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Guide for Risk Assessment in Small and Medium Enterprises

3 Chemical Hazards

Identification and Evaluation of Hazards; Specification of Measures

issa | INTERNATIONAL SOCIAL SECURITY ASSOCIATION

Section for Electricity
Section for Iron and Metal
Section for Machine and System Safety

Guide for
Risk Assessment in
Small and Medium Enterprises

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Section for Electricity
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Imprint

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Introductory Note

This brochure is intended to meet the requirement for a risk assessment for work with hazardous substances.

The brochure is divided into the following chapters:

1. **Principles**
2. **Risk Assessment**
3. **Specification of Measures**
4. **Annexes**

Note:

This brochure serves for implementing the Framework Directive on the introduction of measures to encourage improvements in the safety and health of workers at work (89/391/EEC) of its adopted specific Directives and of the relevant provisions transposed into national law.

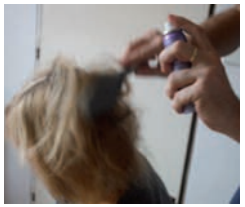
The documentation of the risk assessment is not subject of this series of brochures as there are great national differences between the individual Member States.

Beside the subject “Chemical hazards”, brochures with the same structure are planned (available) on the following issues:

- **Hazards caused by machinery and other equipment**
- **Hazards caused by electricity**
- **Hazards caused by fire and explosions**
- **Hazards causes by whole-body/hand-arm vibrations**
- **Falling on the plane and falling from a height of persons**
- **Physical strain (e.g. heavy and one-side work)**
- **Noise**
- **Mental workload**

1. Principles

Hazardouds substances can be found at nearly all workplaces, including small and medium enterprises e.g.:

	workplace	hazardous substances	danger symbols old RL 67/548/ECC	danger symbols new GHS/CLP
Sites		paint removers, paints and varishes, cements, auxiliary, building materials etc.		
Hairdressers		hair colours, hairspray, decolorants, bleaching agents		
Cleaning agents		cleaning agents desinfecting agents, etc.		
Shops		oils, solvents, diluents and thinners, …		

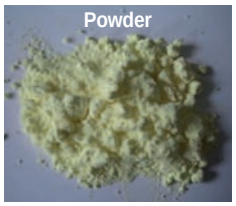
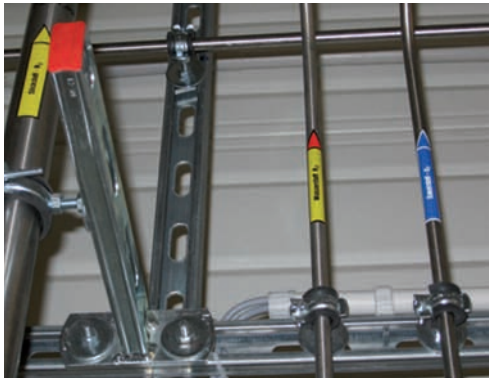
	workplace	hazardous substances	danger symbols old RL 67/548/ECC	danger symbols new GHS/CLP
Farms, plant nurseries		pesticides and, herbicides etc.		
Electroplating shops		acids bases, nickel chloride, potassium cyanide, chromic acid etc.		
Production and application of coating materials		binders, solvents, additives, pigments		
etc.				

Hazardous substances are any liquids, gases or solids that affect workers' health or safety.

These are also substances which are generated or released (welding fumes, emissions from diesel engines, wood dust, flour dust etc.) during processing as well as those where no labelling is required. These substances are delivered or stored in different types of packaging.

Hazardous materials are shipped and stored in different packaging forms.

Different types, storage and packaging of chemicals

solid	 Powder	 Granules	 Tablets
liquid			
gas			

These are also substances which are generated or released (welding fumes, emissions from diesel engines, wood dust, flour dust etc.) during processing as well as those where no labelling is required.

These substances are delivered or stored in different types of packaging.

Legal bases

The Council Directive 98/24/EC of 7 April 1998 (14th individual Directive of the Framework Directive 89/391/EEC on worker protection), regulates the minimum prescriptions for the protection of workers from the risks related to chemical agents at work. This Directive was transposed into national law by the Ordinance on Hazardous Substances.

Manufacturers, importers and users

On 1 July 2007, the REACH Regulation, a new law on chemicals applicable within the European Union came into force (EC No. 1907/2006).

REACH is the short form for **R**egistration, **E**valuation, **A**uthorisation and restriction of **Ch**emicals.

REACH is intended to force manufacturers and importers of chemical substances by means of a registration and assessment procedure to provide sufficient data for a safety assessment of the chemicals. This information is entered in the safety data sheets and serves as an important base for risk assessment.

There is a new global classification and labelling of chemicals regulated by the GHS system (**G**lobally **H**armonized **S**ystem). GHS is implemented in Europe by the **CLP** Regulation (**c**lassification, **l**abelling and **p**ackaging of Substances and Mixtures) and will apply to substances from 1 December 2010, including transition periods, and to mixtures from 1 June 2015.

Concerning different labelling of chemicals according to the regulation on carriage of dangerous goods by road and rail, to the hazardous substances regulation and to GHS/CLP see the following figure.

Identification of Dangerous Chemical Substances

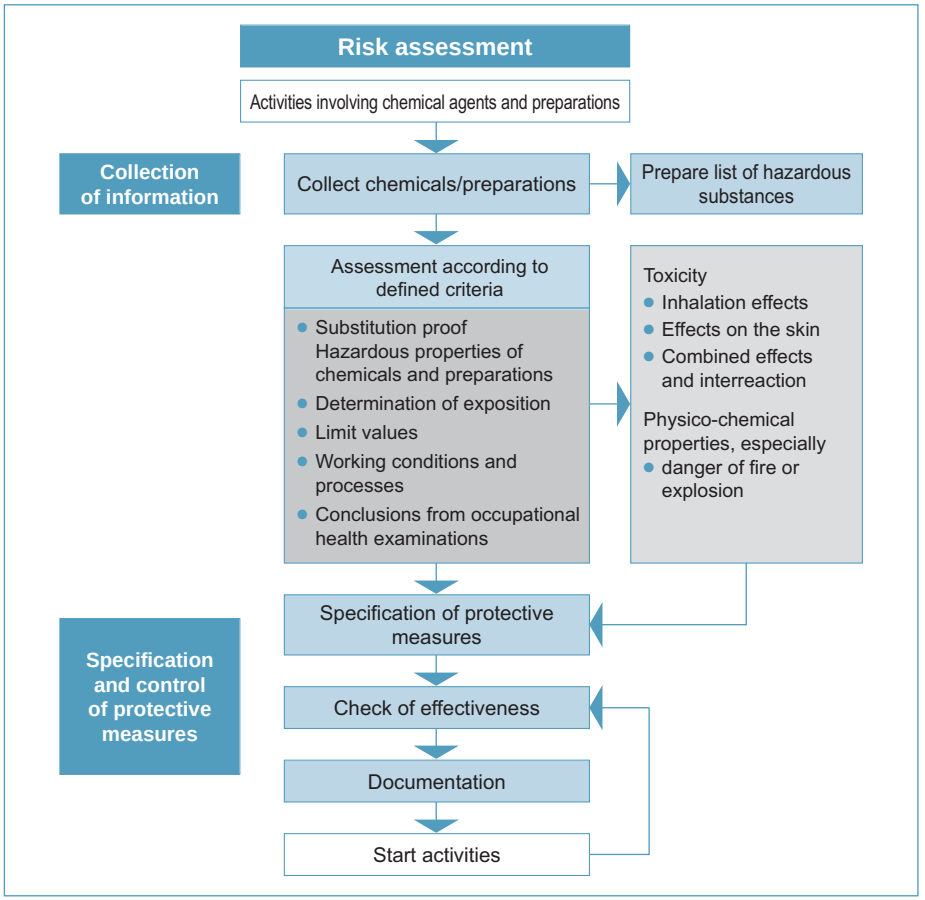
ADR/RID	EC-Directive 67/548/ECC	GHS
		

2. Risk Assessment

The employer shall ensure that hazards of employees caused by hazardous substances are identified, eliminated or reduced to a minimum by means of protective measures.

2.1 | Systematics of Risk Assessment

The individual steps for the risk assessment (see scheme) are described in the following clauses.



2.2 | Identification of hazardous Substances at the Workplace

Pursuant to the Hazardous Substances Ordinance, the employer shall first determine whether hazardous substances are present at the workplace.

How can we find out, whether a working substance is a hazardous substance?

- labelling of chemicals (danger symbols, R-sentences/H-statements)
- Safety Data Sheets
- list of occupational exposure limit values
- list of occupational diseases

A lot of information can be taken from the product label (see label for methanol with labelling according to previous Directive 67/548/EEC and future labelling for GHS/CLP).

During working with hazardous substances, the following items shall be considered when performing risk assessment:

- hazardous properties (labelling, SDS)
- health and safety information of the manufacturer or of the importer (SDS)
- level, type and duration of exposure, taking all ways of exposure into account
- working conditions and processes, including working substances and the amount of hazardous substances
- exposure limit values including short-term values (exceeding factor) or biological limit values

- effect of preventive measures taken or to be taken
- conclusions from occupational health examinations already carried out

Registration of hazardous substances, their properties and their effects

Hazardous substances are systematically registered in the table of hazardous substances (see Annex 1). This table can be prepared related to the workplace, work area or department.

If many working substances are used at a workplace or in a work area (e.g. in chemical laboratories, pharmacies), also representative substance groups such as acids/bases (key components) may be chosen. The risk assessment is then prepared for these key components.

Examples of hazardous substances

	**Hydrofluoric acid** T+; C; R 26/27/28, R35
	**Methanol** T, F; R11, R23/24/25, R39/23/24/25
	**Glass Cleaner/AAA** F, Xi; R11, R36, R36/38, R67 (contains Isopropanol, Ethanol)
	**Hydrochloric acid > 25 %** C; R34, R37

Health effects

Hazardous substances may have acute (acute toxic, caustic, irritative) and/or chronic (carcinogenic, toxic to reproduction, mutagenic) properties. Hazard characteristics and warnings of danger (R-sentences/H-statements) point out these properties.

On the basis of the R-sentences R 20 up to and including R 68 (with the exception of R 44, R 50 and R 59) different health hazards can be derived.

Health effects

Acute effects	**poisoning** T, e.g. R23, R24, R25, R26, R27, R28, R29, R31, R32
	chemical burn C, e.g. R34, R35
	suffocation by lack of oxygen
Chronic effects Long-term effects	**fires and explosions** E, e.g. R1, R2, R3, R4, R5, R6, R9, F +, F, e.g. R7, R8, R10, R11, R12
	respiratory diseases T+, T, Xn, e.g. R39, R48
	carcinogenic R40, R45, R49
	mutagenic R46
	toxic to reproduction R60, R62 **teratogenic** R61, R63, R64
	sensitising and allergies T, Xn, Xi, e.g. R42, R43

2.3 Further Information on hazardous Substances (safety data sheets, exposure scenarios)

Hazards caused by hazardous substances may be influenced by the following items

- their hazardous properties
- processing temperature, vapour pressure and saturation concentration
- particle size
- by displacement of atmospheric oxygen

Required and useful documents:

- up-to-date safety data sheet (should not be older than 3 years) including exposure scenarious according to REACH
- labelling of the working substance with danger symbols and R-sentences/H-statements or information for use and/or package insert text for working substances, which are covered by other regulations (e.g. pharmaceuticals, cosmetics, fertilizers, hazardous wastes)
- occupational exposure limit values
- results from occupational health examinations

2.4 | Further Information about the Workplace

Working conditions shall be identified by taking into account technical, organisational and personal measures. This shall be done in cooperation with the workers and superiors concerned.

Technical measures

Technical protective measures available at the workplace such as local ventilation or forced ventilation shall be considered. The efficiency of this equipment shall be checked at regular intervals.

Processing conditions

For the type of processing, workplace specific circumstances such as increased temperature or pressue shall be considered. Furthermore, the processing technology shall be taken into account, e.g. spraying, dip coating, painting.

Quantity used

Limitation of hazardous substances present at the workplace to a quantity required for the relevant work.

Level of exposure

The evaluation is carried out on the basis of reliable measuring values representing the exposure level at the workplace. If no limit value is specified, international limit values shall be used. If no international limit value exists, limit values for homologous substances or substances with comparable chemical effect shall be used.

Work intensity

The respiratory volume and hence the intake of hazardous substances is influenced by different intensities of work.

Exposure time (duration of exposure)

A crucial criterion for the weigth of exposure of persons by a hazardous working substance is the duration of exposure at the workplace of the worker concerned.

Co-exposed persons, exposure of bystanders

Are other, possibly noninvolved employees also exposed due to the working method at the workplace?

Aptitude, training, instruction

Employees shall regularly, at least annually, be instructed and trained in working with hazardous substances.

Required PPE (personal protective equipment)

The provided PPE shall meet the requirements of the safety objective and be consequently used. It shall always be in perfect condition. The employer is responsible for its provision and functionalibity.

Eye/skin contact

Skin/eye contact shall be prevented, e.g. by using suitable protective gloves (e.g. acid-proof, oil resistant, solvant resistant) particularly for work with toxic, caustic, irritant, allergising or skin-resorptive substances. Information is given in the safety data sheet. Eye contact is prevented, if complete spectacles (e.g goggles) or a face screen are used.

2.5 | Risk estimation

On the basis of the “substance properties” (degree of possible harm) and „probability of occurrence of harm“, the risk of handling a working substance is evaluated. Risk elimination is actually the first principle for prevention.

Carcinogens and mutagents shall be replaced at the workplace by less dangerous substances. This obligation exists whenever it is technically and economically possible to do so. This process is supported by registration, evaluation, authorization and restriction of chemicals according to the REACH ordinance. Thus, Annex XVII of the REACH Regulation contains restrictions for manufacturers for the placing in the market and use of certain substances, preparations and products.

Such chemicals have special health risks or hazards (carcinogenic (K), mutagenic (M) and/or toxic to reproduction (RF) or teratogenic (RE) in ***categories 1*** or ***2***).

Categorie 1:
explicitely proven in human beings

Categorie 2:
proven in animal experiments

The substances are labelled with the danger symbol toxic (T) and the R-sentences R45, R49, R46, R60 and R61 and all combinations with other R-sentences.

Examples for such substances:

K1: benzene, asbestos, chromate (VI) compounds

K2: hydrazene, cadmium compounds

M2: cadmium and its compounds

R_E1: passivesmoking, lead, carbon monoxide

R_F1: special hormones

When these listed substances are used at workplaces, they have to be substituted.

To help employers, there is a list of substances subject to authorisaton in Annex XIV of REACH. The manufacturer and the importer shall indicate on the safety data sheet for which process the substance is authorised. The user wanting to work with the authorized substances shall check whether his/her process conditions comply with the authorisation.

The purpose of a risk assessment is to evaluate the riks for exposed persons and the possible hazards depending on the conditions given at the workplace.

The risk occurring during work with hazardous substances may depend on the following factors:

- risk generated due to hazardous chemical reactions which may affect the health and safety of workers (chemical reactivity and instability of hazardous substances etc.)
- risk due to inhalation of substances depending on the toxicity of the substances, exposure time, and sensitising properties
- risk due to absorption through the skin depending on the toxicity of the substance as well as on the type, duration and frequency of contact

- risk due to contact with the skin or eyes
- risk due to ingestion depending on the toxicity of the substance and on personal hygiene habits
- risk due to penetration through the parenteral route (toxicity of the hazardous chemical agent, damage to the skin etc.)
- risk of fire and explosion depending on the physical condition: gas, liquid, solid, dust, temperature, pressure, flammability, heat capacity, explosion limits, ignition sources: smoking, welding, electrostatic charge, mechanical sparks and exotermic chemical reactions

Based on the obtained findings, the work of employees has to be evaluated. First the inhalative, dermal, and physical-chemical hazards are to be identified and assessed and then be consolidated in the overall assessment.

Prolonged contact with the hazardous substances (from a few minutes to years) may possibly affect the health of the employees even if contact was relatively short. In individual cases, occupational diseases may occur as a result of exposure. In case of an accident the risk is also due to the property of the hazardous substance.

The EU Member States have different systems of risk assessment. The employer may obtain relevant information from the national health and safety authorities.

Further information can be found in the clause on National Aspects.

3. Specification of Measures

It is not always possible to eliminate risks. Therefore, appropriate protective measures are nessessary, the efficiency of which must be checked.

During work with hazardous substances, it shall in principle be checked whether the hazardous substance can be substituted by a less dangerous substance (substitution test) or whether exposure can be prevented or reduced by changing the working process.

When carrying out protective measures, the following sequence of measures shall be observed:

- Use of working substances as non-hazardous as possible, i.e. use of working substances with the smallest hazard possible for persons.
- Working processes and working operations shall, if technically possible, be so designed that employees cannot come into contact with hazardous working substances and that hazardous gases, vapours or suspended matter cannot be released. Minimization of the capability of release or improvement of technical equipment. Written working instructions shall be laid down in which individual safety requirements and their monitoring are specified.
- If measures cannot prevent hazardous gases, vapours or particulate matter from being released, they shall be completely captured at their outlet or point of generation and then removed without any hazard for the employees, as far as allowed by the state of the art. If such a capture is not possible, ventilation measures shall be provided which correspond to the state of the art.
- Limitation of quantity of available hazardous working substances to the extent essential for work.
- Limitation of duration and intensity of a possible exposure of employees to hazardous substances to the essential extent. This obligation is of special importance in case of carcinogenic substances. This could be accessed by providing sufficient ventilation of premises or by an effective room ventilation.
- Limitation of number of employees who are exposed to hazardous working substances, e.g. by limiting acces to certain work areas at risk or by spatial separation.
- Where despite the measures given in the different items a sufficient protection can still not be obtained for the employees, the employer shall ensure that appropriate personal protective equipment is used, e.g. eye, skin protection, respiratory equipment.

The following figures describe the hierarchy and the principle of protective measures. The photos show good respective incorrect practical examples of decanting and storing of hazardous substances in practice

Elimination or reduction of danger by using non hazardous substances

Isolation of danger by the selection of a low-emission working process, e.g. by using closed systems (gases, vapours or fumes shall not release and skin contact shall be eliminated)

Extraction of the released hazardous substances at the occurrence or leak source

Local exhaust ventilation measures in addition to extraction at the source of generation (supply air and discharge air for a proper balance)

PPE Personal Protective Equipment e.g.: protective gloves, protective clothing, respiratory protective equipment

Decanting of hazardous substances

– incorrect –

- smoking
- missing PPE
- missing sign
- missing impounding basin

Decanting of hazardous substances

– correct, but ... ? –

Use of mask is not nessesary.
It is discomfort for employee.
You have to think about PPE.

Decanting of hazardous substances

– correct –

- ventilation
- earthing
- PPE
- impounding basin (room)

Pouring of flammable liquid

– incorrect –

- missing PPE
- missing sign
- missing impounding basin

Pouring of flammable liquid

– correct –

Improvements are possible!

Storage of chemicals

– incorrect –

Chemicals shall be stored in appropriate, labelled containers.

These shall be resistant to the substances so that leaking or decomposition is prevented

Storage of chemicals

– correct –

- suitable containers
- labelling available
- impounding basin available

Use of personal protective equipment (PPE)

There is a variety of PPE on the market. Protective equipment against hazardous substances can be identified by the icon with the filled receptacle (Erlenmeyer flask).

If this icon is missing, e.g. on gloves, they are not suitable.

Chemicals

Provides protection against hazardous substances

Refrigeration

Weather

Flame

Chainsaw

Examples of PPE for work with hazardous substances:

Eye protection

Eye protection/breathing protection

Breathing protection

Breathing protection

Hand protection

Foot protection

Protective clothing against chemicals

3.1 | Evaluation of protective Measures

Check if the measures are sufficient or not.

See also check list in annex 2.

You have to fill in the checklist and check the color smilies:

☹	Protective measures are *immediately required
😐	You have to think about improvement
🙂	O.K.! Protective measures are sufficient
○	Irrelevant

3.2 | Documentation

Based on the check list, risks and protective measures shall be documented. It shall also be laid down how protective measures are controlled.

Other applicable documents for the documentation are the hazardous substances list, safety data sheets and operating instructions.

3.3 | Operating instructions and instruction

Further measures shall be initiated by the employer for work with hazardous substances. Employees shall have access to written operating instructions in a form and language they understand.

The operating instructions shall contain information on hazardous substances occurring at the workplace. In particular, the following information shall be given:

- designation of the hazardous substance
- hazards to human beings and to the environment
- information on protective measures and rules of behaviour
- behaviour in case of danger
- first aid
- correct disposal

On the basis of the operating instructions, employees shall annually receive oral instruction by the employer on occurring hazards and corresponding protective measures. The instructed persons shall confirm this by signature. The proof of instruction (content, time, participants) shall be kept.

An example for operating instructions is given in Annex 3.

Annex 1

Table of hazardous substances

Workplace/area: _____

Identified by: _____ Date: _____

No.	Trade product/ manufacturer	Substitutability checked?		Current safety data sheet available?			Average		Hazard marking R-sentences/ S-sentences	Limit value mg/m³
		yes	no	yes	no		Consumption/ time unit	Quantity in stock		Classification TWA/STEL
1	Glass cleaner Firma X	X		X			24 kg/year	2 kg	F, Xi R11, R36, R36/38, R67, S2	Isopropanol – 500/2 (II) Ethanol – 960/2 (II)
2	Paint Firma X	X		X			150 kg/year	30 kg	Xn, R10, R20/21, R38, S2, S25	Xylene – 440/2 (II)
3	Pipe cleaner Firma X		X	X			3 kg/year	0,5 kg	C R35, S1/2, S26, S37/39, S45	Sodium hydroxide – 2/=1=
4	Solvent Firma X	X		X			120 kg/year	10 kg	Xi R10, R20/21, R36/37/38, R41, S2, S23, S24/25, S26, S36/37/39, S46, S51	Butan-1-ol – 310/1 (I) Xylene – 440/2 (II) Acetone – 1200/2 (I)
5	Anti rust Firma X	X		X			30 kg/year	6 kg	C R20/21/22, R34, R36/38, S1/2, S28, S36/37/39, S45	Phosphoric acid – 2/2 (I)

Annex 1

Table of hazardous substances

Workplace/area: _____

Identified by: _____ Date: _____

No.	Trade product/ manufacturer	Substitutability checked?		Current safety data sheet available?			Average		Hazard marking R-sentences/ H-sentences S-sentences/ P-sentences	Limit value mg/m³
		yes	no	yes	no		Consumption/ time unit	Quantity in stock		Classification TWA/STEL
1										
2										
3										
4										
5										

Annex 2

Example of Checklist of principles with activity involving chemical agents

This Checklist is about the principles with activity involving chemical agents regarding the application of protective measures at workplace.

				
Information and labelling				
Hazardous substances are known in the company				
• Substances or products with hazardous labelling				
• Substances or products without hazardous labelling				
• Substances are realeased during working processes				
Hazardous substances can be easily identified and are correctly labelled				
Labelling of containers and pipes				
Collection of safety data sheets is complete and up-to-date and accessable to employees				
Table of hazardous substances				
• Available and up-to-date				
• Reference to safety data sheets				
Operating instructions available				
Instruction of employees is realised				
First-Aid measures are implemented, e.g. emergency- and eye-showers				
Worksite/workplace design				
Sufficient forced or natural ventilation of the working room				
Warning device in case of ventilation failure				
Clean air recirculation does not cause any stress				
Easy to clean surfaces (e. g. floor)				
Anti-slip floor				
Possibilities for dust deposits				
Separate rest room of area				
Design of working process and working organisation				
Number of empoyees exposed to hazardous substances is limited				

				
Duration and extent of exposure to hazardous substances is kept as low as possible				
• inhalative exposure (take a breath)				
• dermal exposure (skin contact)				
Periodic testing of function and efficiency or technical protection measured and documentation				
Low-dust working and waste removal technologies				
Wet cleaning or use of industrial vacuum cleaners				
Appropriate means for removing leaked or spilled working substances				
Containers are kept closed and are only opened for taking substances				
Lockable containers for waste disposal				
Approriate disposal of no longer required hazardous substances, fully emptied containers and cleaning cloths				
Safekeeping and storage of hazardous substances				
Quantity of hazardous substances at workplace limited to daily requirement				
Do not store in containers which may be confound with food				
Marked storage areas/rooms				
Storage cabinets for chemicals/acids/bases				
Safety storage cabinets for flammable liquids/solvents				
Safety storage cabinets for gases				
Storage of highly toxic and toxic substances in loked facility				
Principles of occupational health				
Required work clothing is worn				
Contaminated work clothing is changed				
Personal protective equipment is used as intended				
Rest areas or rooms for duty staff are not used with contaminated work clothing				
Splatter or contaminants of hazardous substances on the skin are immediately removed				
Cleaning cloths/rags are not used for hands				
Dusty work clothing is not shaken out or blown off				
Work places are regularly cleared and cleaned				

Annex 3

Operating Instructions

Company: _____

Working area: _____

Responsible: _____
Signature

OPERATING INSTRUCTIONS
According to ....

State: _____

Workplace: Cleaning place

Activity: Cleaning and degreasing of metal parts

Hazardous material description

Cleaning agent "Super clean" **contains isoparaffins**

Hazards for human and environment

- skin contact leads to degreasing; irritation possible
- vapours may lead to drowsiness and breathing difficulties
- vapours are heavier than air (sink to the floor) and are inflammable
- hazardous to water, do not put into sewerage

Protective measures and behaviour rules

- work only with exhaustion switched on; always keep cleaning containers closed in case of non-use
- exclude skin contact by using auxiliary tools (baskets, strainers etc)
- wear protective gloves e.g. nitril- or butyl rubber and goggles
- use skin protecting agents:
  protection (before work) product: _____
  cleaning (before rests and end of work) product: _____
  care (after work) product: _____
- do not smoke, eat or drink at the workplace and do not keep food there
- keep away other ignition sources (flame of burner, welding operations et al.)

Behaviour in case of danger

- absorb spilled material with binding agents product: _____ and put it in collecting receivers product: _____; wear protective gloves (see above)
- in case of fire: use existing fire extinguishers e.g. CO_2- or powder extinguishers, inform superior

Emergency call _____

First Aid

- Rinse splatter in the eyes immediately with a lot of water (eyewash station)
- skin contact: clean with skin cleaning agent (see above) under running water
- change soaked clothes immediately
- inform superior in case of drowsiness or breathing difficulties

Emergency call _____

Proper disposal

- put soaked rags and binding agents in collecting receiver _____
- disposal of full collecting receivers _____ Tel.: _____