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HEALTH AND ENVIRONMENTAL RISKS OF CHEMICALS AT ORAS TAP FACTORY

Degree Programme in Environmental Engineering

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Satakunnan ammattikorkeakoulu
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KEMIKAALIEN YMPÄRISTÖ- JA TERVEYSRISKIT ORAS OY:N HANATEHTAALLA

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TIIVISTELMÄ

Tämä opinnäytetyö tehtiin Raumalla sijaitsevalle Oras Oy:lle. Opinnäytetyön aiheena oli perehtyä prosesseissa käytettyjen kemikaalien ympäristö- ja terveysriskeihin sekä Oraksen kemikaaliturvallisuuden soveltamiseen. Työtä varten kehiteltiin eräänlainen tutkimuspohja kemikaalien kulusta tehtaalla, jossa tutkittiin kemikaalien käsittelyä, varastointia ja hävitystä koskevien määräysten ja säädöksien lisäksi kemikaalien vaarallisia ominaisuuksia ja kemikaalimerkintöjä.

Toimintaan perehdyttiin vielä tarkemmin tapaamisilla ja tehdaskierroksella. Aineistona käytettiin kemikaalien käyttöturvallisuustiedotteita, kemikaalikortteja, kirjallisuutta, tutkimusraportteja sekä asiantuntijoilta saatua tietoa.

Vaarallisiksi luokitelluilla kemikaaleilla tulee olla käyttöturvallisuustiedote, joka sisältää kemikaalin ominaisuudet, varastointiolosuhteet sekä turvalliseen käyttöön liittyvät määräykset. Kemikaalikorteista löytyvät aineen fysikaaliset ominaisuudet, kemialliset vaarat, altistumisen vaikutukset ja oireet, palo- ja räjähdysvaara ja sen torjunta.

Tehtaan kymmenestä vaarallisimmista ja yleisimmistä kemikaaleista päivitettiin selkeä lista, josta selviää aineiden kemialliset ja fysikaaliset ominaisuudet sekä vaaraluokitukset. Kemikaaleista on kerätty käyttöturvallisuustiedotteita apuna käyttäen kattava tiivistelmä niiden terveys- ja ympäristövaikutuksista sekä myrkyllisyydestä. Oraksen prosesseista kirjattiin päällimmäiset riskit, niiden suuruus, mahdolliset aiheuttajat ja seuraukset sekä mahdolliset onnettomuustilanteet.

Suuret kiitokset Oras Oy:n kromaamon esimiehelle Sari Sulinille, Specialist, management systems Katja Äärilälle, sekä tietysti SAMKin opinnäytetyön ohjaajalle Timo Hanneliukselle hyvästä yhteistyöstä.

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ABSTRACT

This thesis was done for Oras, located in Rauma. The subject was to examine health and environmental risks of chemicals used in the processes and application of chemical safety at the factory.

The research of chemicals progress at the factory was developed to examine handling, storage and disposal, provisions and regulations, hazardous properties and labelling of chemicals. Further introduction on Oras' operations was given on arranged meetings and on a factory tour.

Material used for this thesis consists of Safety Data Sheets, International Chemical Safety Cards, chemical literature, research reports and information obtained from the experts. Chemicals Safety Data Sheets are excellent documents that include the necessary information about the hazard classification of chemicals, their characteristics, storing and provisions. Safety Data Sheet is required if the chemical is classified as hazardous to health and/or to the environment.

The list of Oras' most hazardous and commonly used chemicals was updated so that the chemical and physical properties, classification and labelling of dangerous chemicals are clarified. Summary of health and environmental effects as well as toxicity of the chemicals was created by using Chemicals Safety Data Sheets as a source. The most severe risks, their magnitude, possible causes and consequences along with possible disasters and risk assessment of Oras' processes were listed in this thesis.

I want to thank Oras supervisor in chrome plating Sari Sulin, specialist in management systems, Katja Äärilä and SAMK's thesis supervisor Timo Hannelius for good co-operation and assistance.

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Abbreviations

CAS	=	Chemical Abstracts Service
CLP	=	Classification, Labelling and Packaging of substances and mixtures
EC_{50}	=	Effective Concentration,50 %
ECHA	=	Europian Chemicals Agency
GHS	=	Globally Harmonised System of Classification and Labelling of Chemicals
LC_{50}	=	Lethal Concentration, 50 %
$LD50$	=	Lethal Dose, 50 %
LD_{Lo}	=	Lowest Lethal Dose
REACH	=	Registration, Evaluation, Authorisation and Restriction of Chemicals
TUKES	=	Suomen turvallisuus ja kemikaalivirasto (Finnish Safety and Chemicals Agency)

1 INTRODUCTION

This thesis is done for Oras, Rauma. The work is research-based and the aim is to study both health and environmental risks of their chemicals, chemical safety and chemicals legislation.

The thesis examines the process of chemicals at the factory, which includes the import and transport, storage, utilization and chemical safety, and finally the disposal of hazardous chemical waste. Oras' processes include overall hundreds of different chemicals and chemical compounds, but this thesis focuses on the most hazardous chemicals and their risk factors. The risk analysis associated with the use of chemicals is an important context in this work as well.

Oras and other companies handling chemicals shall follow up the latest legislation and regulations. In Finland, utilization of chemicals is governed by Tukes and Chemicals legislation (599/2013) as well as the European Commission Directives, especially the REACH and CLP Regulations.

Chemicals classified as hazardous must have Safety Data Sheets that include the chemical properties, storage conditions, and the regulations of safe use. International Chemical Safety Cards have the physical properties of the substance, possible hazardous effects of the exposure and the symptoms, as well as the danger of fire and explosion and its control.

This bachelor's thesis was commissioned by supervisor in chrome plating Sari Sulin and Specialist, management systems Katja Äärilä. On behalf of Satakunta University of Applied Sciences, the supervisor was Lecturer Timo Hannelius.

2 ORAS

Oras is a Finnish company manufacturing bathroom and kitchen faucets. The company was founded in Rauma in 1945 and it is owned by Oras Invest Co. Oras manufactures, markets and develops innovative products that emphasize user-friendliness, quality, energy saving and environmental values.

Oras is a significant supplier of water equipment for building technology and the leading Nordic Marketing Director in its sector. The company's goal is to make the use of water easy and environmentally friendly and its vision is to become the European leader in water equipment. Oras' head office is located in Rauma and the other office in Stuttgart, Germany. The products are manufactured at four factories in Rauma, Burglengenfeld in Germany, Kralove in Czech Republic and Olesno in Poland. Oras Group's products are marketed in almost every European country.

In September 2013, Oras acquired Hansa Metallwerke AG manufacturer of tap water. Oras Group's net sales for the year 2015 were approximately 245 million € and they are employing a total of 1370 employees, orasgroup.com, /1/

2.1 History

Mr. Paasikivi started the business operations of Oras in 1945, but the manufacturing itself began in 1951 when Oras launched its first double socket faucets. In the 1970s, the company proceeded to new plastic technology. Oras produced its first thermostat in the 1980s. Then, in the 90s, the production processes specialized in the electronics and creating their very first touch-free faucets.

2.2 Location and the environment

Oras has started its operations in Rauma in the Isometsä industrial area, 1969. There are no significant areas concerning to surface water or groundwater, see Oras' Environmental Permit Decision, /2/

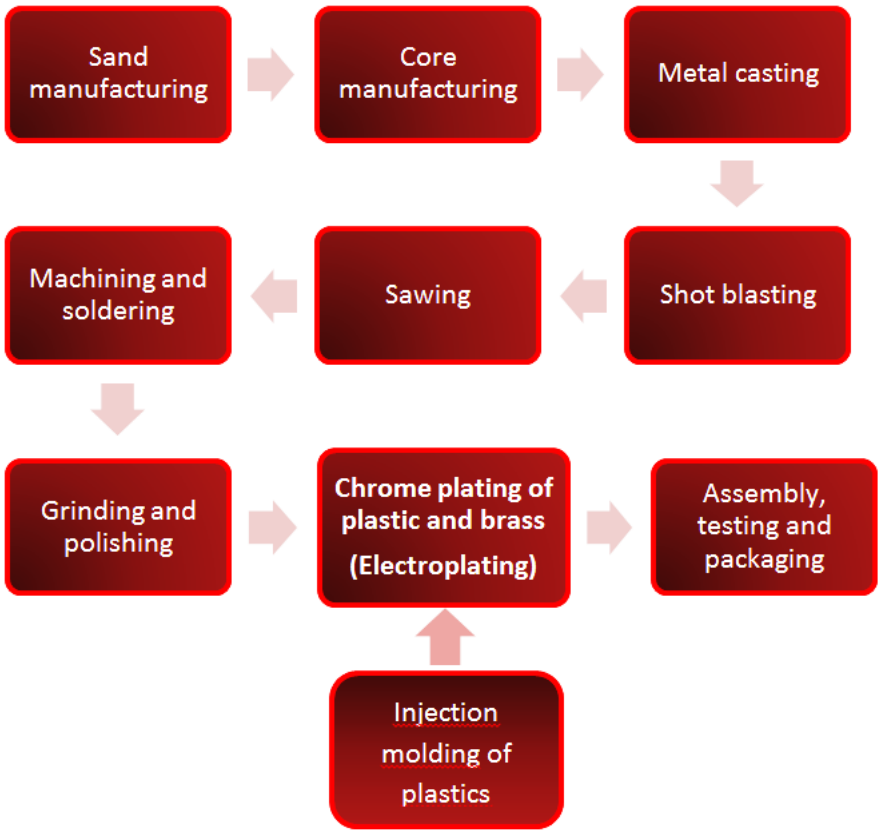
Picture 1. Satellite view of the factory and its environment (Google maps)

- The nearest settlement is located on the west side of the factory about 60−70 meters away.
- Raumanmeri school, high school, elementary school and day care centre are located approximately 500 meters from the factory.
- Rauma regional hospital and health center are 400 meters away.
- Rauman energia, Raumaster Paper Oy and Satatuote Oy are located near the factory.

3 PRODUCTION PROCESSES

3.1.1 General

Oras' factory manufactures electronic taps, bathroom and kitchen faucets and shower accessories. Production processes include these following operations:
Sand manufacturing, core manufacturing, metal casting, shot blasting and sawing, machining and soldering, grinding and polishing, injection molding of plastics, chrome plating of plastic and brass and assembly, testing and packaging. Strict quality control plays an important role in every operation.



Picture 2. Oras' production process

The most significant production operation concerning chemicals is chrome plating 3.8, since many kinds of chemicals and chemical compounds are used in brass and plastic plating processes. More information about chemicals and chemical safety can be read on paragraphs 5, 6 and 7.

3.2 Sand manufacturing

The sand mixture consists of granules, binders and additives. Quartz sand, which has a chemical composition of silica (SiO_2), is the most commonly used granule. The additives used in the sand manufacturing are coal powder and iron oxide (Fe_2O_3). Binders are either powder, such as bentonite, or liquid such as resin.

The powdery binder requires a liquid-based solution to blend in the sand. The purpose of the binders is to fasten the sand granules to each other, allowing the sand mixture to harden.

3.3 Core manufacturing

The core (*Keerna*) is a cured piece manufactured from quartz sand with hot-box machinery, wherein the hardening of sand is based on the reaction of high temperature and sand blend binders where phenol and furfuryl alcohol form a furan resin. Furfuryl alcohol contains small amounts of formaldehyde.

The sand blend is shot with compressed air into a metal mold where it is cured in high temperature. A good quality core should be so strong that it can withstand the stress caused by the transport and the thermal stress caused by the molten metal, see valuatlas.fi, /3/

3.4 Metal casting

The raw material used in casting is brass, which is an alloy of copper and zinc ((63% Cu) and (35% Zn), and small amounts of Al, Pb, As, Fe metals). This yellowish alloy is easy to cast and it is stronger and cheaper than pure copper. Metal casting work takes its place at the factory's foundry department where automated low pressure casting is utilized. Sand core’s main purpose is to shape the casted metal piece’s core and form its distinctive shapes. The fused brass is soldered with compressed air into the casting mold. The molds are soaked in graphite water, preventing the casted piece from sticking to the mold while cooling it down, see valuatlas.fi, /3/

3.5 Shot blasting and sawing

After the casting process, the excess sand left in the product is must be removed by cleansing shot blasting method. Then, the redundant parts and pieces will be cut out by sawing. The parts removed in the sawing are collected and thus the excess casting material can be recycled for reuse.

3.6 Machining and soldering

Machining is executed with a variety of machinery tools because of the difference in characteristics and functions. Each product requires specific dimensions. The quality is carefully monitored because the machining tracks must remain in the given dimensions. The metal parts are soldered with silver-containing, cadmium-free hard brazing at about 700 ° C. The soldering is heated by liquefied petroleum gas.

3.7 Grinding and polishing

Machining is followed by the grinding of frames, where any surface defects created during casting operation are removed from the products either manually or mechanically. In grinding, the polishing of the product’s surface is executed by using polishing wax and fabric pads.

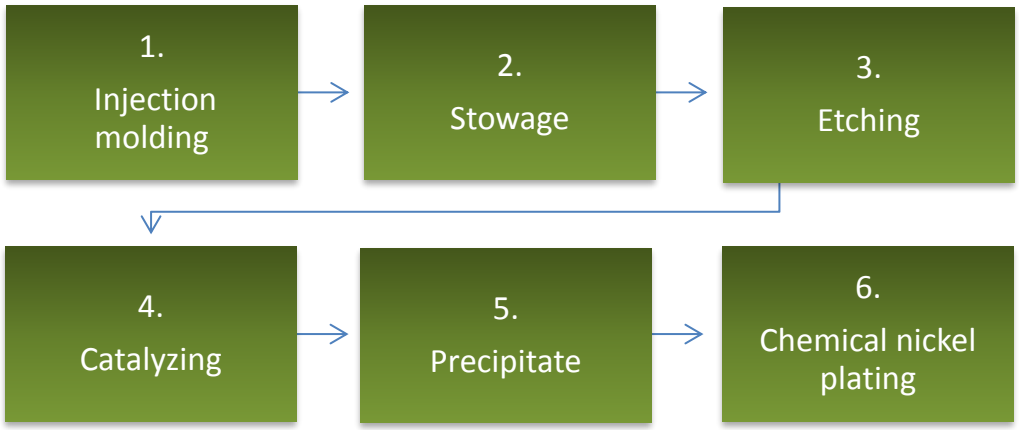
3.8 Chrome plating

Chrome plating of brass and plastic are the most important industrial processes concerning this thesis, since variety of chemicals and chemical compounds are utilized within these operations. Both brass and ABS-plastic products are processed separately at their specific chrome plating department. The plastic parts are individually molded by automatic injection molding machines from which the finished plastic products are transferred to the plastic’s chrome plating department.

Chrome plating is executed electrochemically in both operations by nickel-chromium plating, but their pre-treatments differ greatly from one another.

3.8.1 Pre-treatment and plating of plastics

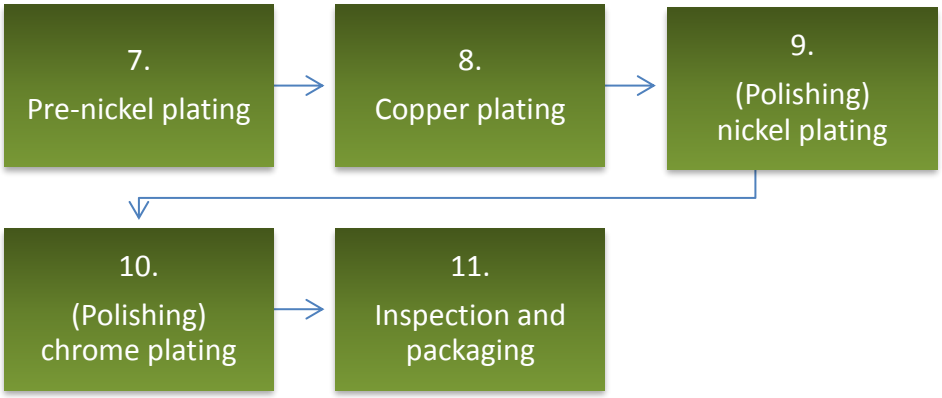
Plastic products are pre-treated on a line with chemical nickel and then electroplating with copper. The plastic is washed in four stages so that the metallic nickel layer can be formed on the surface of the product in a chemical nickel bath. After each step, the products are washed carefully.



Picture 3. Pre-treatment of plastics (Oras Oy, Sari Sulin)

1. Injection molding utilizes ABS- plastic (*acrylonitrile butadiene styrene*). Plastic resin is melted at high temperature (210−250 ° C), after which the molten plastic is injected by pressure into steel mold.
2. On stowage, the plastics should be string up properly so that they are tensionless and the excess liquid can be removed.
3. Etching is an operation that uses both chromium trioxide (CrO_3) and sulfuric acid (H_2SO_4). The butadiene (C_4H_6) is etched from the surface of the product by 0.5 µm of roughness.
4. Catalyzing uses palladium-tin chloride colloid, which molecules attach to the etched surface of the product.
5. Precipitating utilizes a chemical reducer that removes the tin chloride colloids from the product's surface. Thus palladium (Pd) is activated.
6. In chemical nickel plating a metallic, electrically conductive layer is formed on the active palladium by nickel sulphate-based chemical.

After chemical nickel plating and pre-washing, the products are pre-nickelized, polished and finally coated with chrome plating.

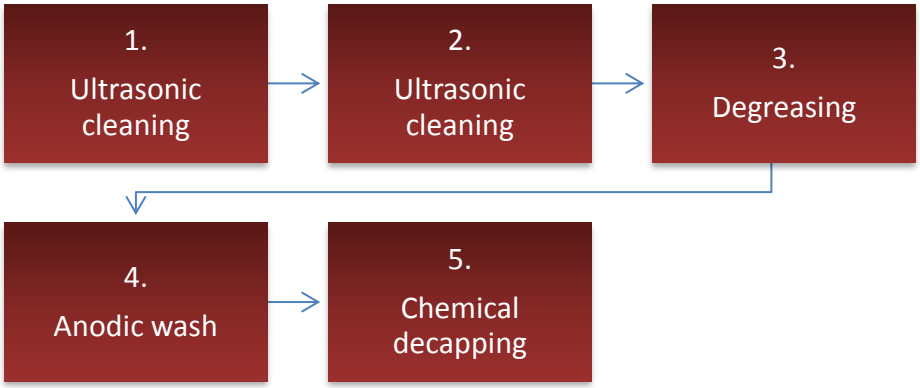


Picture 4. Plating of plastics (Oras Oy, Sari Sulin)

7. Pre-nickel plating nickel utilizes sulphate-based electrolysis, which flattens the pre-treated product forming 2 µm layer. The adhesion to the plastic is enhanced by the physical force.
8. Thereafter copper plating is done, where copper sulphate-based electrolyte is utilized. The surface formed by the copper alloy is about 15−25 µm thick layer, which increases corrosion protection.
9. Polishing nickel plating uses nickel sulphate-based electrolyte containing polishing additives. This form about 8−15 µm polished surface.
10. Polishing chrome plating utilizes hexavalent electrolytic chromium. Approximately 0.3−0.5 µm thick layer is applied to the product giving it a nice polished look and corrosion protection over the nickel plating.
11. Inspection is made visually. Some of the packaged products are stamped with laser.

3.8.2 Pre-treatment and plating of brass

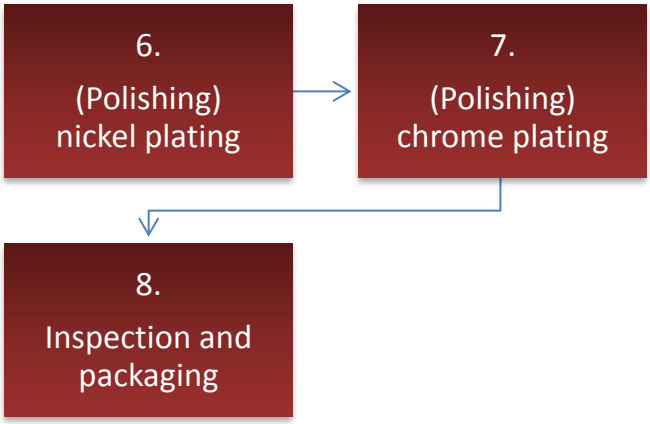
Brass products are pre-treated by various cleansing and activation operations. After each phase, the products must be washed.



Picture 5. Pre-treatment of brass (Oras Oy, Sari Sulin)

1. and 2. Ultrasonic cleaning is based on ultrasound-induced cavitation and emulsifying detergent chemicals interaction. Cavitation bubbles form pressure shocks that remove impurities from the surface of the product, such as grease, wax, and other liquids. After the treatment, the surface is hydrophobic, i.e *water-repellent*.
3. Degreasing removes the remaining grease residues. After the treatment, the surface is hydrophilic, i.e. *water absorbing*.
4. Anodic wash on is an electrolytic wash, in which the washable body acts as an anode. The surface develops oxygen (O_2) which cleans the body chemically. At the same time, there is gas that cleans the product mechanically. Washing removes the residues of organic impurities while improving the adhesion of the plating.
5. Chemical decapping's purpose after degreasing and acidification is to adjust the pH of the product to the same level as the plating solution. The silicates are removed with hydrofluoric acids (HF) from the surface, which is acidified to give an active surface for the electrolytic plating operation. Thus a homogeneous layer is formed.

When brass products are chrome plated, the products must be washed properly. Polishing nickel and chrome plating treatments are done the same way as in the plastic plating operations.



Picture 6. Plating of brass (Oras Oy, Sari Sulin)

6. Polishing nickel plating uses nickel sulphate-based electrolyte containing polishing additives. This form about 8−15 µm polished surface.
7. Polishing chrome plating utilizes hexavalent electrolytic chromium. Approximately 0.3−0.5 µm thick layer is applied to the product giving it a nice polished look and corrosion protection over the nickel plating.
8. Inspection is made visually. Some of the packaged products are stamped with laser.

The electrolytic chromium in industrial chrome plating is based on hexavalent chromium oxide, which is very toxic. Electrolytes are aggressive liquids, even in dilute solutions. The work must comply with strict safety regulations. The chrome-solution basins must be equipped with suction pipes and proper ventilation to clean air from impurities. The most common risks are related to maintenance and disturbance situations, such as leakage, chemical negligence and splatter of chemicals. Chemical reactions can cause dangerous toxic fumes.

3.9 Assembly, testing and packaging

Finally, the faucet products are assembled at the assembly workstations in the cells of a couple of employees. Each finished faucet is checked for possible errors and tested with a specific water/air test device. In the end, the products are packed and ready for transport. Packages include the product's operating instructions.

4 CHEMICALS LEGISLATION

4.1 General

Chemicals Legislation's supreme goal is to protect human health and the environment. Legislation requires companies to ensure the safety of chemicals they use and market. European chemicals legislation has changed significantly with the implementation of the REACH Regulation on the Registration, Evaluation, Authorization and Restriction of Chemicals and of the CLP Regulation on Classification, Labelling and Packaging.

The governing executor of the Regulations is the European Chemicals Agency (ECHA). The Finnish Safety and Chemicals Agency (TUKES) is the competent supervisory authority here in Finland and are governed by the Chemicals Act (Finlex 599/2013). The basis of the Chemicals Act is to identify the chemicals, their properties, utilization and the conditions for safe use, kemikaalineuvonta.fi, /4/ and tukes.fi, /5/

4.1.1 Hazardous chemicals

Chemicals classified as hazardous can be physical, health and/or environmental hazards. Hazardous chemicals can cause much harm that may occur due to short exposure or over a period of time to the effects of accumulated toxins.

The packaging of such chemicals shall be provided with warning labels containing the trade name of the chemical, dangerous ingredients, hazard pictograms, hazard and precautionary statements, supplier contact details and sales volume information.

4.2 REACH (EY) N:o 1907/2006

The REACH Regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals) Is a regulation of the European Parliament which was established on 1.6.2007. The Regulation applies to every European Union member state and it aims to maintain the high level of health and environmental protection, to promote the competitiveness of the international chemical industry and to guarantee the free movement of chemicals within the EU's internal market.

The REACH Regulation has ordered even more responsibility for the chemical industry in case of environmental and health risks caused by chemicals. The Regulation demands manufacturers and importers to investigate the safety of their chemicals, to register them at the European Chemicals Agency and to provide consumers with up-to-date information on chemicals.

The European Chemicals Agency's database recordds all chemicals which manufacture or import exceeds one tonne annually. About 30,000 of these chemicals are utilizes in the EU and an average of 300 new substances enter the EU market each year. The REACH has imposed the use and handling of hazardous chemicals to require permit.

4.3 CLP (EY) N:o 1272/2008

The CLP Regulation (Classification, Labelling and Packaging) is a regulation imposed by the European Parliament and the Council. The CLP Regulation was established on 20.1.2009 and it applies to every European Union member state. The regulation focuses on the criteria that make a particular chemical classified as hazardous.

CLP has replaced the past regulations on the classification, labelling and packaging of chemicals, namely the substance and mixtures directive. GHS hazard pictogram system is for classification and labelling of chemicals approved by the EU and the UN. The aim of this system is to apply the same international principles in the classification and labelling of chemicals.

The hazard pictograms and their codes changed on 1.6.2015, but the transition period of chemicals used by consumers such as paints will last until 1.6.2017. The following pictures depict the current GHS hazard pictograms (Pic 7.) and the former pictograms (Pic 8). Anyone, whose work involve chemicals, should recognize the necessary hazard pictograms, classification and statements, tukes.fi, /5/

4.3.1 GHS hazard pictograms

Picture 7. GHS hazard pictograms and their codes:

(GHS01) Explosive: Unstable explosives, self-reactive substances and mixtures

(GHS02) Flammable: Flammable gases, aerosols, liquids or solids, self-reactive substances and mixtures, self-heating substances and mixtures, prganic peroxides

(GHS03) Oxidiser: Oxidizing gases, liquids or solids, substances oxidizing other substances

(GHS04) Compressed gas: Compressed gases, liquefied gases, refrigerated liquefied gases, dissolved gases (*at least 2 bar*)

(GHS05) Corrosive: Corrosive to skin, can cause serious eye damage, corrosive to metals

(GHS06) Hurtful: Immediately if eaten, cause skin, or respiratory tract

(GHS07) Harmful: Cause skin and eye irritation, allergic reactions, respiratory irritation, acute toxicity, dizziness and nausea

(GHS08) Nausea: Cause chronic health risks such as cancer, impaired fertility, and fetal damage, allergy and poisoning

(GHS09) Environmental hazard: Chemicals dangerous for the environment and aquatic organisms(*Daphnia magna*)

4.3.2 Classification and Hazard statements

As a result of the CLP Regulation, chemicals are classified into three hazard categories, which are physical, health and environmental hazards. These categories include the specific H-statements, www.ttl.fi , /6/

Physical hazards:

H200 Unstable explosive
H201 Explosive; mass explosion hazard
H202 Explosive; severe projection hazard
H203 Explosive; fire, blast or projection hazard
H204 Fire or projection hazard
H205 May mass explode in fire
H220 Extremely flammable gas
H221 Flammable gas
H222 Extremely flammable material
H223 Flammable material
H224 Extremely flammable liquid and vapour
H225 Highly flammable liquid and vapour
H226 Flammable liquid and vapour
H227 Combustible liquid
H228 Flammable solid
H240 Heating may cause an explosion
H241 Heating may cause a fire or explosion
H242 Heating may cause a fire
H250 Catches fire spontaneously if exposed to air
H251 Self-heating; may catch fire
H252 Self-heating in large quantities; may catch fire
H260 In contact with water releases flammable gases which may ignite spontaneously
H261 In contact with water releases flammable gas
H270 May cause or intensify fire; oxidizer
H271 May cause fire or explosion; strong oxidizer
H272 May intensify fire; oxidizer
H280 Contains gas under pressure; may explode if heated
H281 Contains refrigerated gas; may cause cryogenic burns or injury
H290 May be corrosive to metals

Health hazards:

H301 Toxic if swallowed

H302 Harmful if swallowed

H303 May be harmful if swallowed

H304 May be fatal if swallowed and enters airways

H305 May be harmful if swallowed and enters airways

H310 Fatal in contact with skin

H311 Toxic in contact with skin

H312 Harmful in contact with skin

H313 May be harmful in contact with skin

H314 Causes severe skin burns and eye damage

H315 Causes skin irritation

H316 Causes mild skin irritation

H317 May cause an allergic skin reaction

H318 Causes serious eye damage

H319 Causes serious eye irritation

H320 Causes eye irritation

H330 Fatal if inhaled

H331 Toxic if inhaled

H332 Harmful if inhaled

H333 May be harmful if inhaled

H334 May cause allergy or asthma symptoms or breathing difficulties if inhaled

H335 May cause respiratory irritation

H336 May cause drowsiness or dizziness

H340 May cause genetic defects

H341 Suspected of causing genetic defects

H350 May cause cancer

H351 Suspected of causing cancer

H360 May damage fertility or the unborn child

H361 Suspected of damaging fertility or the unborn child

H362 May cause harm to breast-fed children

H370 Causes damage to organs

H371 May cause damage to organs

H372 Causes damage to organs through prolonged or repeated exposure

H373 May cause damage to organs through prolonged or repeated exposure

Environmental hazards:

H400 Very toxic to aquatic life

H401 Toxic to aquatic life

H402 Harmful to aquatic life

H410 Very toxic to aquatic life with long lasting effects

H411 Toxic to aquatic life with long lasting effects

H412 Harmful to aquatic life with long lasting effects

H413 May cause long lasting harmful effects to aquatic life

4.3.3 Precautionary statements

In addition to H-statements, the CLP Regulation has ordered Safety Data Sheets to involve specific P-statements as well.

General precautionary statements:

P101 If medical advice is needed, have product container or label at hand

P102 Keep out of reach of children

P103 Read label before use

Prevention precautionary statements:

P201 Obtain special instructions before use

P202 Do not handle until all safety precautions have been read and understood

P210 Keep away from heat/sparks/open flames/hot surfaces – No smoking

P211 Do not spray on an open flame or other igntion source

P220 Keep/Store away from clothing/…/combustible materials

P221 Take any precaustion to avoid mixinn with combustibles

P222 Do not allow contact with air

P223 Keep away from any possible contact with water, because of violent reaction and possible flash fire

P230 Keep wetted with…

P231 Handle under inert gas

P232 Protect from moisture

P233 Keep container tightly closed

P234 Keep only in original container

P235 Keep cool

P240 Ground/bond container and receiving equipment

P241 Use explosion-proof electrical/ventilating/light/…/equipment

P242 Use only non-sparking tools

P243 Take precautionary measures against static discharge

P244 Keep reduction valves free from grease and oil

P250 Do not subject to grinding/shock/…/friction

P251 Pressurized container – Do not pierce or burn, even after use

P260 Do not breathe dust/fume/gas/mist/vapours/spray

P261 Avoid breathing dust/fume/gas/mist/vapours/spray

P262 Do not get in eyes, on skin, or on clothing

P263 Avoid contact during pregnancy/while nursing

P264 Wash… thoroughly after handling

P270 Do not eat, drink or smoke when using the product

P271 Use only outdoors or in a ventilated area

P272 Contaminated work clothing should not be allowed out of the workplace

P273 Avoid release to the environment

P280 Wear protective gloves/protective clothing/eye protection/face protection

P281 Use personal protective equipment as required

P282 Wear cold insulating gloves/face shield/eye protection

P283 Wear fire/flame resistant/retardant clothing

P284 Wear respiratory protection

P285 In case of inadequate ventilation wear respiratory protection

P231+232 Handle under inert gas. Protect from moisture

P235+410 Keep cool. Protect from sunlight

Response precautionary statements:

P301 IF SWALLOWED:

P302 IF ON SKIN:

P303 IF ON SKIN (or hair):

P304 IF INHALED:

P305 IF IN EYES:

P306 IF ON CLOTHING:

P307 IF exposed:

P308 IF exposed or concerned:

P309 IF exposed or you feel unwell:

P310 Immediately call a POISON CENTER or doctor/physician

P311 Call a POISON CENTER or doctor/physician

P312 Call a POISON CENTER or doctor/physician if you feel unwell

P313 Get medical advice/attention

P314 Get Medical advice/attention if you feel unwell

P315 Get immediate medical advice/attention

P320 Specific treatment is urgent (see… on this label)

P321 Specific treatment (see… on this label)

P322 Specific measures (see… on this label)

P330 Rinse mouth

P331 Do NOT induce vomiting

P332 If skin irritation occurs:

P333 If skin irritation or a rash occurs:

P334 Immerse in cool water/wrap in wet bandages

P335 Brush off loose particles from skin

P336 Thaw frosted parts with lukewarm water. Do not rub affected areas

P337 If eye irritation persists:

P338 Remove contact lenses if present and easy to do. continue rinsing

P340 Remove victim to fresh air and keep at rest in a position comfortable for breathing

P341 If breathing is difficult, remove victim to fresh air and keep at rest in a position comfortable for breathing

P342 If experiencing respiratory symptoms:

P350 Gently wash with soap and water

P351 Rinse continuously with water for several minutes

P352 Wash with soap and water

P353 Rinse skin with water/shower

P360 Rinse immediately contaminated clothing and skin with plenty of water before removing clothes

P361 Remove/Take off immediately all contaminated clothing

P362 Take off contaminated clothing and wash before reuse

P363 Wash contaminated clothing before reuse

P370 In case of fire:

P371 In case of major fire and large quantities:

P372 Explosion risk in case of fire

P373 DO NOT fight fire when fire reaches explosives

P374 Fight fire with normal precautions from a reasonable distance

P375 Fight fire remotely due to the risk of explosion

P376 Stop leak if safe to do so

P377 Leaking gas fire – do not extinguish unless leak can be stopped safely

P378 Use … for extinction

P380 Evacuate area

P381 Eliminate all ignition sources if safe to do so

P390 Absorb spillage to prevent material damage

P391 Collect spillagee

P301+310 IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician

P301+312 IF SWALLOWED: Call a POISON CENTER or doctor/physician if you feel unwell

P301+330+331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting

P302+334 IF ON SKIN: Immerse in cool water/wrap in wet bandages

P302+350 IF ON SKIN: Gently wash with soap and water

P302+352 IF ON SKIN: Wash with soap and water

P303+361+353 IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower

P304+312 IF INHALED: Call a POISON CENTER or doctor/physician if you feel unwell

P304+340 IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing

P304+341 IF INHALED: If breathing is difficult, remove victim to fresh air and keep at rest in a position comfortable for breathing

P305+351+338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do -continue rinsing

P306+360 IF ON CLOTHING: Rinse immediately contaminated clothing and skin with plenty of water before removing clothes

P307+311 IF exposed: Call a POISON CENTER or doctor/physician

P308+313 IF exposed or concerned: Get medical advice/attention

P309+311 IF exposed or you feel unwell: Call a POISON CENTER or doctor/physician

P332+313 IF skin irritation occurs: Get medical advice/attention

P333+313 IF skin irritation or a rash occurs: Get medical advice/attention

P335+334 Brush off loose particles from skin. Immerse in cool water/wrap in wet bandages

P337+313 Get medical advice/attention

P342+311 Call a POISON CENTER or doctor/physician

P370+376 In case of fire: Stop leak if safe to do so

P370+378 In case of fire: Use… for extinction

P370+380 In case of fire: Evacuate area

P370+380+375 In case of fire: Evacuate area. Fight fire remotely due to the risk of explosion

P371+380+375 In case of major fire and large quantities: Evacuate area. Fight fire remotely due to the risk of explosion

Storage precautionary statements:

P401 Store…

P402 Store in a dry place

P403 Store in a well ventilated place

P404 Store in a closed container

P405 Store locked up

P406 Store in a corrosive resistant/… container with a resistant inner liner

P407 Maintain air gap between stacks/pallets

P410 Protect from sunlight

P411 Store at temperatures not exceeding…°C/…°F

P412 Do not expose to temperatures exceeding 50 °C/122 °F

P420 Store away from other materials

P422 Store contents under…

P402+404 Store in a dry place. Store in a closed container

P403+233 Store in a well ventilated place. Keep container tightly closed

P403+235 Store in a well ventilated place. Keep cool~

P410+403 Protect from sunlight. Store in a well ventilated place

P410+412 Protect from sunlight. Do not expose to temperatures exceeding 50 °C/122 °F

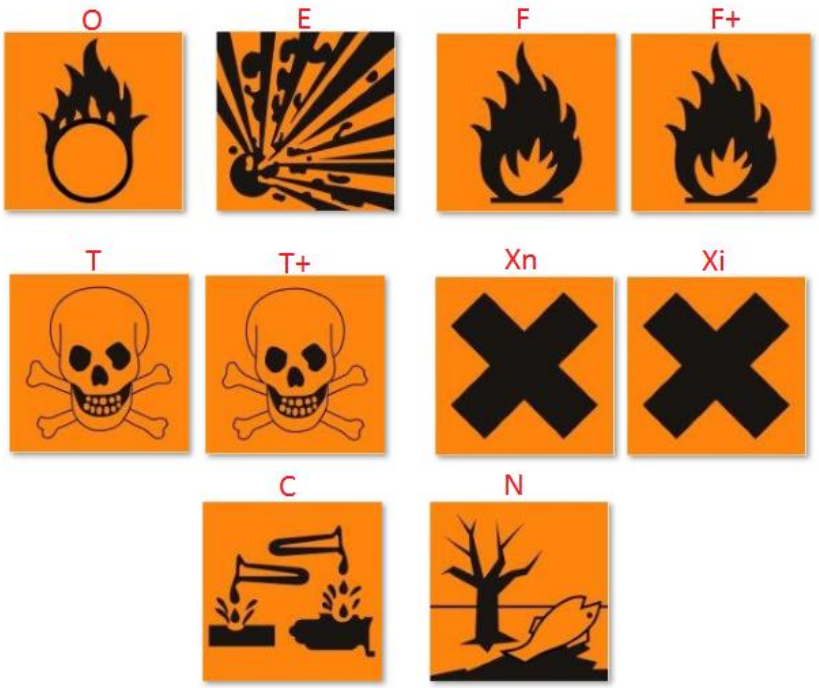
P411+235 Store at temperatures not exceeding…°C/…°F. Keep cool

Disposal precautionary statements:

P501 Dispose of contents/container to…

P502 Gain information about reuse/recycling from the manufacturer or supplier.

4.3.4 Former pictograms



Picture 8. Old pictograms and their codes

O: Oxidizing

E: Explosive

F: Flammable

F+: Extremely flammable

T: Toxic

T+: Very toxic

Xn: Harmful

Xi: Irritant

C: Corrosive

N: Dangerous for the environment

4.4 Safety Data Sheet

Safety Data Sheet (SDS) is an international guidebook to observe chemicals and their properties. Manufacturer or importer of chemicals shall prepare a Safety Data Sheet from the chemical classified as hazardous, which is given to the recipient as the chemical is delivered.

Safety Data Sheet provides comprehensive information about chemical's risks, health and environmental hazards, fire and explosion susceptibility, information on storage, safe use and the necessary safety measures. In addition, SDS provides information on the classification and labelling of chemicals, the regulations on transporting and on the treatment of hazardous chemical waste. For users, the most important information considers handling, prevention on exposure, protective equipment, first aid guidelines and instructions in case of accidents.

Especially hazardous chemicals should be provided with separate working instructions and chemical safety cards to identify their dangerous properties and exposure conditions. Safety precautions and first aid instructions are important to take into account. In addition, if the chemical substance is persistent, bioaccumulative and toxic or very persistent and very bioaccumulative, it should contain its specific safety data sheet.

4.4.1 International Chemical Safety Cards

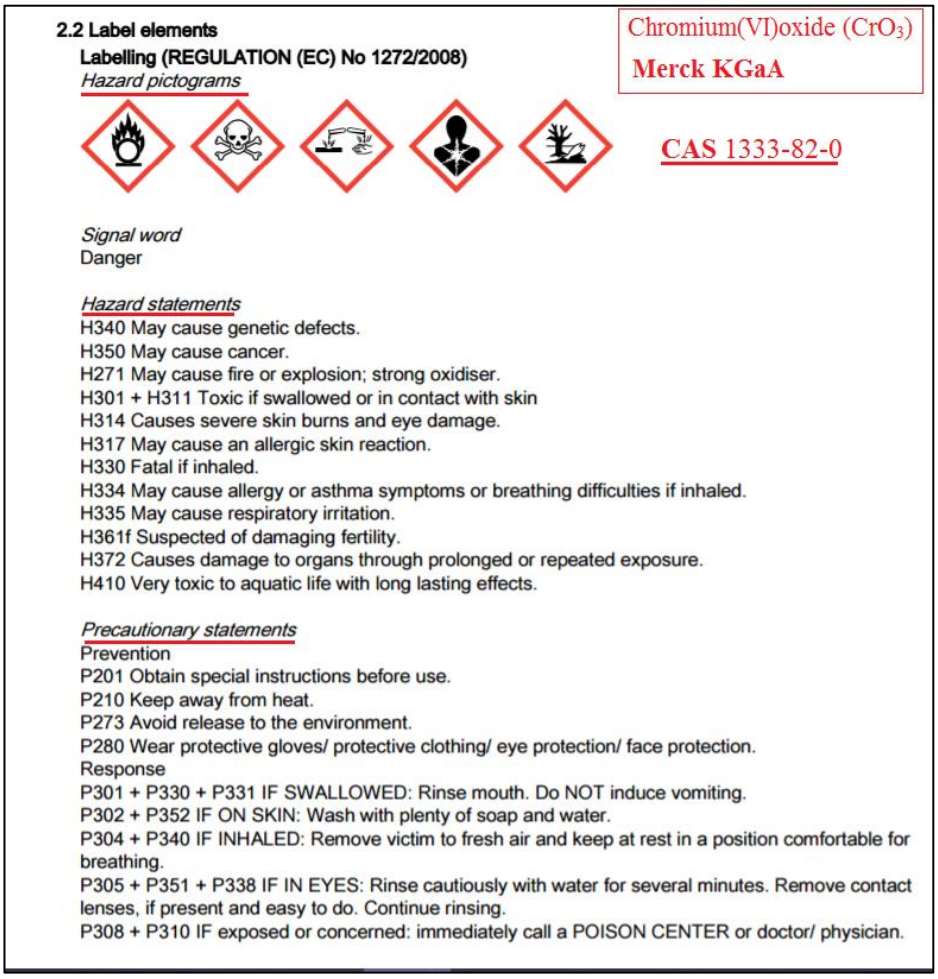
It is very important to know that International Chemical Safety Card (ICSC) is not the same as Safety Data Sheet. Chemical safety cards and Safety Data Sheets can be quite similar, but they have certain differences. The International Expert Group coordinated by the World Heatlth Organization has selected substances for which chemical safety cards have been designed to.

Chemical safety cards are prepared by chemistry specialists and the final approval is given by an expert working group. The information deals with clean substances and contains a summary on health risks and protection, ks. kappa.ttl.fi, /7/

4.4.2 Chromium trioxide's Safety Data Sheet −Example

Safety Data Sheet for chromium trioxide, chromium(VI)oxide (CrO_3) is used as an example of P- and H-statements and the GHS hazard classification.

The CAS (Chemical Abstracts Service) register number shown below is the identification number system used in every safety data sheet and chemical safety cards to facilitate chemical identification, database and the Internet searches. Chromium trioxide's CAS number is 1333-82-0.



2.2 Label elements

Labelling (REGULATION (EC) No 1272/2008)

Hazard pictograms

Chromium(VI)oxide (CrO_3)

Merck KGaA

CAS 1333-82-0

Signal word

Danger

Hazard statements

H340 May cause genetic defects.
H350 May cause cancer.
H271 May cause fire or explosion; strong oxidiser.
H301 + H311 Toxic if swallowed or in contact with skin
H314 Causes severe skin burns and eye damage.
H317 May cause an allergic skin reaction.
H330 Fatal if inhaled.
H334 May cause allergy or asthma symptoms or breathing difficulties if inhaled.
H335 May cause respiratory irritation.
H361f Suspected of damaging fertility.
H372 Causes damage to organs through prolonged or repeated exposure.
H410 Very toxic to aquatic life with long lasting effects.

Precautionary statements

Prevention
P201 Obtain special instructions before use.
P210 Keep away from heat.
P273 Avoid release to the environment.
P280 Wear protective gloves/ protective clothing/ eye protection/ face protection.
Response
P301 + P330 + P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.
P302 + P352 IF ON SKIN: Wash with plenty of soap and water.
P304 + P340 IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
P305 + P351 + P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P308 + P310 IF exposed or concerned: immediately call a POISON CENTER or doctor/ physician.

Picture 9. Safety Data Sheet, 16.01.2015, Chromium trioxide (Merck KGaA, Germany)

5 ORAS' CHEMICALS AND THEIR CHARACTERISTICS

Hundreds of different chemicals and chemical compounds are used at Oras's industrial processes, but the most common chemicals are chromic acid, other acids and bases as well as liquefied petroleum gas. Departments, such as chrome plating departments, are equipped with safety cabinets, spill trays and air conditioning.

Extremely accurate risk assessments of chemicals have been prepared. The staff has been trained to work with chemicals, practice chemical safety, prevent and act on possible chemical accidents. The following table represents the most common hazardous chemicals used at Oras and a description of their physical and chemical properties.

Table 1 List of the most hazardous and commonly used chemicals.

Chemicals	**CAS-number**	**Chemical formula**	**Mole mass (g/mol)**	**Appearance**	**Density (g/cm3, 20 °C)**	**Boiling point (°C)**	**GHS-classification [link 4.3.1]**
Chromium trioxide (100 %)	**1333-82-0**	CrO_3	100	Dark red, granular solids, deliquescent	2,7	250 °C	**GHS03, GHS05, GHS06, GHS08, GHS09**
Ammonium hydroxide (25 %)	**1336-21-6**	NH_4OH	35,04	Colorless liquid	0,91	24,7 °C	**GHS05, GHS09**
Sulfuric acid (25–99 %)	**7664-93-9**	H_2SO_4	98,08	Colorless liquid	1,84	337 °C	**GHS05**
Sodium hydroxide (50 %)	**1310-73-2**	NaOH	39,9	Colorless liquid	2,13	1388 °C	**GHS05**
Hydrochloric acid (35 %)	**7647-01-0**	HCl	36,46	Colorless liquid	1,2	57 °C	**GHS05, GHS07**
Nitric acid (60 %)	**7697-37-2**	HNO_3	63,01	Colorless liquid	1,37	120,5 °C	**GHS03, GHS05**
Nickel(II)chloride hexahydrate (99 %)	**7791-20-0**	$NiCl_2 \cdot 6H_2O$	237.69	Green crystals	1,92	337 °C	**GHS06, GHS08 GHS09**
Liquified propane gas	**74-98-6**	CH_3-CH_2-CH_3	44,1	Colorless liquidfied gas	0,5 (neste) 1,5(kaasu)	-44 °C	**GHS03**
Ethyl acetate	**141-78-6**	$C_4H_8O_2$	88,1	Colorless liquid	0,9	77 °C	**GHS02, GHS07**
Nickel(II)sulfate hexahydrate (99 %)	**10101-97-0**	$NiSO_4 \cdot 6H_2O$	154,8	Green, granular solids	3,7	840 °C	**GHS07,GHS08, GHS09**

5.1 Health and environmental risks of chemicals

The previous chemicals and their health and environmental risks as well as toxicity has been compiled into a simple summary by using various Safety Data Sheets as a source, ttl.fi/ova, /8/ , sigmaaldrich.com, /9/

Chromium trioxide (Chromium(VI)oxide, 100 %)

Chromium trioxide, or chromic acid, is widely exploited in industrial metal plating, such as chrome plating processes. The electrolytic chromium used in industrial chrome plating is based on hexavalent chromium oxide, which is very toxic to both human health and the environment.

This carcinogenic chemical is a hazardous respiratory irritant and it can absorb through the lungs and digestive tract. Prolonged exposure can produce target organs damage. Over-exposure can cause lung damage or even lung cancer. It is a corrosive acid that can cause damage to the skin and to mucous membranes, as well as damage in the nasal mucosa. Eye contact can result in corneal damage or blindness. In the worst possible case, chromium trioxide can be lethal.

Ingestion of chromium trioxide causes severe symptoms in the digestive system, which are bloody diarrhea, vomiting, convulsions, circulatory collapse, unconsciousness, and formation of methaemoglobin. The absorption of this chemical leads to damages in the liver and kidneys. Scientific studies have proven that respirable chromium trioxide compounds can cause lung cancer. The chemical may also cause damage to the fetus and affect fertility. Access to the environment or to sewage system must be prevented as chromium trioxide is listed as highly noxious to the environment and aquatic organisms.

Toxicity:

- Lowest lethal dose for humans, ingested: LDLo = 0.5 g.
- Lethal dose for rats, ingested: LD50 = 80 mg/kg
- Lethal dose for rats, inhaled: LC50 = 0.217 mg/L; 4 h
- Toxicity to aquatic organisms (*Daphnia magna*): EC50 = 0,162 mg/l; 48 h

Ammonium hydroxide (25 %)

Ammonium hydroxide is utilized in chrome plating process and as a neutralizing agent. A strong aqueous solution of ammonia (25 % or higher) is corrosive to skin, harmful to eyes and very hazardous to aquatic organisms. Especially eyes must be protected by wearing safety glasses as the substance is corrosive to the eyes. The solution's access into the environment must be prevented since ammonium hydroxide is classified as hazarous to the environment.

The chemical solution damages mucous membranes, respiratory tract, eyes and skin tissues and it is harmful to health by ingestion. Ammonium hydroxide causes corrosion and ulceration and may be harmful when absorbed through the skin. The symptoms of exposure are burning sensation, cough, laryngitis, shortness of breath and bronchial inflammation.

Toxicity:

- Lowest lethal dose for humans, ingested: LDLo = 43mg/kg
- Lethal dose for rats, ingested: LD50 = 350 mg/kg
- Lethal dose for rats, inhaled: LC50 = 2000 mg/L; 4 h
- Toxicity to aquatic organisms (*Daphnia magna*): EC50 = 101 mg/L; 48h

Sulfuric acid (25–99 %)

Sulfuric acid is the most commonly used industrial chemical. It is used in the etching phase of plastic plating process and in the chemical treatment of Oras' wastewater plant. Etching is the pre-treatment operation of plastics plating process, where 99 % sulfuric acid and chromium trioxide are utilized. In machining the solders are purified with diluted, 25 % sulfuric acid. Also, the chemical water used for wastewater treatment contains diluted 25 % sulfuric acid solution.

Sulfuric acid is an oily, corrosive liquid. Although sulfuric acid itself is not susceptible, it reacts violently with metals, generating highly flammable hydrogen gas. Sulfuric acid fume is formed in plating process of metals and it irritates the respiratory tract, causing burning sensation and severe cough.

Exposure concentrations of 40−80 mg/m3 are unbearable. Splattering of the chemical causes serious eye damage and corrosion to skin. Based on the valid criterias, sulfuric acid is not classified as hazardous to the environment.

Toxicity:

- Lowest lethal dose for humans, ingested: LDLo = 135 mg/kg
- Lethal dose for rats, ingested: LD50 = 2,14 mg/kg
- Lethal dose for rats, inhaled: LC50 = 510 mg/L; 2 h
- Toxicity to aquatic organisms (*Daphnia magna*): EC50 = 29 mg/l; 24h

Sodium hydroxide (50 %)

Sodium hydroxide i.e. lye is used as aqueous solutions that are alkaline and highly corrosive. The solution is an industrial chemical used in the factory's water treatment processes in the alkalization of raw water, which increases the pH of the water.

Most strong acids react quite violently with sodium hydroxide. Acids are corrosive to metals and this combination could release highly flammable hydrogen gas. Sodium hydroxide is corrosive to eyes and in severe cases the contact can result in corneal damage or even blindness.

If sodium hydroxide is ingested, it will damage gastrointestinal tract, causing intensive pain, vomiting and diarrhea. Based on the existing criterias, sodium hydroxide is not classified as hazardous chemical to the environment.

Toxicity:

- Lowest lethal dose for humans, ingested: LDLo = 0,1 dl;72h
- Lethal dose for rats, ingested: LD50 = 2000 mg/kg
- Lethal dose for rats, inhaled: LC50 = 1200 mg/L; 4 h
- Toxicity to aquatic organisms (*Daphnia magna*): EC50 = 40,4 mg/L; 48h

Hydrochloric acid (35 %)

Hydrochloric acid is diluted in water to create 30−35% solution. It is used in chrome plating process, mainly in etching, and as an ion exchange resin's recovery solution. Hydrochloric acid is very corrosive.

Exposure of 75−150 mg/m^3 for an hour causes severe nasal irritation, coughing and breathing difficulties. Five minute exposure of 4500 mg/m^3 and half an hour at 2000 mg/m^3 may be lethal.

Hydrochloric acid can cause rash and even flesh wounds on the skin, if the exposure is longer than usual. Splashing of the chemical solution can cause corrosive injuries on the skin and eyes. Swallowing hydrochloric acid will corrode the gastrointestinal tract causing intensive pain, vomiting and diarrhea. Swallowing a large number can even cause death. Based on the existing criterias, hydrochloric acid is not classified as hazardous chemical to the environment.

Toxicity:

- Lowest lethal dose for humans, ingested: LDLo = 60 mL;29h
- Lethal dose for rats, ingested: LD50 = 700 mg/kg
- Lethal dose for rats, inhaled: LC50 = 4.7 mg/L; 1 h
- Toxicity to aquatic organisms (*Daphnia magna*): EC50 = 0.492 mg/L; 48h

Nitric acid (60 %)

Nitric acid is an important industrial chemical product. As a strong solution it works as an oxidizing agent. It reacts quite violently with acetic acid, liquefied gases, hydrogen sulphide, chromic acid and hydrogen cyanide. This reaction may cause a risk of ignition and release dangerous nitrogen oxides. It is important to know that nitric acid releases nitrogen oxides when in contact with metals, such as copper and iron, and even when it's dissolved in water.

In case of potential nitric acid leakage, Oras' departments 4, 5, 6 and 8 must be evacuated as nitrogen oxides may cause pulmonary edema. Symptoms of acid fumes and nitrogen dioxide exposure are moderate eye and respiratory irritation.

An exposure of 200−1000 mg/m^3 may cause dyspnoea or even death. Nitric acid is corrosive to eyes and in severe cases the contact can result in corneal damage or even blindness. The solution will corrode the skin causing burning sensation and the skin may become scarred. Based on the existing criterias, nitric acid is not classified as hazardous chemical to the environment.

Toxicity:

- Lethal dose for rats, ingested: LD50 = 430 mg/kg
- Lethal dose for rats, inhaled: LC50 = 2500 mg/L; 1 h
- Toxicity to aquatic organisms (*Daphnia magna*): EC50 = 180 mg/l; 48h

Nickel(II)chloride hexahydrate (99 %)

Nickel chloride hexahydrate is a stable, crystalline-liquid form of nickel chloride at room temperature. Nickel chloride is used in the nickel plating process and it is classified as hazardous to health and the environment. It's harmful if ingested or inhaled and it irritates the skin and even damages internal organs for long periods of exposure, if inhaled. Nickel chloride hexahydrate is very toxic to aquatic organisms, causing long-term adverse effects.

Nickel chloride hexahydrate may damage the fetus. If ingested, the chemical will cause painful symptoms in the digestive tract, such as diarrhea, vomiting and convulsions. The chemical is absorbed through the respiratory tract, causing burning sensation, cough, breathing difficulties, as well as irritation in the respiratory tract and possible damage to the nasal mucosa. It also irritates the skin.

Inhaled compounds of nickel chloride have been researched to be carcinogenic in animal experiments. Access to the environment or to sewage system must be prevented as nickel chloride hexahydrate is listed as highly noxious to the environment and aquatic organisms.

Toxicity:

- Lethal dose for rats, ingested: LD50 = 105 mg/kg
- Toxicity to aquatic organisms (*Daphnia magna*): EC50 = 6-9 mg/L; 48h

Liquified propane gas

Liquified propane gas is highly flammable mixture of gaseous hydrocarbons, which is stored and transported in liquefied gas cylinders and tanks. For instance, the heating of foundry's ladle nozzles and machining's solderings is executed with liquefied propane gas. A $15m^3$ storage tank is located outside the department of the foundry, from which it is passed through an air duct to the evaporator.

Propane leak from the storage tank may appear in a liquid or gas form. Liquified propane produces partially visible fumes, but in a gas form the fumes are invisible. The liquefied propane gas/air mixture formed in the leak is heavier than air. The leaking propane is easily flammable and the formed gas fog ignites in a couple of seconds.

An ignition of gas and air mixture formed in the enclosed space may cause an interior explosion and the liquefied gas tank is in danger of tearing apart because of the excess heat caused by flames. It is an order to evacuate the factory, if any of the previous accidents occur.

Toxicity:

- Lethal dose for rats, inhaled: LC50 = 12,190 mg/L; 4 h
- Toxicity to aquatic organisms (*Daphnia magna*): EC50 = 27.1; 48h

Ethyl acetate

Ethyl acetate is a synthetic chemical, which can be produced from ethanol and acetic acid. The chemical is used as a solvent and a raw material. At room temperature, ethyl acetate is a highly flammable, colorless liquid.

When handling ethyl acetate, the space must not contain any fire. The chemical reacts violently with strong oxidants, bases and acids. It is highly corrosive for metals, such as aluminium, and even for plastics.

When inhaled, ethyl acetate may cause bad cough, dizziness, headache, nausea and unconsciousness in large quantities. The chemical can be absorbed into the body by inhaling its fumes. Ethyl acetate irritates skin and may cause redness in the eyes.

Based on the existing criterias, ethyl acetate is not classified as hazardous chemical to the environment.

Toxicity:

- Lethal dose for rats, ingested: LD50 = 5620 mg/kg
- Lethal dose for rats, inhaled: LC50 = 16000 mg/L; 6 h
- Toxicity to aquatic organisms (*Daphnia magna*): EC50 = 717 mg/L; 48h

Nickel(II)sulfate hexahydrate (99 %)

Nickel(II)sulfate hexahydrate is a green, water-soluble compound produced by the chemical reaction of sulfuric acid and metallic nickel or nickel oxide. It is used in the nickel plating process as a polishing agent and catalyst. The chemical is classified as a carcinogenic substance and it's very hazardous to aquatic organisms and to the environment.

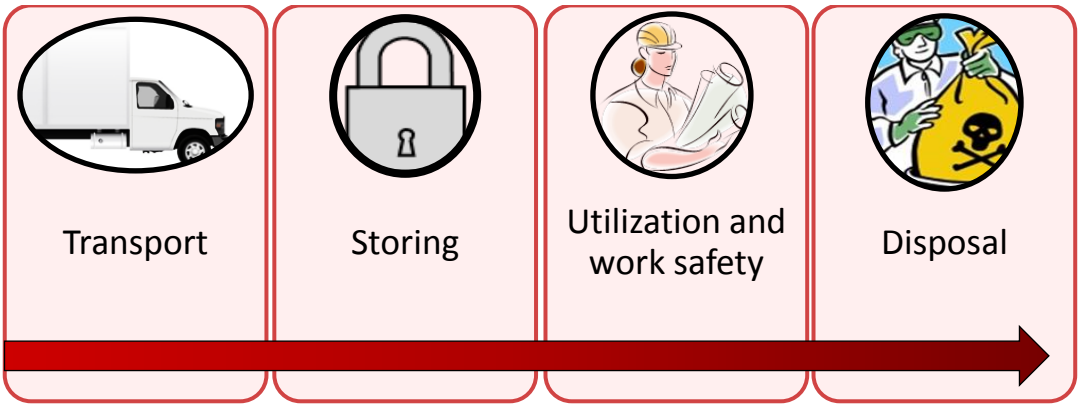
Nickel sulfate hexahydrate decays when heated (840 ° C) forming toxic fumes of sulfur trioxide and nickel monoxide. The chemical irritates the eyes and skin, causing redness, cough, sore throat and dizziness. Ingestion of nickel sulfate hexahydrate causes a painful stomach pain, dizziness, nausea and vomiting. It may even damage the fetus. Access to drains, surface water, groundwater and to the environment must be prevented.

Toxicity:

- Lethal dose for rats, ingested: LD50 = 264 mg/kg
- Toxicity to aquatic organisms (*Daphnia magna*): EC50 = 4,2 mg/l ; 48h

6 CHEMICALS PROCESS AT ORAS' FACTORY

This thesis focused on the chemicals process throughout the factory, which includes the transportation and import of chemicals, storage, utilization of chemicals in different processes, their risks and work safety, and finally the waste disposal and disposal of hazardous chemicals. Oras' clean and wastewater treatment plants operations are explained as well.



Picture 10. Chemicals process step-by-step at Oras

6.1 Chemicals transport

Oras purchases its chemicals from well-known chemical manufacturers, whose responsibility is to ensure that those chemicals are properly packaged and labelled and that the transport shall be in accordance with the given regulations. The main responsibility of the safe use, storage and transport of chemicals at the factory will be exchanged to Oras, when chemicals enter the factory site. Liquified propane gas is transported in liquefied gas cylinders and tanks.

In Finland, Tukes monitors the compliance of transportable chemicals, while Trafi is responsible for the safety of transport. The objective of transporting the noxious substances is to handle those chemicals efficiently while taking health and environmental aspects into account. The purpose of transport legislation for hazardous substances is to prevent any risks that hazardous chemicals may cause to humans or the environment.

The transport legislation ensures that people carrying out transport tasks must have a specific training to ensure safe transport. Staff training provides training on the provisions and regulations about the transport of hazardous chemicals, trafi.fi, /10/

6.2 Storage of chemicals

The chemical storage at Oras is designed to prevent chemicals from leaking into the work environment or to sewer system. Acidic, alkaline and hazardous chemicals have their own storage rooms. The most hazardous chemicals storage is locked behind a pin code where only the employer has an access to.

The spill trays, i.e. floor-installed pools, collect possible chemical leaks leading them to the embankment tank. If there is any hazardous chemical in the leakage, the hazardous wastewater is treated in Oras' wastewater plant before letting it flow into the sewer. Chemical spill trays have been built in every storage room to prevent the mixing of chemicals.

The storages are equipped with air ventilation systems so that the gas or fumes released from the chemicals does not pose a risk to human health. Alarming gas sensors and emergency showers are also installed there. The real estate monitoring system is responsible for the alarm situations and the overall functionality is tested on a regular basis.

6.3 Utilization of chemicals and their risks

The safe use of chemicals requires precise training and induction. Various chemicals are used at Oras' operations, like sand and core manufacturing, metal casting, soldering, grinding and polishing, and especially chrome plating processes and wastewater treatment.

Sand and core manufacturing

Quartz sand is utilized in the production of core, manufactured with hot-box machinery. Hardening of the sand is based on the reaction of high temperature and sand blend binders where phenol and furfuryl alcohol form a furan resin. Furfuryl alcohol contains small amounts of formaldehyde. The risks of core manufacturing, such as the risk of burning, fire, and various physical injuries, are mainly caused by the use of hotbox machines.

Metal casting

Metal casting is operated at the foundry department, where automated low pressure casting is utilized. The material used in casting is brass, which is an alloy of copper and zinc. The heating of foundry's ladle nozzles is executed with liquefied propane gas. The basement cellar is equipped with automatic gas alarms in case of propane leakage. Major risks are the high temperature of the casting ovens, the molten brass, zinc burning and the risk of gas leakage and fire due to the use of propane.

Soldering

The metal parts are soldered with silver-containing, cadmium-free hard brazing at very high temperature. The solderings are heated by liquefied petroleum gas and they are cleaned with a 25 % sulfuric acid solution and then rinsed with water, which is treated at the wastewater treatment plant. The risks of soldering process are mostly caused by the hot equipment and the use of sulfuric acid and propane.

Grinding and polishing

In the grinding process, polishing of the product is executed by polishing wax and fabric pads The risks of grinding and polishing are related to the use of machinery and the possible ignition of polishing waste.

Chrome plating

The most important chemicals utilized in the chrome plating processes are chromium trioxide, ammonium hydroxide, sodium hydroxide, sulfuric acid, hydrochloric acid, nitric acid and nickel chloride.

Electrolytic chrome plating is based on hexavalent chromium oxide, which is very hazardous. The handling of hazardous chemicals is already a significant risk, so the employees must be well-trained.

The management of any chemical leakage poses a safety risk, and therefore both brass and plastic chrome plating departments are placed over the spill trays in order to treat the hazardous leakage separately. The chrome plating departments organize regular training concerning the safety issues related to possible chemical accidents and dangers.

Wastewater treatment

Oras' wastewater treatment plant is designed to precipitate heavy metals from the rinsing water. Chemicals, such as lye i.e. sodium hydroxide, hydrochloric acid and sulfuric acid, are stored in the same site. Chemical tanks and sewage treatment pools are placed in their own spill trays to control possible leaks, which poses a safety risk. For more detailed information, see 6.4.1.

6.3.1 Water plant and containers

Oras acquires its raw water from Rauma's water supply network and receives about 130 m^3 of water each day. The clearest rinsing water is recycled to the production operations. The factory owns its separate clear water plant, which primary task is to produce deionized water for chrome plating processes. Ionized water is produced by ion exchangers, i.e. with anionic and cation exchangers, for the water storage system.

The groundwater in Finland is acidic (pH <7), so alkalinization, i.e. raising the pH level, is necessary to reduce the corrosiveness of raw water. Water's alkalinity and hardness must be adjusted so that it does not cause any problems in the water network or equipment. Alkalization is produced by adding chemicals such as lye (NaOH) and lime ($Ca(OH)_2$).

However, using lye involves the risk of overdosing, resulting in too high pH level of water. For this reason, the use of lye is attempted to change into other alkalization methods, if it is efficient for the water quality.

There are five clear water tanks and four chemical tanks containing sodium hydroxide, sulfuric acid, hydrochloric acid, and chemically purified sulfuric acid.

6.3.2 Work safety

Chemicals and their safety risks are carefully assessed in Oras. The overall responsibility of work safety is on the employer to provide that every chemical is listed and that comprehensive information and safety data sheets are available on their properties and safety.

Employees working with hazardous chemicals wear protective clothing such as gloves, goggles, respirators, protective clothing and safety shoes. They are trained in handling and protection in case of exposure or dangerous situations. Use of chemicals, storage and disposal is managed in accordance of given regulations.

6.4 Disposal of chemical waste

According to the Waste Act (Finlex 646/2011), waste is classified as a hazardous waste, if it poses a risk to health and/or to the environment due to their chemical nature. Hazardous waste sets precise requirements for the transport and handling of the waste. Oras, like any other industry, has the responsibility to sustain a professional waste management system. Hazardous waste can be placed on a special landfill site designed for these purposes, ymparisto.fi, /11/

The most hazardous chemical waste generated by Oras's production processes is delivered to Ekokem Oyj for post-processing. Ekokem is a Finnish environmental management company specializing in the handling and disposal of hazardous waste. Norilsk Nickel Oy in Harjavalta utilizes a certain part of nickel-containing waste. Waste sand, nickel and copper waste are mainly utilized at Boliden Harjavalta Oy.

A small amount of the waste sand is delivered to the landfill, because large sand granules cannot be post-processed. However, most of the hazardous chemicals can be handled at Oras's wastewater treatment plant. The wastewater plant has three batch tanks and a variety of chemicals are utilized in the treatment process.

6.4.1 Wastewater treatment

Oras' wastewater treatment plant is designed to precipitate heavy metals from the rinsing water. Chemicals, such as sodium hydroxide, hydrochloric acid and sulfuric acid, are stored in the same site. Chromic acid, acidic and alkaline containing waste has their own collection points and waste of different purity levels have their own wastewater treatment processes. Chemical water contains sodium hydrogen sulfate, calcium chloride, sulfuric acid (diluted from 99 % to 25 %) and an aluminum chloride-containing chemical mixture.

Wastewaters should be treated so precisely that they can be discharged into Rauma's wastewater plant. The water is treated with a continuous waste treatment line to ensure the desired heavy metal content and clearness. Samples of wastewater are taken daily as the limit values are set in Oras' Environmental Permit.

Table 2 Maximum permissible concentrations (Oras, Environmental permit decision).

Total -Cr	Cr 6+	Cu	Ni	pH
0,5 mg/l	0,1 mg/l	0,5 mg/l	1,0 mg/l	10,5

The most concentrated waters containing heavy metals are handled manually in the batch process. Plant workers treat the mixture in a batch tank in which they add polyaluminium chloride. The pH of the water should be adjusted, whereby a white precipitate is formed in the water and the clear, treated water rises to the surface. A dry, chemical waste residue is left in the chamber where it is collected on the platform. This way, the chemical waste can be transported for post-processing.

7 THE APPLICATION OF CHEMICAL SAFETY MANAGEMENT

7.1 General

The priority of Oras' chemical safety is to identify work-related accident and consequences as well as preventing health, environmental and property risks caused by the manufacture, transfer, storage or other utilization of chemicals, www.tyosuojelu.fi, /12/

Selection of personal protective equipment is based on the risk assessments. Chemical workers must use protective equipment if the risk cannot be removed by separate arrangements or technical solutions. Personal protective equipment comprises tools, equipment and clothing that protect human health from any potential accidents and dangers. These include goggles, safety shoes, gloves, helmet, hearing and respirator protection and protective overalls.

Isolating emissions from Oras' work environment through efficient ventilation is the primary mechanism against any harmful air pollutant. With a mixing air distribution system, indoor air cleanliness and temperature can be balanced throughout the departments.

Work departments are built separately from one another at Oras, thus it's more efficient to manage impurities and emissions generated by different work operations. Hazardous chemicals, their risks and potential accidents are risk assessed systematically. Different risk analysis methods as well as safety data sheets are used in the process. Safety data sheets are kept organized for employees at Oras.

7.2 Risk assessment and management

Risk assessment is a process of assessing potential health and safety risks concerning the workers. The process focuses on the identification of hazards and disadvantages at work, the identification of risk factors, the determination and assessment of the magnitude of the risks, and measures to prevent or reduce potential risks.

The assessment of risks associated with chemicals utilizes advice and more detailed information from the professionals. Occupational health care expertise is needed to address the importance of risks related to tertiary and welfare and occupational hygiene. The purpose of the risk assessment is to identify the magnitude of the risk on the risks and to set the risk factors in the order of magnitude of the risk:

Table 3 The magnitude of the risks.

Risk probability	**Consequences**		
	(1) Low	**(2) Harmful**	**(3) Severe**
Improbable	Insignificant risk (1)	Low risk (2)	Moderate risk (3)
Possible	Low risk (2)	Moderate risk (3)	Significant risk (4)
Probable	Moderate risk (3)	Significant risk (4)	**Unbearable risk (5)**

- **Risk magnitude (1−5):**

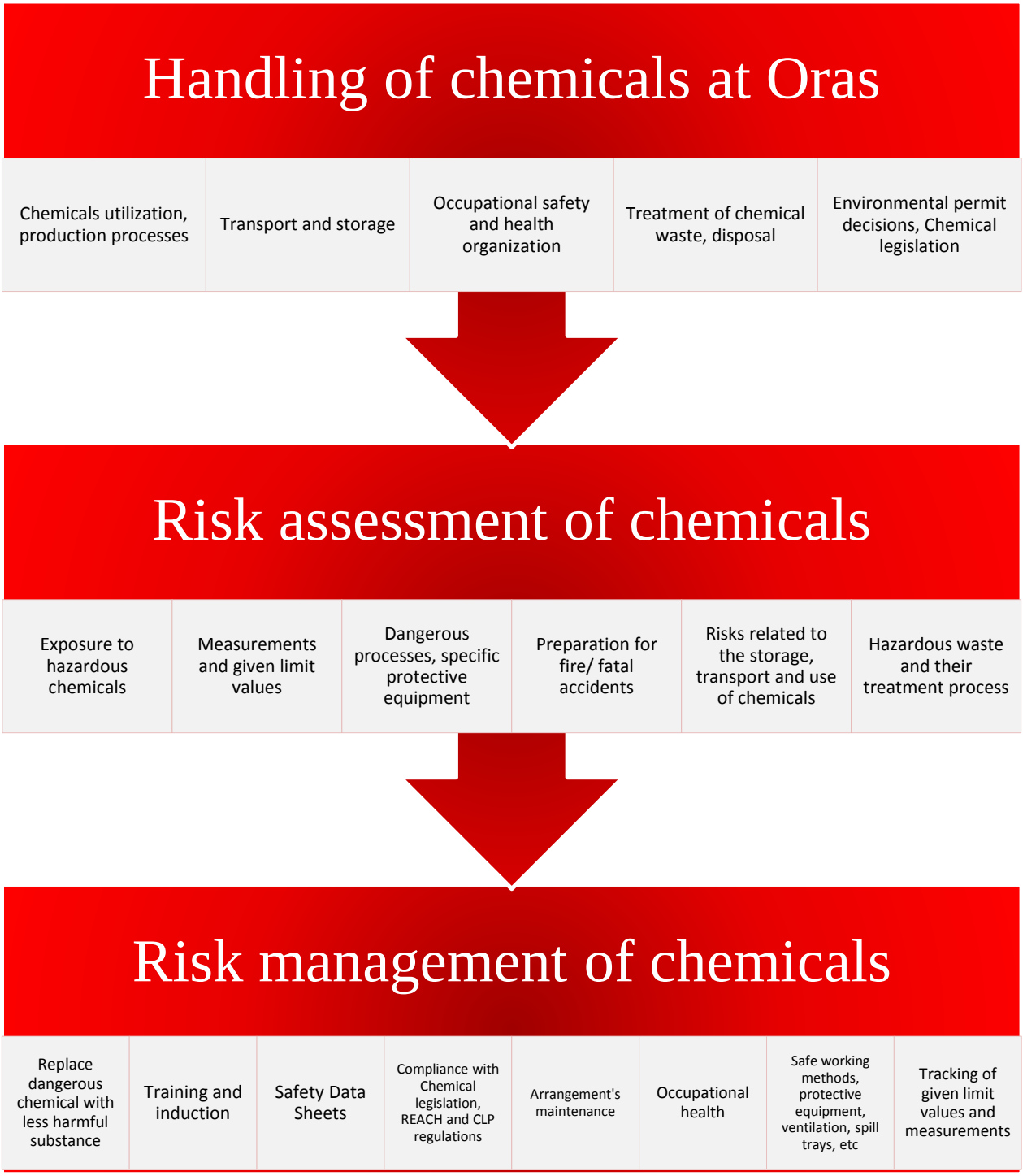
1. **Insignificant:** No measures needed.
2. **Low**: Requires monitoring so that risk remains under control.
3. **Moderate**: Measures should be taken to reduce the risk. If a reasonable risk involves adverse consequences, further evaluation is required to establish a likelihood of a disadvantage that will determine the need for more effective measures.
4. **Significant:** Work must not start until the risk has been reduced. There may be a need for large amounts of resources to be taken. If there is a risk associated with ongoing work, the problem must be corrected in a shorter timeframe than in the case of reasonable risks.
5. **Unbearable:** Work must not be started or resumed. If risk reduction is not possible, work must be permanently prohibited.

Risk management is a systematic estimation of significant risks and it provides effective measures to improve work safety and accident prevention. Management methods are evaluated based on the level of safety, the magnitude of the risks, and the overall cost-effectiveness.

Risk management purpose is that immediate risks are addressed and minimized. Even low risks must be minimized or eliminated. In Oras, departmental meetings are arranged by the foremen, where risk management measures are decided.

The most common measures to reduce chemical risks are:

- Designing and monitoring safe work methods
- Use of safe equipment and tools
- Use of personal protective equipment
- Exposure and emission intensity control through efficient air conditioning
- General cleanliness and hygiene
- Reduce the amount of hazardous chemicals, if possible
- Appropriate working methods for the utilization of chemicals, waste management, transport and storage
- Replace hazardous chemicals with less harmful substances or methods, if possible.



Picture 11. Segment of chemicals, risk assessment and risk management

7.3 The most severe risks of processes

Table 4 The most severe risks of processes, their magnitude, causes and consequences.

Risks	Utilization of hazardous chemicals	Foundry work accident	Fire	Liquified propane gas leakage
Risk magnitude (1–5)	Moderate (3) – Significant (4)	Moderate (3)	Moderate (3)	Moderate (3)
Causes	**Negligence** **Maintenance/interference** **Leakage** **Contact with other hazardous-substances** **Contact with metals** **Splatter**	**Negligence** **Zinc fire** **Device breakage** **Malfunctions** **Interference**	**Negligence** **Machine failure** **Malfunctions** **Electrical fire** **Zinc fire** **Fire work** **Smoking cigarettes**	**Negligence** **Storage tank leakage** **Tube/tank breakage** **Storage tank rupture** **Malfunctions**
Consequences	**Fatal** **Health hazard** **Fire** **Explosion** **Environmental contamination**	**Fatal** **Health hazard** **Fire** **Physical injuries**	**Fatal** **Damage property** **Suspend the work**	**Fatal** **Fire** **Explosion** **Damage property**

Based on the risk assessments, utilization of chemicals should not cause any major accident outside Oras' factory. However, the departments must be evacuated if severe fire, hazardous chemical leakage (like nitric acid leakage) or liquefied propane gas leak is noticed. The probability of fire accident is prominent in the foundry's metal casting operations, soldering and grinding and polishing. Utilization of nitric acid and propane include the risk of fire as well.

There have been very few cases of fire in Oras and the consequences have been small property losses. Zinc fires has occurred a couple of times and they have been caused by malfunctions. The worst case scenario, associated with the use of hazardous chemicals, would be the leakage of nitric acid to chemicals storage caused by valve breakage, Satakunnan pelastus, ulkoinen pelastussuunnitelma, /13/

7.3.1 Training on work safety

Specific work training and induction has been taught so that staff can work properly in dangerous situations. The safe use of hazardous chemicals require proper training to prepare workers for potential chemical risks such as leakage, liquefied gas leakage or even fire.

The handling of hazardous chemicals and waste are considered a safety risk, and for this reason, chrome plating departments provide regular training to examine safety issues related to hazardous chemicals and accidents.

Training organized at Oras:

- Fire extinguishing training
- Chrome plating departments chemical and occupational safety training
- Fire works
- Foundry's occupational safety training
- Liquified propane gas usage training

Along with Oras, the Satakunta rescue department has participated in providing chemical safety, equipment, training and induction for the factory workers in case of possible accidents. Every three years, the factory organizes training involving both Satakunta rescue department team and Oras' staff. In the end of the training, there will be an evaluation phase of potential safety issues and suggestions for possible improvement methods.

8 CONCLUSIONS

The purpose of this thesis was to study Oras's production processes and the utilization of hazardous chemicals, their health and the environmental risks and chemical safety. Part of this work was to examine the process of chemicals throughout the factory, from transport to storage, to utilization and eventually to the disposal.
This thesis was translated from Finnish to English, since the objective for Oras was to receive the work in Finnish.

List of the most hazardous chemicals was updated, presenting the chemical and physical properties of the substances as well as the hazard classifications. Comprehensive summary of their health and environmental risks and toxicity of chemicals was collected by using different Safety Data Sheets as a source.

This thesis studied general chemicals legislation and the changes implemented by the REACH and CLP regulations. The goal was to examine Oras' chemical safety, which included very important chemical safety issues. Different processes and chemicals risks, their magnitude, potential causes and consequences and potential accidents were evaluated.

Oras complies commendably with the regulations and related provisions. It's great that the factory has left gold potassium cyanide out of production processes, since it is very hazardous chemical for both human health and the environment. The possibility whether or not the amount of any other hazardous chemical could be reduced or replaced with less harmful substance in the future was discussed. For example, chromium trioxide is known to be a dangerous chemical, which is intended to be replaced with less harmful alternatives in many industries.

Carcinogenic chromium trioxide, i.e. hexavalent chromium, is more toxic compared to the more environmentally friendly dichromium trioxide, i.e. trivalent chromium. Because chromium trioxide causes hazardous exposure and potential diseases, an alternative choice is to replace the conventional chromating process with a more ecological plating method, if possible.

The two chrome plating processes are different in their operating principles and a trivalent chromium plating is not yet suitable for every purpose, as the basins do not precipitate hard chromium layers. Use and maintenance of trivalent chromium basins is way more complex than hexavalent chromium basins and the cost of alteration is quite significant.

However, the plating obtained from trivalent chromium is almost equal to the conventional chromium plating in the properties like resistance to corrosion and shine, even though the shade is darker. Trivalent chromium has many advantages over hexavalent mostly in health and environmental aspects, although the technology, quality and cost-effectiveness are not at the same level yet.

However, the utilization of hazardous chromium trioxide is very challenging, as continuously requests of authorization is demanded. Oras has a four-year permission to use chromium trioxide in their chrome plating processes. In 2021, chromium trioxide is prescribed to be replaced with some less harmful chemical.

In particular, REACH encourages companies to develop more environmentally friendly technology that would match the quality of hexavalent chromium oxide based electrolytic chrome plating. The international goal is to promote the development safe and environmentally friendly technologies and the deployment of chemicals.

REFERENCES

1. Oras Oy, Factory, Rauma. Company information. The Internet website. Available: orasgroup.com/fi/

2. Oras Oy, Environmental permit decision, 2007. Available: ymparisto.fi (PDF-DOK)

3. ValuAtlas. Foundry work. The Internet website. Referred:10.11.2016. Available: valuatlas.fi/

4. Chemical Information, 2013. REACH and CLP Regulations. The Internet website. Referred:1.12.2016. Available: kemikaalineuvonta.fi (REACH ; CLP)

5. Tukes, 1995. Chemicals legislation, REACH, CLP, GHS hazardous pictogram. The Internet Websites. Referred:16.12.2016. Available: tukes.fi/ (Chemicals legislation; REACH ; CLP ; GHS)

6. Occupational safety and health department. GHS, hazardous statements, precautionary statements. The Internet website Available: ttl.fi/ova/varoitusmerk_CLP.html

7. International chemical safety cards. The Internet websites. Referred:19.1.2017. Available: kappa.ttl.fi/kemikaalikortit/

8. Work safety department. Information about the chemicals. The Internet website. Available: ttl.fi/ova/ (Kromitrioksidi ; Ammoniakkivesi ; Rikkihappo ; Natriumhydroksidi-liuos ; Suolahappo ; Typpihappo ; Nestekaasu/Propaani (In Finnish))

9. Sigma-Aldrich, 1975. Safety Data Sheets. The Internet website. Available: www.sigmaaldrich.com/catalog/ (Chromium ; Ammonium ; Sulfuric ; Sodiumhydr ; Hydrochloric ; Nitric ; Nickelchloridehex ; Propane ; Ethylace ; Nickelsulfhex)

10. Trafi. Chemicals transportation. The Internet website. Available: trafi.fi/liikennejarjestelma/vaaralliset_aineet

11. Network service for environmental management. Disposal of chemical waste. The Internet website. Available: ymparisto.fi (Jätteet ja jätehuolto ; Vaarallinen jäte)

12. Occupational safety and health administration web service. Application of chemical safety, risk assessment and management. The Internet website. Referred:16.3.2017. Available: tyosuojelu.fi/tyoolot/

13. Satakunta rescue department. Rescue plan (Oras Oy), 2013. Processes and possible accident situations. The Internet website. Available: satapelastus.fi/ (PDF-DOK)

IMPORTANT:

Sulin, S. 2016. Oras. An interview and induction to the factory. 19.10.2016

Sulin, S. 2016. Oras. Chrome plating -theory. 19.10.2016

Oras Oy. Presentation. Summer 2016. Production processes. Intranet.

Oras, Environmental permit decision, 2007. Available: ymparisto.fi (PDF-DOK)

Institute of Occupational Health. 2005. Book: Kemikaalit ja työ, selvitys työympäristön kemikaaliriskeistä. Helsinki. 13−18 ; 30−43.

Merck KGaA, Germany. Chromium(VI)oxide safety data sheet (EY) N:o 1272/2008. Available: merckmillipore.com

Galvanotech SGY ry, Aalto Yliopisto, Metropolia Ammattikorkeakoulu.Environmentally friendly chrome plating. Arranged:27.1.2017. Utilized in the conclusion of this thesis. Available: sgy-ry.fi/ (Ympäristöystävällisen kromauksen kehittäminen)