48 hours in a closed petri dish at room temperature before applying the OrmoStamp.	

5.1.2 OrmoStamp® Processing

Substrate preparation	1. Use the glass wafer coated with OrmoPrime®08. 2. Take your PDMS mould.
OrmoStamp® Casting 	3. Put your PDMS mould in the fumehood, flat on the surface. 4. Take precisely 1.5 ml OrmoStamp® using a disposable plastic pipette and drop cast it onto the **PDMS mould** (from the centre). Place small cleanroom tissue pieces at the edges of PDMS mold as a gap-keeper between the PDMS and glass mould. Then carefully place the glass wafer on top as shown in fig 1. Let the OrmoStamp® flow and fill the gap between the glass mould and PDMS by capillary force (at least 20 min), then slowly remove the spacers accordingly. <u>CRITICAL STEP: Tips for minimizing air bubbles in your OrmoMould:</u> - Do not shake the OrmoStamp® bottle. - The drop-casting should be performed in one go, in a continuous flow from the pipette onto the PDMS mould. - Avoid sucking air into the pipette, always apply a certain amount of pressure whilst handling to make sure no air is going inside the tube.

	- The glass wafer should be placed very slowly to avoid trapping air in between topographical features. Let the air escape.
UV Curing 	5. Switch on the UV-LED Light Source Machine. The minimum dose is 1000 mJ/cm^2 set the intensity to 12 mW/cm^2. Intensity should remain below 20 mW/cm^2 6. The machine calculates the time automatically if the correct dose is entered. Note: UV curing leads to volume shrinkage in the range of 4–6 %. Applying a UV overdose during curing does not affect OrmoStamp®'s properties. Keep the substrate-mould stack always horizontal until the resin is fully cured.
Hard bake 	7. Peel the PDMS mould from the glass wafer. 8. Hard bake the Glass with OrmoStamp® on a hot plate @ 130°C for 30 min. Use the hot plate for temperature ramp up @ 5°C/min and ramp down. Note: The final thickness of the OrmoStamp® will be around 150 – 170 µm. The exact thickness of the film may depend on master stamp structures.

See below Figure 1 and Figure 2 to visualise the critical steps described in 5.1.1 to process the OrmoStamp® to fabricate an OrmoMould. Drop casting of the OrmoStamp® polymer and the manual placement of the glass wafer coated with OrmoPrime®08 on top of the PDMS mould are the two critical steps (Figure 1) that could result in introducing air bubbles into the polymer. For instance, if the glass wafer is placed on top of the OrmoStamp® hurriedly, there will not be enough time for the air that is in between the glass wafer and the PDMS mould to escape resulting in the entrapment of unwanted small air pockets which will cause loss of topographic features and the overall lifetime yield of the OrmoMould.

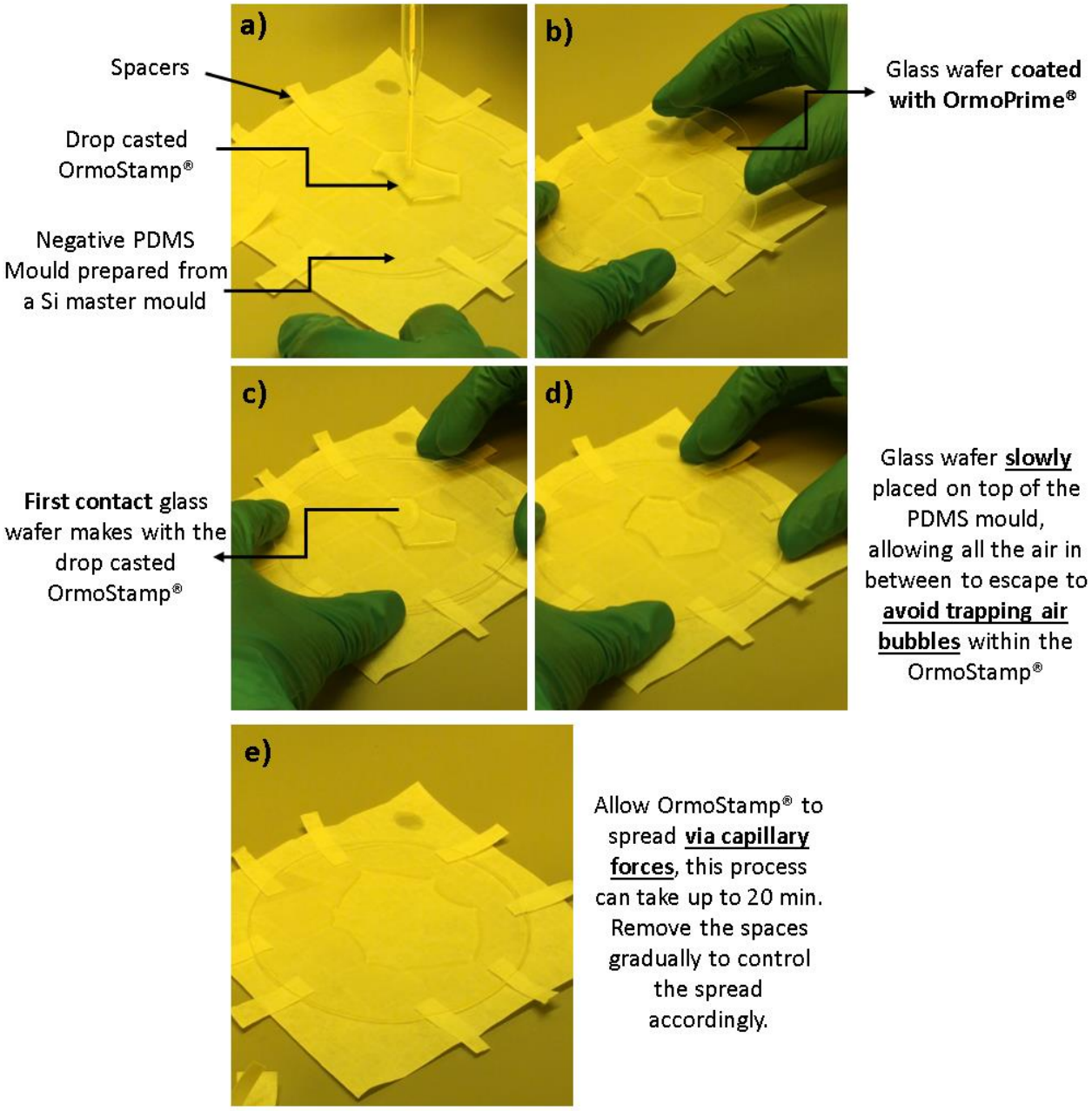


Figure 1. (a-e) The critical steps of the OrmoStamp® drop-casting and glass wafer substrate placement.

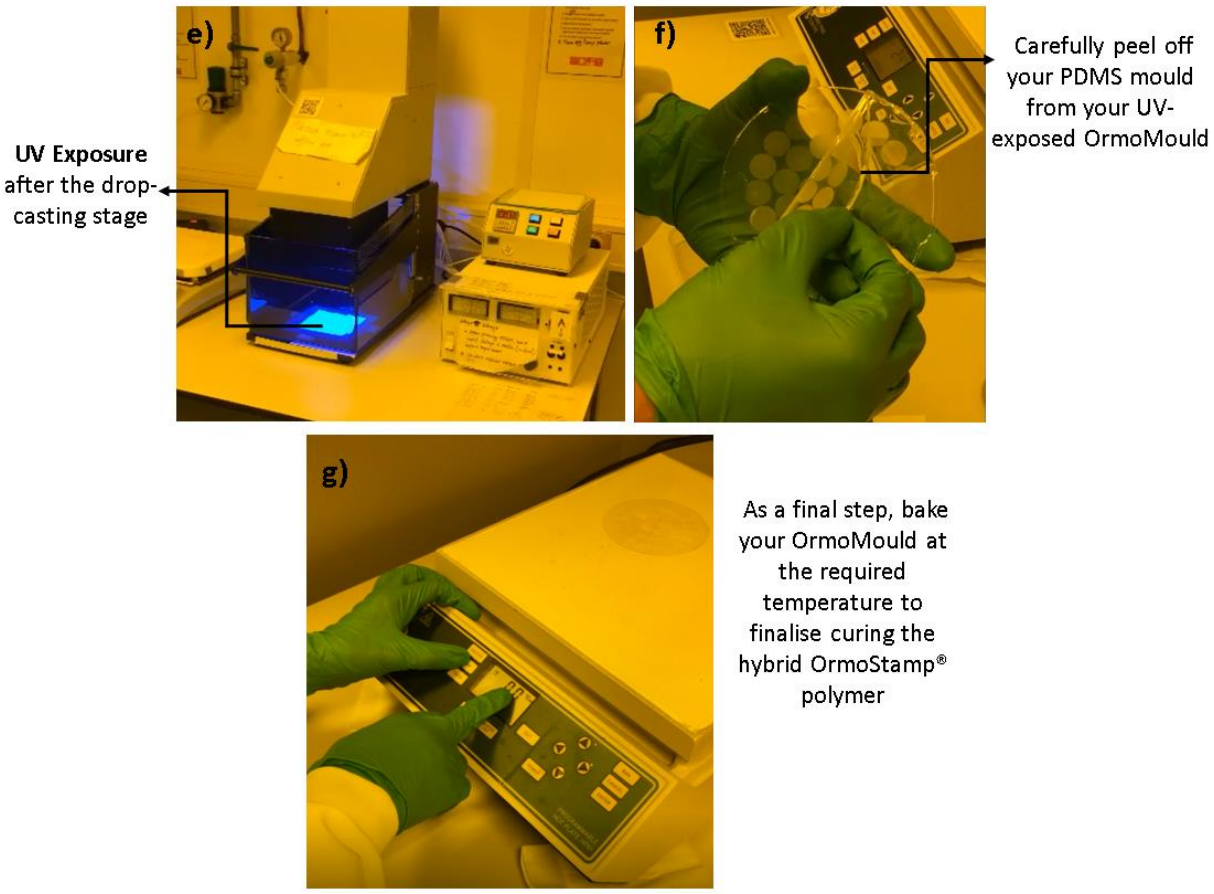


Figure 2. (e-g) The following required processing steps to fabricate the OrmoMould after the OrmoStamp® casting.

It is important that the fabricated OrmoMoulds are plasma treated (SOP 1.2 – Oxygen Plasma Treatment) and then silane treated (SOP 1.3 – Silanization Treatment) after completing the hard baking step described above.

An OrmoMould could be used many times to imprint polymer films as long as it remain intact. As OrmoStamp® forms a three-dimensional polymer network during curing, drastic conditions for removal are necessary. The solvent PGMEA or NMP-based solvents in an ultrasonic bath at higher temperature (40-60 °C) for several hours will usually result in a peel off. Alternatively, dry etching with O_2/CHF_3 plasma can be used to remove the cured hybrid polymer.

Do not use pure oxygen plasma! Porous SiO_2 will be formed.

5.2 Safety

Work in the Feynman lab in Gemini-Noord according to the safety regulations. Follow the instructions given in the lab introduction by the lab managers

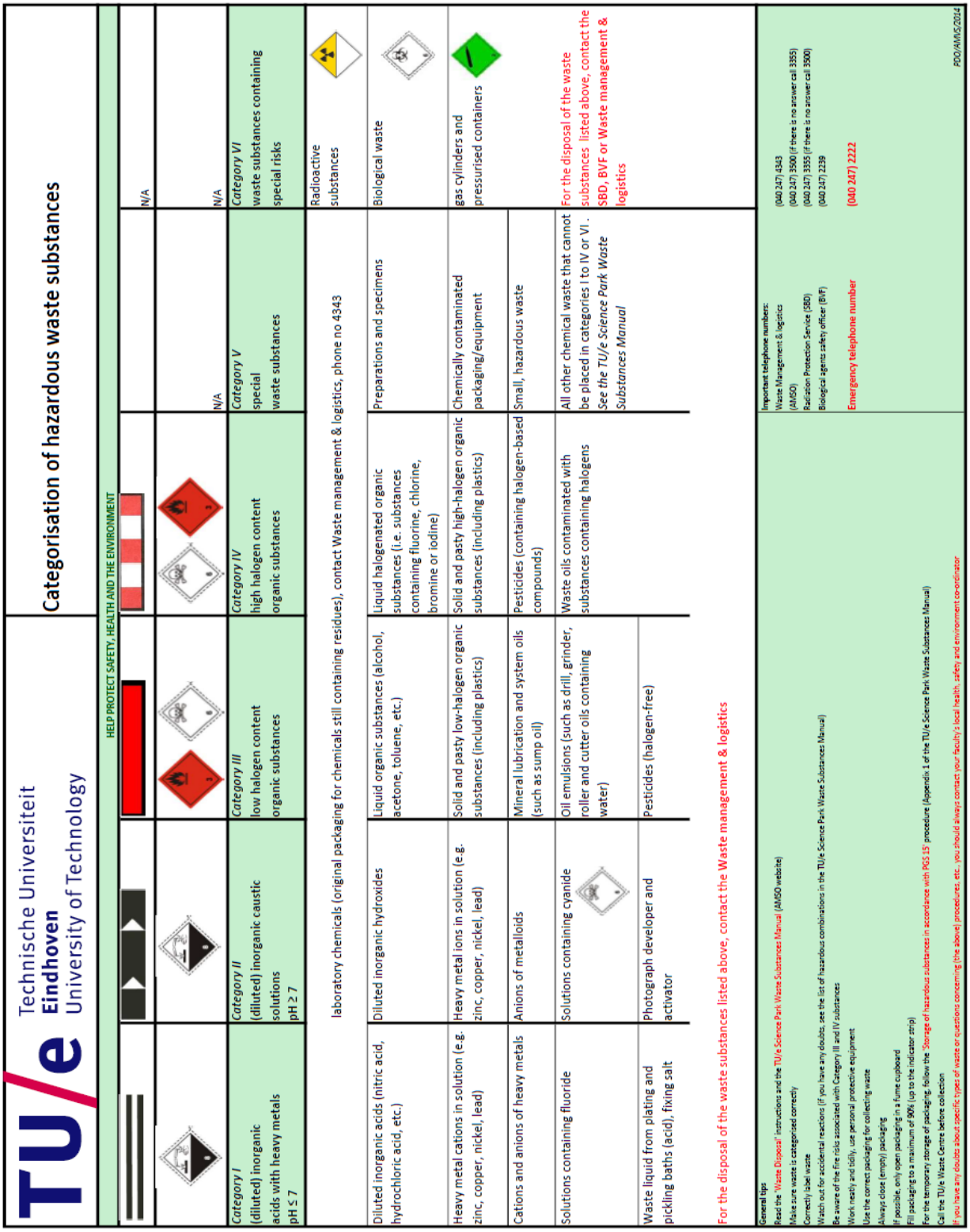
6 Waste

When working in the Feynman lab, handle waste according to guidelines which are labelled at the waste disposal based on its categories as given below in the Table 1.

If you are unsure how to dispose of OrmoStamp®, follow below guidelines:

- Unexposed material: dispose of as halogen-poor solvent.
- Exposed material: dispose of as solid chemical waste.

OrmoPrimo08® should be disposed of as halogen-poor solvent.



Technische Universiteit Eindhoven University of Technology

Categorisation of hazardous waste substances

HELP PROTECT SAFETY, HEALTH AND THE ENVIRONMENT

					N/A	
				N/A	N/A	
Category I (diluted) inorganic acids with heavy metals pH ≤ 7	*Category II* (diluted) inorganic caustic solutions pH ≥ 7	*Category III* low halogen content organic substances	*Category IV* high halogen content organic substances	*Category V* special waste substances	*Category VI* waste substances containing special risks	
laboratory chemicals (original packaging for chemicals still containing residues), contact Waste management & logistics, phone no 4343					Radioactive substances	
Diluted inorganic acids (nitric acid, hydrochloric acid, etc.)	Diluted inorganic hydroxides	Liquid organic substances (alcohol, acetone, toluene, etc.)	Liquid halogenated organic substances (i.e. substances containing fluorine, chlorine, bromine or iodine)	Preparations and specimens	Biological waste	
Heavy metal cations in solution (e.g. zinc, copper, nickel, lead)	Heavy metal ions in solution (e.g. zinc, copper, nickel, lead)	Solid and pasty low-halogen organic substances (including plastics)	Solid and pasty high-halogen organic substances (including plastics)	Chemically contaminated packaging/equipment	gas cylinders and pressurised containers	
Cations and anions of heavy metals	Anions of metalloids	Mineral lubrication and system oils (such as sump oil)	Pesticides (containing halogen-based compounds)	Small, hazardous waste		
Solutions containing fluoride	Solutions containing cyanide	Oil emulsions (such as drill, grinder, roller and cutter oils containing water)	Waste oils contaminated with substances containing halogens	All other chemical waste that cannot be placed in categories I to IV or VI . *See the TU/e Science Park Waste Substances Manual*	For the disposal of the waste substances listed above, contact the SBD, BVF or Waste management & logistics	
Waste liquid from plating and pickling baths (acid), fixing salt	Photograph developer and activator	Pesticides (halogen-free)				

For the disposal of the waste substances listed above, contact the **Waste management & logistics**

General tips
Read the 'Waste Disposal' instructions and the TU/e Science Park Waste Substances Manual (AMSO website)
Make sure waste is categorised correctly
Correctly label waste
Watch out for accidental reactions (if you have any doubts, see the list of hazardous combinations in the TU/e Science Park Waste Substances Manual)
Be aware of the fire risks associated with Category III and IV substances
Work neatly and tidily, use personal protective equipment
Use the correct packaging for collecting waste
Always close (empty) packaging
If possible, only open packaging in a fume cupboard
Fill packaging to a maximum of 90% (up to the indicator strip)
For the temporary storage of packaging, follow the 'Storage of hazardous substances in accordance with PGS 15' procedure (Appendix 1 of the TU/e Science Park Waste Substances Manual)
Call the TU/e Waste Centre before collection
If you have any doubts about specific types of waste or questions concerning (the above) procedures, etc., you should always contact your faculty's local health, safety and environment co-ordinator

Important telephone numbers:
Waste Management & logistics (AMSO) (040 247) 4343
Radiation Protection Service (SBD) (040 247) 3500 (if there is no answer call 3355)
Biological agents safety officer (BVF) (040 247) 3355 (if there is no answer call 3500)
(040 247) 2239

Emergency telephone number (040 247) 2222

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Table 1: Categories of hazardous liquid waste