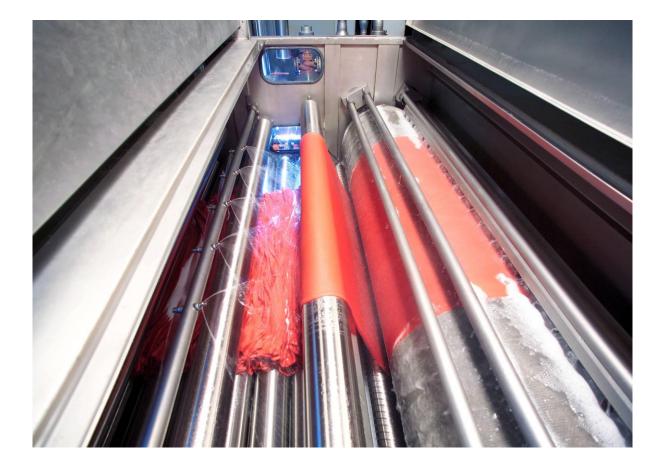
# IAMC Toolkit

Innovative Approaches for the Sound Management of Chemicals and Chemical Waste



# Technical Manual **Textile Finishing Industry**

July 2016

### **Masthead**

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Unless otherwise mentioned, all references to sums of money are given in United States dollars. References to "tons" are to metric tons, unless otherwise stated.

### Contents

| 1                        | INTRODUCTION   | 4               |
|--------------------------|--|-----------------|
| 2                        | GENERAL ASPECTS OF THE TEXTILE AND FINISHING INDUSTRY  | 7               |
| 2.1                      | Importance of the textile market   | 8               |
| 2.2                      | Textile finishing processes  | 9               |
| 2.2.1                    |  | 9               |
| 2.2.2                    | 5 0  | 12              |
| 2.2.3                    | e  | 13              |
| 2.2.4                    | e  | 13              |
| 2.3                      | Chemicals in the textile finishing processes   | 13              |
| 2.3.1                    |  | 15              |
| 2.3.2                    | Dyestuffs  | 15              |
|                          | INNOVATIVE SOLUTIONS   | 18              |
| 3.1                      | Reduction of utilities and chemicals consumption   | 18              |
| 3.1.1                    | e e  | 18              |
| 3.1.2                    |  | 19              |
| 3.1.3                    | *  | 20              |
| 3.1.4                    |  | 22              |
| 3.1.5                    |  | 23              |
| 3.1.6                    |  | 24              |
| 3.1.7                    |  | 25              |
| 3.1.8                    |  | 26              |
| 3.1.9<br>3.1.1           |  | 28              |
| <b>3.1</b> .1 <b>3.2</b> | 0 Caustic soda recovery<br>Substitution of hazardous chemicals   | 30<br><b>32</b> |
| <b>3.2</b> .1            |  | 32              |
| 3.2.1                    |  | 32              |
| 3.2.2                    |  | 33              |
| 3.2.4                    | e  | 34              |
| 3.2.5                    |  | 34              |
| 3.2.6                    |  | 35              |
| 3.2.7                    |  | 36              |
| 3.2.8                    | • •  | 37              |
| 4                        | CROSS-CUTTING INNOVATIVE APPROACHES  | 38              |
| 4.1                      | Chemical leasing and other innovative business models  | 38              |
| 4.1.1                    |  | 38              |
| 4.1.2                    |  | 38              |
| 4.1.3                    |  | 41              |
| 4.2                      | Prevention of major accidents  | 42              |
| 4.2.1                    |  | 42              |
| 4.2.2                    | 5  | 43              |
| 4.2.3                    | 1 5  | 44              |
| 4.2.4                    | 5  | 44              |
| 4.2.5                    |  | 48              |
| 4.3                      | Safe handling of chemicals   | 49              |
| 4.3.1                    |  | 50              |
| 4.3.2                    | •  | 56              |
| 4.3.3                    | L Contraction of the second seco | 57              |
| 4.3.4                    | 6  | 62<br>62        |
| 4.3.5<br><b>4.4</b>      |  | 62              |
| <b>4.4</b> 4.4.1         | Storage of hazardous chemicals   | <b>62</b><br>63 |
| 4.4.1                    |  | 63              |
| 7.4.2                    | Crassifications/categories   | 05              |

| 4.4.3 Technical solutions  | 65         |
|--|------------|
| 4.5 Fire protection  | 70         |
| 4.5.1 Classification/categories  | 71         |
| 4.5.2 Technical solutions (risk reduction measures)                                    | 72         |
| 4.6 Management of chemical waste   | 75         |
| 4.6.1 Waste management options   | 76         |
| 4.6.2 Good practices in hazardous waste management                                     | 77         |
| 4.6.3 Additional sources of information  | 83         |
| 4.7 Energy efficiency and chemicals  | 84         |
| 4.7.1 Heat transfer systems  | 84         |
| 4.7.2 Fuel type  | 85         |
| 4.7.3 Emission reduction measures  | 85         |
| 5 CASE STUDIES   | 89         |
| 6 SUPPORTING POLICIES  | 96         |
| 6.1 Market-based instruments to promote efficient technologies and preventive          | 20         |
| environmental practices  | 97         |
| 6.2 Optimization of the use of natural resources and raw materials, minimization of    |            |
| emissions  | 98         |
| 6.3 Reward for good environmental performance and practices                            | 99         |
| 6.4 Minimization of practices leading to the exclusive use of end-of-pipe technologies | 100        |
| 6.5 Industry-lead initiatives  | 101        |
| 6.6 Regulatory instruments: command and control for environmental protection and s     |            |
| 102  | v          |
|  | 104        |
| <ul><li>7 FUNDING OF INNOVATIONS</li><li>7.1 Funding in Peru</li></ul>                 | 104<br>104 |
| <ul><li>7.1 Funding in Peru</li><li>7.1.1 Green Credit Trust Fund</li></ul>            | 104        |
| 7.2 Funding in El Salvador   | 104        |
| 7.2.1 FONDEPRO   | 105        |
| 7.2.2 BANDESAL-KfW Environmental Conversion Line                                       | 105        |
| 7.3 Funding in Egypt   | 105        |
| 7.3.1 Private Public Sector Industry Project   | 106        |
| <ul><li>7.3.2 Environmental Compliance Office Revolving Fund Programme</li></ul>       | 106        |
| 7.4 Funding in Morocco   | 107        |
| 7.4.1 National Fund for the Environment (FNE)  | 107        |
| 7.4.2 Fund for Industrial Depollution (FODEP)  | 107        |
| 7.4.3 Voluntary Mechanism of Industrial Wastewater Treatment                           | 107        |
| 7.4.4 Business Advisory Service Programme  | 107        |
| 8 WHERE DO I FIND SUPPORT?   | 108        |
| 9 BIBLIOGRAPHY   | 110        |
| APPENDICES   | 113        |
| APPENDIX 1: IMPORTANT AUXILIARIES AND BASIC CHEMICALS USED IN TEX                      | TILE       |
| PRODUCTION   | 114        |
|  | -          |
| APPENDIX 2: CHEMICAL RESISTANCE SELECTION CHART FOR PROTECTIVE<br>GLOVES               | 192        |
|  | 123        |
| APPENDIX 3: STORAGE  | 126        |
| APPENDIX 4: FIRE PROTECTION  | 128        |

### **1** Introduction

The United Nations Industrial Development Organization's (UNIDO) overarching objective is to reduce poverty through sustainable industrial development. In response to this global challenge, UNIDO launched the *Green Industry* initiative with the aim of fostering the positive role of industry in achieving sustainable economic growth. According to UNIDO's Green Industry vision, the industries' role is to constantly provide creative and innovative solutions and alternatives to countries' economies, focusing on a well-balanced economic, environmental and social impact of industry. Sustainable development has indeed become a core determinant of economic competitiveness and allows industries to decouple their economic growth and revenues from excessive and increasing resource use and pollution by minimizing waste in every form, using renewable resources, taking precautions to avoid harming workers, communities as well as the environment [1].

The joint global *UNIDO-UNEP Resource Efficient and Cleaner Production (RECP) Programme* endorses the Green Industry vision. The programme is based on a multi-pronged programmatically and geographically focused approach to scale up and mainstream the application of RECP concepts, methods, techniques, technologies and policies in developing and transition countries in order to improve resource efficiency and environmental performance of enterprises and other organizations, in particular small and medium-sized operators in the manufacturing and associated sectors.

The multi-faceted reliance on chemicals across industries makes chemicals production one of the major and most globalized industrial sectors with a high impact on the overall sustainability performance of supply chains. The essential economic role of chemicals and their contribution to improved living standards needs to be balanced under consideration of all potential costs. An adequate cost analysis thus has to include the *chemical industry's use of resources*, such as water and energy, and the potential adverse impacts of chemicals on the environment and human health. The potential severity and complexity of such impacts highlights the fact that sound chemicals management is a key issue for sustainable development [2].

Under this programme, the project entitled *Innovative Approaches for the Sound Management of Chemicals and Chemical Waste* aims at providing three groups of industries, namely producers of chemicals, formulators and industrial users of chemical products, with innovative approaches and specific technical solutions to chemicals and chemical waste management. The main target is to achieve a reduction of chemical consumption in both production and application of chemicals. Further targets also address the replacement of hazardous chemicals by chemicals with a lower risk, the reduction of chemical wastes, the safe handling of chemicals and risk reduction related to accidents with chemicals. In each of the five participating countries (as of 2013: Colombia, Egypt, El Salvador, Morocco and Peru) and the three groups of industries concerned by the project, the identification and implementation of innovative alternatives and solutions is made on a subsector basis (i.e. industries in the paint formulation, paint application, textile finishing and polymers domains). Assessments in subsectors in each of the participating countries led to the development of the present *technical manual*, which aims at triggering innovative ideas, providing cost-effective innovative solutions and at enabling companies in these countries and subsectors to implement environmentally sound management of chemicals and chemical waste with high impact.

### Introducción

El principal objetivo de la Organización de las Naciones Unidas para el Desarrollo Industrial (ONUDI) es reducir la pobreza por medio del desarrollo industrial sostenible. En respuesta a este desafío global, ONUDI lanzó la iniciativa *Industria Verde* con el objetivo de promover el papel positivo de la industria a la hora de conseguir un crecimiento económico sostenible. Según la visión de la Industria Verde de ONUDI, el papel de las industrias es el de ofrecer constantemente soluciones y alternativas creativas e innovadoras a las economías de los países, centrándose en un impacto social de la industria bien equilibrado, económico y medioambiental. De hecho, el desarrollo sostenible se ha convertido en un factor decisivo central de la competitividad económica y permite a las industrias separar su crecimiento económico y sus ingresos del uso de recursos excesivo y creciente y de la polución, así como minimizando el gasto en todas las formas, usando recursos renovables, tomando precauciones para evitar dañar a los trabajadores, así como a las comunidades y al medioambiente [1].

El **Programa ONUDI-PNUMA para la Eficiencia en el uso de Recursos y Producción Más Limpia** (**RECP**) respalda la visión de la Industria Verde. El programa está basado en una estrategia multidual con enfoque programático y geográfico para aumentar y hacer prevalecer la aplicación de los conceptos, métodos, técnicas, tecnologías y políticas RECP en los países en desarrollo y en transición. El objetivo es de mejorar la eficiencia en el uso de los recursos y el rendimiento medioambiental de las empresas, con especial enfoque a los medianos y pequeños operadores de los sectores manufactureros y asociados.

La interdependencia de las industrias en relación con las sustancias químicas a lo largo de las industrias hace que la producción de sustancias químicas sea uno de los mayores sectores industriales y más globalizados con un alto impacto sobre el rendimiento global de la sostenibilidad de las cadenas de suministro. El papel económico esencial de las sustancias químicas y su contribución a la mejora del nivel de vida debe ser equilibrado considerando todos los costes potenciales. Así, un análisis de costes adecuado debe incluir el **uso de recursos por la industria química** como el agua y la energía, así como los impactos potenciales adversos de las sustancias químicas sobre el medioambiente y la salud humana. Teniendo en cuenta la potencial severidad y complejidad de dichos impactos, subraya el hecho de que la buena gestión de las sustancias químicas constituye un factor clave para el desarrollo sostenible [2].

Bajo este programa, el proyecto titulado Enfoques Innovadores para una Buena Gestión de las Sustancias y de los Desechos Químicos pretende ofrecer a tres grupos de industrias, en concreto a los productores de sustancias químicas, a los formuladores y a los usuarios industriales de productos químicos, enfoques innovadores y soluciones técnicas específicas a la gestión de sustancias y desechos químicos. El principal objetivo es lograr una reducción del consumo de sustancias químicas tanto en su producción como en su aplicación. Además, se pretende afrontar la sustitución de sustancias químicas peligrosas por sustancias químicas de menor riesgo, la reducción de los desechos químicos y el tratamiento seguro de sustancias químicas y la reducción de riesgos relacionados con los accidentes con sustancias químicas. En cada uno de los 5 países participantes (en 2013: Colombia, Egipto, El Salvador, Marruecos y Perú) y en los tres grupos de industrias interesados en el proyecto, la identificación y la implementación de alternativas y soluciones innovadoras se realiza sobre una base subsectorial (es decir, industrias de formulación y aplicación de pinturas, acabado de textiles y polímeros). Las evaluaciones en subsectores en cada uno de los países participantes condujo al desarrollo del presente manual técnico que pretende desencadenar ideas innovadoras, ofreciendo soluciones innovadores efectivas a nivel de costes y permitiendo a las empresas y a los subsectores en estos países implementar una buena gestión medioambiental de las sustancias y desechos químicos con un gran impacto.

### Introduction

L'objectif prioritaire de l'Organisation des Nations Unies pour le développement industriel (ONUDI) est de réduire la pauvreté à l'aide du développement industriel durable. Pour répondre à ce défi mondial, l'ONUDI a lancé l'initiative en faveur de *l'industrie verte (Green Industry)* dans le but de promouvoir le rôle positif de l'industrie dans la croissance économique durable. Selon la vision de l'industrie verte de l'ONUDI, le rôle des industries est de fournir en permanence des solutions et des alternatives créatives et innovantes aux économies des pays, en recherchant un équilibre entre les impacts économiques, environnementaux et sociaux. Le développement durable est en effet devenu un facteur déterminant de la compétitivité économique et permet aux industries d'assurer la croissance économique et les revenus, tout en limitant la pollution et l'utilisation excessive des ressources, en réduisant toutes les formes de déchets, en utilisant des ressources renouvelables et en prenant des précautions pour éviter de nuire aux travailleurs, aux communautés et à l'environnement [11].

Le **Programme mondial commun de production propre et économe en ressources (PCER) de l'ONUDI-PNUE** sanctionne la vision de l'industrie verte. Le programme est basé sur une approche à plusieurs volets dont les objectifs (en termes de contenu et de géographie) sont d'étendre et d'intégrer l'application des concepts, méthodes, techniques, technologies et politiques du PCER dans les pays en développement et en transition. Le programme vise à améliorer l'efficacité des ressources et la performance environnementale des entreprises et des autres organisations, en particulier les acteurs de petite et moyenne taille dans les secteurs de la production.

La dépendance multiple des industries vis-à-vis des produits chimiques fait de leur production l'un des secteurs industriels les plus mondialisés, générant un impact important sur la durabilité des chaînes d'approvisionnement. Le rôle économique essentiel des produits chimiques et leur contribution à l'amélioration du niveau de vie doivent être pondérés au regard de l'ensemble des coûts potentiels. Une analyse adéquate des coûts doit donc inclure *l'utilisation des ressources par l'industrie chimique*, comme l'eau et l'énergie, ainsi que les impacts négatifs potentiels des produits chimiques sur l'environnement et la santé humaine. Prendre en considération la gravité potentielle et la complexité de ces impacts, met en évidence le fait que la gestion rationnelle des produits chimiques est une question clé pour le développement durable [2].

En vertu de ce programme, le projet intitulé Approches novatrices pour la gestion rationnelle des produits chimiques et des déchets chimiques vise à fournir à trois groupes d'industries, à savoir, les producteurs de produits chimiques, les formulateurs et les utilisateurs industriels de produits chimiques, des approches novatrices et des solutions techniques spécifiques pour la gestion des produits chimiques et des déchets chimiques. L'objectif principal est de parvenir à une réduction de la consommation de produits chimiques tant dans leur production que leur application. D'autres objectifs portent également sur le remplacement des produits chimiques dangereux par des produits chimiques moins risqués, la réduction des déchets chimiques, la manipulation en toute sécurité des produits chimiques et la réduction des risques liés aux accidents avec des produits chimiques. Dans chacun des cinq pays participants (depuis 2013 : la Colombie, l'Égypte, le Salvador, le Maroc et le Pérou) et des trois groupes d'industries concernés par le projet, l'identification et la mise en œuvre d'alternatives et de solutions innovantes ont été faites pour les sous-secteurs industriels suivants : soit formulation de peinture, application de la peinture, finissage textile et polymères). Les évaluations des sous-secteurs dans chacun des pays participants ont mené à l'élaboration du présent manuel technique, qui vise à susciter des idées novatrices produisant des solutions innovantes et rentables ainsi qu'à permettre aux entreprises de ces pays et aux sous-secteurs de mettre en œuvre une gestion écologiquement rationnelle des produits chimiques et des déchets chimiques à fort impact.

### 2 General aspects of the textile and finishing industry

Textile manufacturing has been around since the dawn of the industrial age – and it is not only one of the oldest but also one of the most complex industries, featuring a wide range of (mainly small and medium) companies. Its products generally meet three different types of demand: the demand for clothes, for household textiles and for industrial fabrics.

The "textile industry" is also a shorthand expression for a wide range of processes, including the production of synthetic fibres, the manufacturing of fabrics and the trade with finished products.

On top of that, it comprises a large number of sub-industries that cover the entire manufacturing cycle from the production of raw materials (such as synthetic fibres) and semi-finished products (yarn, woven and knitted fabrics with their finishing processes) to the end products (rugs and carpets, household textiles, clothes and industrial fabrics).

The first step in the production of any textile product is always the manufacturing of the fibres. Natural fibres are made of animal wool and cellulose products such as cotton and flax. Additionally, there are many different synthetic fibres such as viscose, acrylic, polyester, polyurethane and polyamide. These fibres, whether natural or synthetic, are then spun or textured into a yarn. Pre-treatment, dyeing and finishing processes can be applied on yarns, fabrics (woven, knitted, non-woven) or on garments.

The so-called finishing processes (i.e. pre-treatment, dyeing, printing, finishing and coating, including washing and drying) have a specifically large impact on the environment and receive special attention in this manual. The upstream processes of synthetic fibre manufacturing, spinning, weaving and knitting, conversely, are ignored.

The pre-treatment, dyeing and finishing processes in particular require the application of large amounts of chemicals, water and energy, since several chemical and physical treatment operations need to be performed, some of them under high temperature, to give the yarn and the fabric the desired properties.

For example, easy care or non-iron features to a cotton garment require several chemical treatments to ensure crease-free or wrinkle-free properties. In a similar way, mercerizing, singeing, flame retardant, water repellent, waterproof, anti-static and peach finishing achieve various fabric properties desired by consumers.

The use of 100 per cent synthetic textiles has increased considerably since the development of textured yarns made of filaments, and the growing production of knit goods.

The properties of man-made fibres based on synthetic polymers, the most important among them being polyester, polyamide and polyacrylonitrile, are essentially different from those of natural cellulosic and wool fibres. Hence the sequence of finishing operations is likely to be different. While cellulosic fabrics require a resin finishing treatment to impart easy-care properties, synthetic fibres already exhibit these easy-care criteria and require only a heat setting operation [3].

The textile industry generally consumes large amounts of chemicals, water and energy, at significant costs to the producer. The textile industry is therefore expected to develop environmentally friendly technologies and processes that reduce pollution and exploit the existing potentials for a prudent use of natural resources. Researchers have established that 25 per cent of all globally produced chemicals are – directly or indirectly – used in the production of textiles [4].

Under current market conditions, it is difficult to increase the price for the manufactured textiles, despite rising costs for raw materials, water and energy. It is therefore vital to deploy modern technologies that allow the factory owners to save money by cutting down on their production costs.

### **2.1 Importance of the textile market**

The textile and clothes manufacturing industry accounts for a large proportion of the global trade volume. The industry is particularly important in developing countries where it is often responsible for a significant share of total exports. According to figures published by the WTO, textile exports around the world reached a total volume of approximately \$195 billion in 2004, not even counting exports of clothes which added another \$258 billion to this sum [5]. It is estimated that more recent figures are significantly higher still.

In 2013, the overall size of the textile and clothing industry in the 28 countries of the European Union represented a turnover of  $\notin$ 166 billion and investments of around  $\notin$ 4 billion. Thanks to a revival in 2010 after the critical year of 2009, the 173,000 textile and clothing companies still employ over 1.7 million workers. EU external trade was more dynamic than the previous year with  $\notin$ 42 billion of textile and clothing products exported and  $\notin$ 92 billion imported from third markets [6].

The total global production of man-made fibres in 2006 rose to 41.27 million tons, of which China and India accounted for 51.8 per cent and 6.2 per cent, respectively, and man-made fibre consumption is steadily increasing [7] (see Figure 2-1).

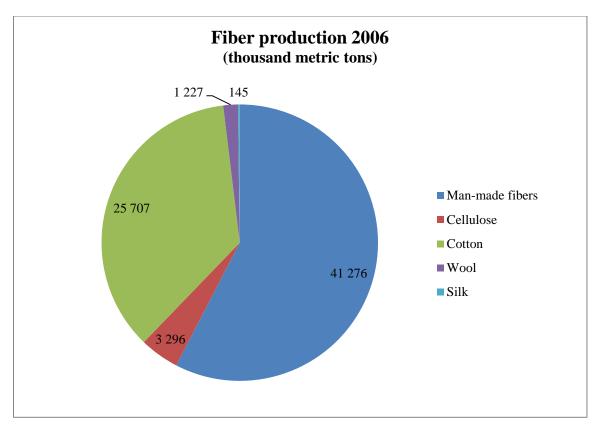


Figure 2-1: Worldwide fibre production in 2006 [based on 7]

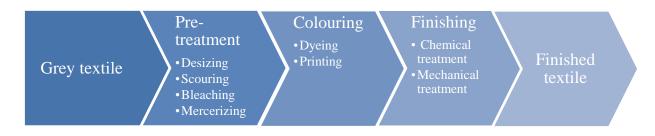
Figures from the European Union show the magnitude of the textile *finishing* industry and its global significance. The total turnover of the EU textile finishing industry amounted to nearly  $\notin$ 11 billion in the year 2000, with more than 117,000 employees. The majority of EU textile finishing companies are SMEs [8].

### 2.2 Textile finishing processes

Textile finishing improves the appearance, durability and overall functionality of fabrics. The term covers all mechanical and chemical/biochemical processes performed to improve the properties of the products, providing them with a specific appearance (for example colour) or function. Finishing processes are performed at any stage of the manufacturing process and are applied to loose fibres, yarns, fabrics or garments. The fabric, however, is the dominant substrate.

To simplify matters, textile finishing is generally sub-divided into the following processing steps:

- Fabric pre-treatment, for example desizing, washing, scouring or bleaching
- Colouring: dyeing and/or printing
- Functional finishing



### Figure 2-2: Textile finishing processes [based on 9]

Depending on the desired properties and quality features of the finished textile, all or only a selected few of the finishing processes may be applied. Further below, we shall explain the most important of these finishing processes in closer detail [10].

### 2.2.1 **Pre-treatment**

Most fabrics undergo pre-treatment before they can be dyed, printed or finished, for example to remove natural contamination such as wax, pectins, earth alkaline metals or biocides from the grey fabrics but also to eliminate size materials that were added during weaving. Synthetic fibres contain spinning oils and lubricants as well as monomers and oligomers.

These by-products, together with the chemicals used in pre-treatment, can cause significant contamination of wastewater and exhaust air.

Pre-treatment is essential for all subsequent finishing steps, cleans the fibres and has the following effects on fibre properties [10]:

- The absorption of dyes is increased.
- The tensions in textiles are minimized and the dimensional stability is improved.
- The wettability of the material is improved.
- A change in crystallinity of the cellulose can be achieved through mercerization, thus improving its lustre.
- The whiteness of the substrates is enhanced through bleaching, which is important for fullwhite fabrics as well as for fabrics dyed in light shades or with a high brilliance.

The three main techniques applied are mechanical, wet and thermal pre-treatment. The processing steps and their sequence depend on the substrate (for example cotton, wool, man-made fibres, woven or knitted fabrics, etc.) and also on the downstream processing steps of the textiles and the equipment used.

Normally, wet processes are carried out with water. Compared to wet and thermal pre-treatment processes, mechanical pre-treatment has only a minor environmental impact.

### Thermal processes

### **Heat setting**

Heat setting is applied to fabrics consisting of man-made fibres or their blends with natural fibres to reduce tensions in the textiles or fibres caused by previous fibre, yarn or fabric processing and to improve the dimensional stability of the textiles. It is applied to grey fabrics at the pre-treatment stage, as intermediate step after dyeing or in the finishing phase. Since the raw material may contain volatile substances, heat setting can generate substantial amounts of smoke gas.

### Singeing

If a smooth surface of the textile is required, singeing will be applied, in particular as pre-treatment before printing. The fabric passes directly over a flame, a metal plate or indirectly between heated ceramic devices to burn off protruding fibres. The process is mainly applied to woven and knitted textiles made of cotton and cotton blends, although synthetic fibres may sometimes also be singed to reduce pilling effects. The exhaust gases produced during singeing contain dust and volatile organic compounds (VOCs) which may cause environmental impact.

### Wet processes

### Desizing

Desizing is a process commonly applied to all woven fabrics to remove sizing agents that were added in weaving mills to improve weaving efficiency. They have to be eliminated before subsequent textile finishing processes. Water-insoluble sizing agents have to be degraded during desizing, water-soluble sizes can be washed out.

The following methods are used:

- Enzymatic desizing for starch sizes and modified starch sizes
- Oxidative desizing (for example with persulphate) for starch sizes and modified starch sizes
- Washing (with or without detergents) for water-soluble sizing agents such as polyvinyl alcohol (PVA) and sizes containing acrylic and polyacrylic acids.

Desizing increases a company's wastewater pollution load considerably and may contribute to 50 per cent of the total, depending on the sizing material used. The biological oxygen demand (BOD) is particularly high if starch has to be removed.

### Scouring

In order to remove natural impurities (waxes, pectins, metal salts, husks), cotton fabrics and cotton blends are treated either discontinuously or continuously with hot alkali.

The scouring process has three main objectives:

- Saponify fatty acids and waxes to make them water-soluble and bind the minerals and metal ions
- Make the raw cotton absorbent
- Crack the cotton husks

Scouring can be applied as separate pre-treatment step or in combination with bleaching or desizing.

### Bleaching

Generally, the bleaching process is applied on natural and man-made fibres in order to increase the whiteness of the material and improve the quality of the subsequent printing and dyeing processes.

Bleaching is carried out for undyed natural material to achieve fullwhite effects and for material to be dyed or printed with high brilliance or in light shades. Loose fibres, slivers, yarns and fabrics can be bleached continuously or in batches. The bleaching technologies and agents used vary depending on the textile substrate. Bleaching with sodium hypochlorite is no longer state of the art, since this substance generates high loads of adsorbable organic halogens (AOX) and free chlorine.

The following bleaching agents are commonly used and may pose environmental risks if the wastewater is not properly treated.

| Textile (substrate) | Peroxide | Sodium chlorite | Reductive |
|---------------------|----------|-----------------|-----------|
| Cellulose fibres    | +        | +               |           |
| Cellulose/Polyester | +        |                 |           |
| Protein fibres      | +        |                 | +         |
| Polyester           |          | +               |           |
| Polyamide           |          |                 |           |
| Polyamide/Wool      | +        |                 | +         |
| Polyacrylonitrile   |          | +               |           |
| Cellulose esters    |          | +               |           |
| Viscose             |          | +               |           |
| Elastane            | +        |                 | +         |

### Table 2-1: Bleaching agents for different textile materials [based on 10]

### Mercerizing

Mercerizing is used to improve the tensile strength, dimensional stability and lustre of cotton. In addition, dye uptake (dyestuff yield) is improved after the process, reducing dyestuff consumption by 30 to 50 per cent [8].



Figure 2-3: Improvement of dye uptake on cotton. Left without mercerizing, right with mercerizing [22]

Mercerizing can be carried out on yarn or woven and knitted fabrics. The following treatment methods are known:

- Mercerizing with tension using caustic soda
- Caustification (without tension, using caustic soda)
- Ammonia mercerizing

### 2.2.2 Dyeing

The process of colouring textiles as a whole is called dyeing. Dye may be fixed on a fabric by using various chemical or physical mechanisms, including covalent, electrostatic and hydrogen bonds and adsorption [10]. Dyeing involves the application of dyestuff but also of auxiliary chemicals that might cause ecological impacts.

In general, two methods of dyestuff application are used:

#### Exhaust dyeing

In a first step, dyestuff is dissolved in water. It then exhausts from the bath and diffuses into the textile fibres. The process is finished by fixing the dye onto the fibres. Exhaust dyeing is always carried out discontinuously.

#### Foulard (padding) technique

With this technique, the textile is dipped in a concentrated dyestuff bath and passes the nip of a squeezing unit to avoid a surplus of dyestuff on the textile. The fixation of the impregnated dyestuff takes place in subsequent steps.

With regard to dyeing processes affecting the wastewater volume and wastewater load, three different types can be defined:

- Batch (discontinuous) dyeing
- Semi-continuous dyeing
- Continuous dyeing

#### Discontinuous dyeing

Discontinuous dyeing, which is also known as batch dyeing, involves applying a dyestuff in solution or suspension at a specific liquor ratio, which determines the depth of the colour obtained. After the dyeing operation, the spent dye-bath liquor is drained off. The subsequent stage consists of washing with water to remove unfixed residues of dyestuff from the textile substrate. In some cases, after-treatment steps are also necessary. Exhaust dyeing can be done with different types of equipment such as beam, winch, soft-flow, jet and jig dyeing machines [11].

### Continuous dyeing

In the continuous dyeing process, the dyestuffs are applied by means of a foulard (padding technique) to the material with direct subsequent dye fixation. The dye is fixed by the use of chemicals, heat or steam followed by washing steps. Pad-steam processes (padding and fixation by steaming) and so-called thermosol processes (padding of disperse dyes with subsequent heating) are commonly used [10].

#### Semi-continuous dyeing

In semi-continuous dyeing processes (pad-jig, pad-batch, pad-roll), the fabric is impregnated in a padding machine with the dye-liquor and later treated as batch in a jigger or stored with slow rotation for several hours for fixation of the dyes on the fibre (pad-batch: at room temperature; pad-roll: at elevated temperature in a heating chamber). Subsequently, the material is washed and rinsed in full width in continuous washing machines.

#### **Optical brightening**

Most fibres contain yellow colouring impurities. In order to obtain bright white or bluish shades, socalled optical brighteners, for example fluorescent whitening agents, are used. These chemicals are generally applied by means of exhaustion or padding techniques, the latter being more important due to economic advantages. The fixation mechanism of optical brighteners is similar to dyestuffs.

### 2.2.3 Printing

In contrast to dyeing, printing involves applying the colour only to specific areas (the so-called pattern) of the textile. This is mainly done using screen-printing systems (flat or rotary screens) to achieve the required design. However, nowadays a strong trend to digital printing, especially for smaller lots, can be observed as well.

Generally, three techniques are applied:

- Printing with diffusing dyestuffs (printing, drying, fixation, washing)
- Printing with pigments (printing, drying, fixation)
- Transfer printing (transfer paper, print on textile, paper waste disposal)

The printing pastes are prepared by dissolving the dyes and additives in a limited quantity of water, to which a thickening agent is added to formulate the printing paste with a specific viscosity. The printing process is followed by a drying and steaming or curing procedure (in case of pigment printing). Except for pigment printing, the textiles are subsequently washed and dried.

Globally, about 50 per cent of textile printing is accomplished with the pigment printing technology. The pigments used have no affinity to the textile fibre. Thus, a binder and fixating agents must be added to the printing paste. One advantage of pigment printing is that it does not require the subsequent washing needed for all other printing technologies.

A typical printing paste for pigment printing comprises water, emulsifiers, thickening agents, pigment dispersion agents, softening agents, binders and fixation agents [10].

### 2.2.4 Finishing

In order to achieve specific properties or effects, the pre-treated and/or coloured/printed textiles (in the form of yarn, fibres or fabrics) are subjected to one or several functional finishing steps. These processes may involve a chemical treatment (for example with stiffening, softening, water repellent, antimicrobial, moth-proofing and fire-proofing agents) and a mechanical treatment to improve smoothness or roughness. In chemical processes, the chemicals are generally applied to the textiles in a watery solution/dispersion by padding machines ("foulards"). Following this, the solution is dried at approximately 120°C. In addition to padding machines, spraying, knife coating and printing as well as exhaustion processes may also be applied.

### **2.3** Chemicals in the textile finishing processes

The most intensive use of chemicals is required for wet finishing processes such as dyeing, washing, printing and finishing [12]. A 1997 study of the Swedish Office for Chemicals estimated that more than 10,000 substances were manufactured for their use in colouring and printing alone, 3,000 of which were regularly used [13].

Moreover, to supply the global textile production 1 million tons of dyes and 7 million tons of other chemicals are used annually [14]. Faced with such a large number of industrial chemicals, it is difficult to procure and provide information and to implement or enforce regulations for the use of such substances.

A good overview of textile chemicals is provided in the "International Textile Auxiliaries Buyers' Guide" (TAG) published by Deutscher Fachverlag and developed in cooperation with the German TEGEWA Association. The TAG gives an overview of more than 5,500 commercial products based on 400 to 600 active components and provides information on the product names and their

13

manufacturers, details of their application, properties and the effects achievable with each product [15]. The guide can also be used for the identification of chemical substitutes. In the technical manual on hand, a table with an overview of chemical compounds applied in textile manufacturing, their technical effects and chemical composition is provided (Appendix 1).

Most of the auxiliaries applied in textile finishing are used as aqueous solutions and dispersions. The amount of active ingredients in these solutions or dispersions varies widely.

Bulk chemicals like inorganic salts (for example sodium chloride or sodium sulphate) are primarily used as basic chemicals in textile finishing followed by lyes (for example sodium hydroxide), acids (acetic acid, formic acid, inorganic acids) and reducing and oxidizing agents (sodium dithionite, hydrogen peroxide).

Apart from a minor amount of water which is evaporated during drying in the textile production processes, the main part is discharged as aqueous effluent. The main environmental concern is therefore the amount of water discharged and the chemical load it carries.

The input of chemicals and auxiliaries added at the finishing mills can be up to 1 kilogramme per kilogramme of processed textiles. Among the products applied during the finishing processes, the highest environmental loads arise from salts, detergents and organic acids (in that order).

Some chemicals that may be used in textile finishing are worth mentioning for their potential negative environmental impact [8]:

- Alkyl phenol ethoxylates (used as detergents, wetting agents, levelling agents and for other purposes): The metabolites octylphenol and nonylphenol are toxic to aquatic life and disturb the reproduction of aquatic species by disrupting the endocrine system.
- Polybrominated diphenyl ethers and chlorinated paraffins (flame retardants), halogenated phenols and benzenes (reagents in the production of flame retardants): Some compounds of these classes of substances (for example pentabromodiphenyl ether, C 10-13 chloroparaffins) have been identified as "Priority Hazardous Substances" for their toxicity, persistency and liability to bioaccumulate.
- Mothproofing agents based on permethrin and cyfluthrin (carpet sector) are toxic to aquatic life.
- Sequestering (complexing) agents such as EDTA, DTPA and NTA may form stable complexes with metals. EDTA and DTPA are also poorly biodegradable.
- Compounds that form chlorine such as sodium hypochlorite (bleaching agent) and sodium dichloroisocyanurate (wool anti-felting agent) may react with organic compounds in water to form adsorbable organic halogens (AOX).
- Chromate-containing substances such as potassium dichromate
- Organic compounds with carcinogenic potential such as some aromatic amines, formed by cleavage of azo dyes, or vinylcyclohexene and 1,3-butadiene that can be present in polymer dispersions due to incomplete polymerization.

There is evidence [8] that more than 90 per cent of the organic chemicals and auxiliaries in pretreatment and dyeing operations does not stay on the fibre. The major part is discharged with wastewater, others being released to air.

In terms of air pollutants, volatile organic compounds (VOCs) may be released from activities such as printing processes (for example organic solvents in pigment printing pastes), cleaning with organic solvents, heat treatments (for example thermofixation, drying, curing), vulcanization (carpet sector) or in cases where the textiles contain substances that evaporate or degrade thermally (for example oils, plasticizers, finishing agents).

Furthermore,  $CO_2$ ,  $SO_2$  and  $NO_x$  emissions and particulates released through burning of fossil fuels, (for example thermal energy produced in boiler houses for baths, drying and curing processes) are also relevant.

### 2.3.1 Auxiliaries

### Surfactants

Surfactants are widely used in the textile finishing industry. They are divided into the classes anionic, non-ionic, cationic and amphoteric substances, however, anionic and non-ionic substances dominate. The effects of surfactants are manifold. In the textile industry, they are used predominantly as detergents, wetting agents, de-aeration agents, levelling agents, dispersing agents, softening agents, emulsifying agents, spotting agents, anti-electrostatics, foaming and defoaming agents, after-treatment agents for fastness improvement, felting agents and fixing acceleration agents for continuous dyeing and printing.

In dyeing and pre-treatment processes, surfactants are generally used in a concentration of approximately 2 grams per litre. With a typical liquor ratio in exhaust processes of 1:10, 20 grams of surfactant are used per kilogramme of textile [10].

### Biocides

Biocides are applied on textiles either in exhaust or padding processes during textile finishing in order to avoid any problems with bacteria, fungi, mould, mildew and algae, and the associated deterioration, staining, odours and health effects that they may cause. However, less than 5 per cent of the textiles for the end-use are finished with biocides.

Particularly fabrics used outdoors (such as sportswear), sanitary products (for example hospital textiles) and carpets are treated with antimicrobial finishing [10]. The sensitivity of the textile fibres varies based on their classes, but generally textiles made from natural fibres are more susceptible to biodegradation than man-made fibres.

The following categories are characteristic for biocides applied in textile finishing:

- Antimicrobial finishing
- Moth proofing
- Preservation agents used to improve the storage stability of textile auxiliaries

Biocides are applied to the textiles in a similar way to other auxiliaries. Mainly continuous padding processes or discontinuous methods comparable to exhaust dyeing are common.

Preservation agents to increase the storage stability are contained in various auxiliaries such as liquid sizing agents, preparation agents, natural thickeners in printing pastes, bonding agents for pigment printing based on polymeric dispersion, coating agents based on polymers, softening agents (especially fatty acid condensation products), finishing agents containing silicone compounds and auxiliaries based on proteins [10].

Generally, the widely used substance permethrin and synthetic pyrethroids are reported to have low toxicity to humans but high aquatic toxicity [8]. However, all biocides entail negative environmental impacts when they are discharged in wastewater, due to their toxicity to aquatic life.

### 2.3.2 Dyestuffs

Successful textile dyeing requires the selection of the right dyestuff and the suitable dyeing process. The composition of the dye bath is essential, and so are a number of other parameters. The dye bath must not only provide the correct ratio of textile and dyeing solution, but also have the correct temperature, water quality (contamination, hardness), electrolyte content and pH value. Wool, for example, requires an acidic colouring liquid whereas cotton has to be treated in an alkaline solution. Additional requirements are proper adjustment of treatment time and appropriate dosing of auxiliary agents [17].

Textile dyes can be classified according to their chemical composition [16], for example:

- Azo dyes
- Antrachinone dyes
- Sulphur dyes
- Triphenylmethane dyes
- Polymethine dyes
- Diarylmethane and triarylmethane dyes
- Indigoid dyes
- Phthalocyanine dyes
- Nitro and nitroso dyes

However, the classification according to the application class of the dyes, that is the performance in the dyeing processes, is more common [8]. These classes might include:

- Acid dyes: anionic dyes with affinity to protein, polyamide and acrylic-functional groups of substrates
- Cationic dyes: cationic salt of a dye base with affinity to protein fibres and synthetic acrylates
- Direct dyes: dyes with a substantivity to cellulose fibres
- Disperse dyes: neutral dyes, which are sparingly soluble in water and which are applied to polyester and polyamide fibres
- Reactive dyes: dyes that form covalent bonds with the fibres (for cellulose fibres and wool fibres)
- Sulphur dyes: water-insoluble dyes based on sulphur compounds, which are normally applied in their reduced form (for cellulose fibres)
- Vat dyes: water-insoluble dyes: The soluble reduced (leuco) form is applied in the dye bath. The reduced form is subsequently re-oxidized on the fibres (for cellulose fibres).

Especially dyeing chemicals entail environmental problems if not used and treated properly. The following table shows different sources and emissions related to textile dyeing.

| Process                               | Sources of emissions                        | Emission type   |  |
|---------------------------------------|---|---|--|
|                                       | Dye preparation                             | Discontinuous, low-   |  |
| Colour kitchen                        | Auxiliaries preparation                     | concentration water emission at<br>the end of each batch (cleaning<br>step)   |  |
|                                       | Manual dispensing of dyes and auxiliaries   | Indirect pollution from<br>inaccurate dosing and handling<br>of chemicals (e.g. spillage)                               |  |
|                                       | Dyeing                                      |   |  |
| Batch dyeing                          | Washing and rinsing operations after dyeing | Discontinuous, low-<br>concentration water emission at<br>the end of each cycle   |  |
|                                       | Cleaning of equipment                       |   |  |
|                                       | Application of dyestuff                     | No emission from the process<br>unless dye bath is drained  |  |
| Semi-continuous and continuous dyeing | Fixation by steam or dry heat               | Continuous emission to air<br>(generally not significant,<br>except for specific situations,<br>e.g. thermosol process) |  |

Table 2-2: Potential sources and emission types in textile dyeing [based on 8]

| Process | Sources of emissions   | Emission type   |
|---------|--|---|
|         | Washing and rinsing operations after dyeing                              | Continuous, low-concentration water emission  |
|         | Discharging of leftovers in the<br>chassis and feed storage<br>container | Discontinuous, concentrated<br>water emission at the end of<br>each lot   |
|         | Cleaning of equipment  | Discontinuous, low-<br>concentration water emission<br>(may contain hazardous<br>substances when reductive<br>agents and hypochlorite are<br>applied) |

Substances in the emissions table above that could be harmful to aquatic life may originate from

- Dyestuffs, for example metals or colours
- Auxiliaries contained in the dye formulation
- Basic chemicals, for example alkali, salts, reducing and oxidizing agents
- Contaminants present on the fibre when it enters the dyeing process, for example residues of pesticides or spin finishes

Unfortunately, in discontinuous dyeing the residual dye liquors from spent dye baths contain a certain amount of unfixed dye. The fixation rates vary significantly based on the specific dyestuff classes. Unfixed rates are generally low for reactive dyes (for cotton) and for sulphur dyes. With the so-called double anchor reactive dyes comprising two reactive groups, an exhaustion rate of more than 90 per cent may be achieved. These bifunctional reactive dyes are associated with an increased probability of chemical reaction with cellulose fibres compared to monofunctional dyes with only one reactive group.

### Dyeing auxiliaries

Textile colouring does not only aim for high levels of evenness, colour fastness and brilliance, but also needs to treat the fabrics gently and make them resistant to high temperatures and abrasion, while remaining economically viable, ecologically sustainable and safe for all users. In order to meet all of these requirements, high-quality dyestuffs are supported by a wide range of auxiliary agents [17].

### **Dye solvents and hydrotropic solutions**

Help the dyestuff to dissolve in the dye bath. These are generally water-soluble solvents such as alcohols or esters.

### **Dispersing agents**

Keep dyestuffs that are insoluble or not readily soluble afloat in the water and establish or stabilize dispersions. These agents are surface-active substances such as sulphited fatty acid esters and amides, alkylaryl sulphonates and fatty acid ethoxylates.

### **Protective colloids**

Wrap themselves around dispersed particles and prevent the dispersions from flocculating, even when the temperature changes or electrolytes are added. Substances used for this purpose include lignin sulphonate and water-soluble polymers such as polyacrylate.

### Wetting agents

Decrease the interface tension between the textile and the dye solution, ensuring that the dyestuff agent will quickly and readily reach the fibre. For this purpose, anionic tensides such as alkyl sulphate, alkane sulphonate and the salts of sulphosuccinic acid and phosphoric acid are frequently used.

#### Levelling agents

Have the task of achieving an even distribution of the dyestuff. This means that substances are required which slow down the up-take of the colouring agents during the heating phase and which stimulate the migration of the dyes and their penetration into the fibre once the final temperature has been reached, without blocking those spots of the fibre which have an affinity for the dyestuffs. Fatty acid esters and amides as well as alkylamines and their ethoxylized variants are often used for this purpose.

#### **Dyeing accelerators**

Are added to the dyeing solution during the exhaust dyeing of polyester fibres with dispersion dyestuffs in order to assist and accelerate the diffusion of the colourants into the fibres and to improve the dyestuff yield. Often, not readily soluble aromatic hydrocarbons and phthalic acid imides are used to accelerate the dyeing process in this way. The low-temperature colouring of wool also requires dyeing accelerators.

### **Post-treatment agents**

Such agents can improve the resistance of the finished colour against abrasion, wetfastness and sunlight. Rubbing fastness is increased by removing non-fixed dyestuff during post-treatment washing through appropriate auxiliary agents. The levels of wetfastness (reactive and direct processes) can be increased by quaternary ammonium compounds and cationic formaldehyde condensation products.

### **3** Innovative solutions

### **3.1 Reduction of utilities and chemicals consumption**

### **3.1.1** Status of textile finishing along the textile value chain

Textile processing requires many resources. Textile finishing is the main contributor to environmental pollution within the textile value chain, since high amounts of water, energy and chemicals are required (**Error! Reference source not found.**).

|           | Spinning | Weaving /<br>knitting | Finishing | Garmenting |
|-----------|----------|-----------------------|-----------|------------|
| Water     | -        | -                     | + + +     | -          |
| Effluent  | -        | -                     | + + +     | -          |
| Energy    | + +      | + +                   | + +       | -          |
| Chemistry | -        | -                     | + + +     | -          |
| Society   | +        | +                     | +         | + + +      |

### Table 3-1: Resource consumption for textile processing [based on 18]

Legend :

- No effect + Some effect ++ Large effect +++ Very large effect

The concept of the carbon footprint is used to describe the total of greenhouse gas emissions which are associated with a product, and it is calculated as  $CO_2$  emissions in grams of  $CO_2$  per kilogramme of fabric. When analyzing the lifecycle of textiles, it appears that about 50 per cent of  $CO_2$  emissions occur along the value-creation chain (fibre production, manufacture, trade, transport), and 50 per cent are caused by daily usage. Figure 3-1 shows the main  $CO_2$  sources during textile production from the fibre to the finished garment.

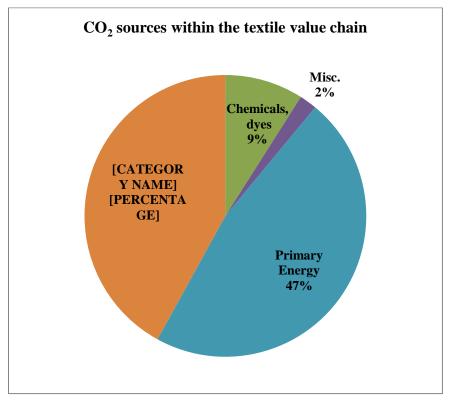


Figure 3-1:  $CO_2$  sources within the textile value creation chain for a pair of trousers made of 100 per cent cotton manufactured in China in 2012 [based on 19]

### **3.1.2** Status of textile finishing

The concept of the carbon footprint is suitable for judging the textile finishing process as well.  $CO_2$  emissions are caused directly by energy consumers and indirectly by consumables such as chemicals, lubricants, etc. The distribution of  $CO_2$  emissions in a fully continuous textile finishing process for cotton textiles shows that about 26 per cent come from drying, 34 per cent from washing and steaming and 29 per cent from the use of chemicals (Figure 3-2).

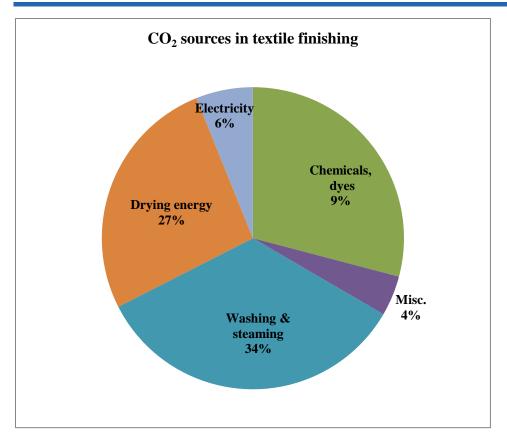


Figure 3-2: CO<sub>2</sub> sources in the textile finishing of trousers made of 100 per cent cotton manufactured in Turkey in 2014 [based on 20]

A number of different approaches are possible to reduce the chemical consumption, both for knitwear and for woven fabrics. This chapter describes methods or equipment used to reduce chemical and utility consumption. It is important to take the entire value-creation chain into account, starting with the selection of the fibre material.

### **3.1.3** Viscose fibres replace cotton

As a result of the progressive worldwide scarcity of agricultural land and the fluctuation in cotton prices, regenerated synthetic fibres such as viscose and Tencel (trade name of Lenzing AG) have recently gained significant market share and also impress with their ecological footprint. In fully integrated fibre factories, it is already possible, under favourable conditions, to produce  $CO_2$  neutral synthetic fibres [21, p. 31].

As for the ecological footprint of dyeing factories and finishing works, regenerated synthetic fibres have significant advantages from the environmental point of view. Viscose fibres may replace the naturally harvested cotton in certain applications. These articles do not require the classic pre-treatment that is needed for cotton as they do not have to be bleached.

All that is needed is the removal of spinning oil and in certain cases a mild peroxide bleach. **Error! Reference source not found.** describes the chemical consumption of classical cotton pre-treatment compared to viscose pre-treatment. The continuous pre-treatment concept used by the Swiss company Benninger involves an impregnation, emulsification and washing process in drum wash compartments. During the emulsifying phase, the chemical-saturated knitwear is placed in loops onto a dwelling system (Figure 3-3). The micro-movement of the individual loops ensures that the knits are continually loosened and promotes free relaxation, and at the same time prevents the formation of creases. In this way, the bi-directional shrinkage of the material is excellent. It is known that so-called hydro-shrinkage is significantly stronger and longer lasting than thermal shrinkage performed, for example,

20

by using hot air. Regardless of the use of subsequent thermal fixing processes, the stretchability and the material's elasticity is maintained, even following several household wash cycles and wear. The fit of the garments is retained.

Another advantage of the prewash process is that the emission of silicone and mineral knitting oils during the fixing process of unwashed knitwear is avoided. The black smoke in the exhaust air of the stenter frame is a thing of the past [23].

Table 3-2: Comparison of chemical consumption for cotton and viscose knitwear during the openwidth continuous pre-treatment process

|                          | Cotton       | Viscose without<br>bleaching<br>(dark shades) | Viscose with bleaching<br>(light shades and full<br>white) |
|--------------------------|--------------|---|--|
| Scouring/De-oiling       |              |   |  |
| Demineralizing agent     | 3-5 ml/kg    |   |  |
| Sequestering agent       | 3-5 ml/kg    | 3-5 ml/kg                                     | 3-5 ml/kg  |
| Wetting agent            | 2-3 ml/kg    | 2-3 ml/kg                                     | 2-3 ml/kg  |
| Bleaching                |              |   |  |
| Peroxide 50%             | 20-30 ml/kg  |   | 5-8 ml/kg  |
| NaOH 100%                | 8-12 g/kg    |   | 3-5 g/kg   |
| Organic stabilizer       | 5-8 ml/kg    |   | 2-3 ml/kg  |
| Wetting agent            | 2-3 ml/kg    |   | 2-3 ml/kg  |
| Mercerizing/Causticizing |              |   |  |
| NaOH 100%                | 220-240 g/kg | 60 g/kg                                       | 60 g/kg  |



Figure 3-3: Prewash and relaxing of viscose knitwear [23]

### **3.1.4** Replacement of exhaust dyeing processes by continuous processes

The exhaust dyeing process, as described in chapter 2.2.2 and shown in Figure 3-4, is widely used in the textile finishing industry. Approximately 90 per cent of the knitted goods are processed by exhaust method, and today most of the fabric is bleached and dye-processed in soft-flow or jet dyeing machines. Various quality problems, high utility consumption and approximately 10 to 15 per cent higher processing costs are forcing the change to open-width continuous processing. This development occurred in the woven goods field 30 years ago. Today open-width processing of woven goods is state of the art.

Despite the massive efforts of machine designers to reduce the liquor ratio, the finishing of knitwear by exhaust dyeing in jet dyeing machines still requires large amounts of water and therefore also large amounts of energy. By contrast, the continuous open-width finishing process not only achieves additional quality benefits but also savings, particularly in terms of water and energy. By using the continuous mode,  $CO_2$  emissions can be reduced by nearly two thirds compared to exhaust dyeing processes (liquor ratio of 1:7). Continuous open-width bleaching and washing plants are perfectly suited for this type of application. Full continuous dyeing as well as semi-continuous dyeing (CPB dyeing) are salt-free dyeing processes that provide a high degree of dyestuff fixation.

### What means continuous processing ?

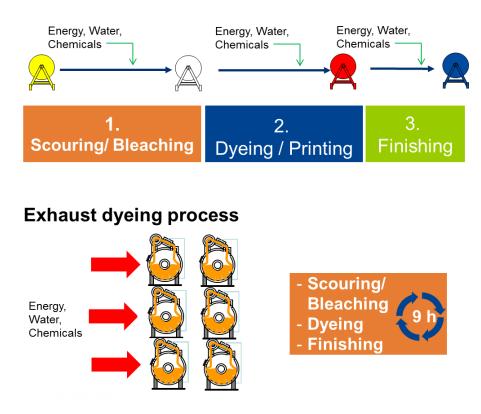


Figure 3-4: Continuous processing vs. exhaust dyeing and finishing [22, p. 3]

| Continuous<br>vs. EXHAUST DYEING<br>Production : 10 tons per day |                    |                    |                    |
|--|--------------------|--------------------|--------------------|
|  | continuous         | (LR 1:8)           | (LR 1:5)           |
| Water for Pretreatment   | 8 m <sup>3</sup>   | 80 m <sup>3</sup>  | 50 m <sup>3</sup>  |
| Water for Rinsing  | 80 m <sup>3</sup>  | 260m <sup>3</sup>  | 160 m³             |
| Water for Dyeing   | 9 m <sup>3</sup>   | 70 m <sup>3</sup>  | 40 m <sup>3</sup>  |
| Salt for Dyeing  | 0.0 To             | 4 To               | 2.5 To             |
| Water for Soaping  | 120 m <sup>3</sup> | 350 m³             | 320 m <sup>3</sup> |
| Softening  | 3 m <sup>3</sup>   | 70 m <sup>3</sup>  | 40m <sup>3</sup>   |
| Total Water  | 220 m <sup>3</sup> | 850 m <sup>3</sup> | 610 m <sup>3</sup> |
| Total Energy (Steam)   | 19 t               | 71 t               | 52 t               |
| Total Salt   | 0.0 t              | 4.0 t              | 2.5 t              |
| Saving on 10 ton/d   | Water              | 630 m3             | 390 m3             |
| production   | Steam<br>Salt      | 52 t<br>4.0 t      | 33 t<br>2.5 t      |

Figure 3-5: Utility consumption: exhaust dyeing and finishing vs. continuous finishing of knitwear [22, p. 9]

### 3.1.5 Cold Pad Batch (CPB) dyeing

Cold pad batch (CPB) dyeing is a salt-free process avoiding the use of large amounts of salt. With this dyeing process, the reactive dye is allowed to set, i.e. to dwell and react at room temperature (Figure 3-6). The liquor ratio used is smaller than 1:1. Modern CPB dyeing centres use controlled dyeing conditions which means that this process is almost universally applicable for all types of cellulosic fibres (woven and knitted fabrics). Savings are achieved because the dye is fixed at room temperature and used at maximum efficiency. The heart of a CPB dyeing station is the padder (Figure 3-7).

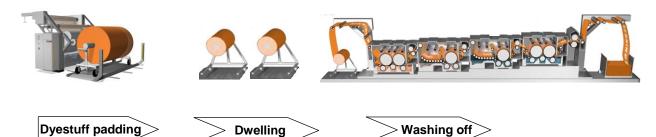


Figure 3-6: Cold pad batch dyeing process [23, p. 4]

23



Figure 3-7: Cold pad batch (CPB) dyeing station [24, p. 13]

### 3.1.6 Nip dyeing

Dyeing in the roller nip of squeezing mangles belongs to the group of foulard padding applications described in chapter 2.2.2. A special advantage is the fact that less than 2 litres of liquor content are used for dyeing in the roller nip. Classical foulard applications with a trough require at least six to ten times higher liquor volumes. The dye solution is produced just-in-time, thus avoiding residue liquor. Both features reduce the danger of hydrolysis and ensure high dyestuff fixation.

<u>Additional information</u>: Hydrolysis reduces the degree of dye fixation. In order to compensate for lower fixation rates, the dyestuff concentration is increased by 5 to 10 per cent in classical applications.

Nip dyeing is suitable for most of the applications mentioned in Figure 3-8.

|                    | Trough dyeing   | Nip dyeing + +   |
|--------------------|---|--|
| Liquor content     | 12 I/m Working width<br>(26 – 27 I for 2200 mm)                                   | 1.8 l/m Working width<br>(4 l for 2200 mm)   |
| Speed              | 60 m/min  | 40 m/min   |
| Process            | CPB Dyeing (Reactive)<br>and CPB Bleaching  | CPB Dyeing (Reactive)  |
| Min/max lot length | 1000 m  | 30 –m  |
| Fabric tension     | low   | Very low   |
| Danger of tailing  | in some cases possible  | No tailing   |
| Applications       | -Cold Bleach or fabric with very bad<br>hydrophility<br>- sometimes Rayon/Viscose | -dyeing Reactive dyestuffs and<br>especially fast hydrolyzing dyestuffs<br>-very elastic fabrics |
| Handling           | Easy  | Very easy, very good visibility  |
| Miscellaneous      |   | -Saving of 30 % Urea<br>-Suitable for dyeing cuffs and collars                                   |

### COMPARISON Trough dyeing vs. Nip dyeing

Figure 3-8: Comparison of trough dyeing vs. nip dyeing [24, p. 11]

CPB dyeing using the nip dyeing option is the most sustainable dyeing process. Despite its considerable advantages it remains in competition with exhaust dyeing processes. The main cause is the lack of knowledge at supervisor level.

### **3.1.7 One-step bleaching with high add-on impregnation**

In recent years, the classical two-step bleaching process has been replaced by a one-step bleaching process, reducing chemical consumption by approximately 30 per cent. At the same time, the steaming time increased by 50 per cent. In order to avoid crease marks from longer steaming, a high liquor pick-up impregnation is required. The liquor film around the fibres acts as a protection shield against undesired partial drying.

One-step bleaching involves the uniform application of a defined quantity of chemicals dissolved in water over the length and width of a wet or dry canvas cloth. During the reaction process in the steamer, the treatment chemicals have to be spread evenly across the fibre structure to achieve a homogeneous pre-treatment effect over the fibre cross-section. A company has developed under the brand name Impacta an aggregate which fulfil this aspects. The Impacta is a high moisture application system for wet on wet impregnation and is mainly used for preliminary treatment. A major advantage of this unit is that a liquor exchange takes place in the bath. In other words, the water is exchanged for chemicals. Overloading the fabric with chemicals is avoided. Not all articles have the same liquor exchange rate and the same liquor uptake. The following quality criteria have to be met:

- Reproducible liquor pick-up
- Fabric-specific liquor pick-up close to the maximum liquor uptake (overloading with chemicals and chemical losses through dropping have to be avoided)

Pure add-on application systems do not fulfil this requirement and overloading with chemicals and chemical losses are common (Figure 3-9). A special two-roller squeezing unit ensures a controlled and speed-independent liquor pick-up. Classical two-roller squeezers were unsuitable with regard to controllability in the high moisture range. A modified design where the dead weight of the squeezing roller has no influence on the liquor pick-up, since the centre of gravity of the squeezing roller lies directly above the pivot point of the squeezing mechanism. The pneumatic system has been designed so that the smallest pressures can be set exactly. Owing to the low pressure there is a danger that the squeezing roller nip would spring open when passing seams or other thick places. This condition is termed an exceptional status in quality management. Independent closing is not possible owing to the minimum nip pressure. A sensor has been positioned to monitor the nip joint, which continuously measures the distance of the two rollers. If an opening of the squeezer takes place for the reasons mentioned above, this is immediately detected and a special nip closing algorithm is activated. The squeezer is returned to its original position within 2 seconds and the bleaching liquor is supplied in its customary uniform and reproducible volume [25].

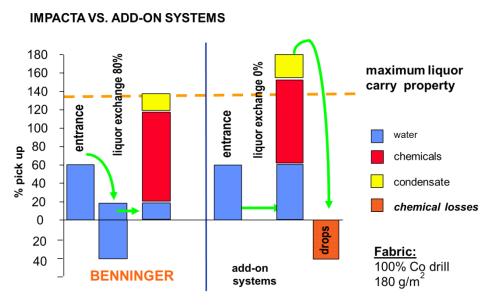


Figure 3-9: Add-on systems vs. systems with liquor exchange (courtesy of Benninger AG)



Figure 3-10: Chemical loss by uncontrolled liquor pick-up [22]

### **3.1.8 Just-in-time chemical preparation systems**

If items with different characteristics are produced in succession without production stop, it is necessary to change the formulation. Conventionally, chemicals and dyestuffs are fed through a preprepared stock tank. It is common practice to always include a safety margin to be sure that enough solution is available. Studies have shown that approximately 15 per cent of excess chemicals and dyes are prepared. To avoid overdosing, newly developed dosing and chemical metering systems are fitted with a programmable logic control (PLC) system to automate this type of processes. Chemical and dyestuff solutions are prepared just-in-time in mixing tubes. Mixing tanks or intermediate stock tanks are no longer required. Just-in-time chemical and dyestuff preparation systems are employed in the following areas:

- Preparation of enzymatic desizing solutions
- Preparation of bleaching and scouring liquors (Figure 3-11)
- Ratio dosing for dyeing with reactive dyestuffs (Figure 3-12)
- Preparation of resin finishing and finishing liquors



Figure 3-11: Single component chemical metering system for peroxide bleaching [25]



Figure 3-12: Contidos just-in-time chemical and dyestuff preparation system for CPB dyeing station [24]

### **3.1.9** Membrane filtration and water recycling systems

Around 7,000 to 10,000 litres of water are needed for every kilogramme of textiles. The largest amount is accounted for by the cultivation of natural fibres and the synthetic production of man-made fibres. Water consumption during the textile finishing process comes in second place. In the textile finishing industry, there is already an awareness of the initial effects of water shortage and the problems associated with wastewater. In China and India, for instance, licences are only granted to new companies if they can prove that their approach to dealing with water consumption and wastewater issues is responsible and sustainable. In Europe, companies face closure if they are unable to stop discharging textile wastewater in rivers and lakes. Textile centres in Asia are reporting that natural reservoirs are dwindling and that groundwater is becoming heavily salinized. As a result, many companies face problems which could potentially affect their entire existence. The recovery of water and valuable materials is becoming more and more important.

The recovery of valuable materials from waste can be achieved by filtration systems. For textile effluents, two types of filtration systems are in use.

### Ultrafiltration

The hot wastewater from textile processes is cleaned of coarse contaminants by means of mechanical pre-filtration and collected in an intermediate tank. With the aid of an ultrafiltration stage, particles are then filtered down to a size of  $0.01\mu$ m or a molecular mass of 20 kDa, in special applications even down as far as to a molecular mass of 1 kDa.

Separation is performed according to the principle of cross-flow filtration. In the ceramic membranes, the medium that is first heated to temperatures of up to 90°C flows through the channels of the membrane carrier. All particles larger than the pore diameter of the membrane are retained. The particles/molecules accumulate in the concentrate, while the filtrate penetrates the pores. A thin covering layer of particles builds up on the membrane, but is constantly carried away by the high flow speeds and is thus concentrated in the circulating water, which is then extracted as concentrate.

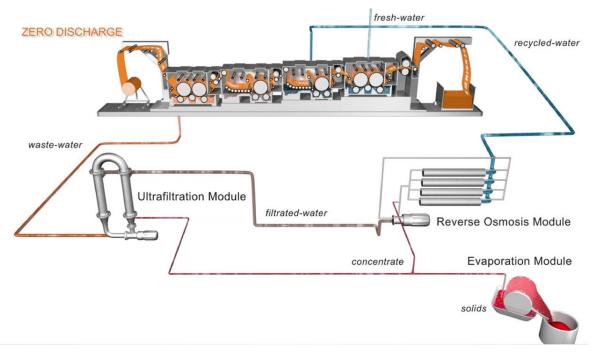


Figure 3-13: Integrated membrane filtration system for a textile dye works [26, p. 3]

### Reverse osmosis

The coloured and salty filtrate obtained from ultrafiltration is normally fed through a reverse osmosis stage, which is the finest filtration level possible. It can filter particles down to ion level. Whereas the water can still pass the membrane, salts and other small molecules are held back. Thus, wastewater from textile processes is desalinated and decoloured and can be recycled in all textile finishing processes.

In textile finishing and dying, three types of wastewater are generated:

### Wastewater from desizing and pre-treatment operations

Wastewater generated in **desizing** processes is characterized by an extremely high chemical oxygen demand (COD) load. At the same time, recyclable materials can be recovered by using water-soluble sizes. For that purpose, an ultrafiltration unit with a temperature and chemical resistant ceramic membrane is required.

### <u>Results</u>

- Water recycling: 85 to 90 per cent
- Recycling of size: 75 to 85 per cent
- Heat recovery: 70 per cent

Wastewater from **pre-treatment** processes (bleaching and scouring) has a high chemical oxygen demand (COD) value due to the organic substances which accompany the fibres. The water is usually yellow, therefore a combination of ultrafiltration followed by reverse osmosis is needed to neutralize the colour. The concentrate cannot be reused and is subsequently reduced even further and processed into solids or burned.

### **Results**

- Water recycling: 80 to 90 per cent
- Heat recovery: 70 per cent

### Wastewater from dyeing operations

Wastewater from **dyeing** processes has a heavy coloration and a high content of electrolytes, so a combination of ultrafiltration and reverse osmosis is required to process the water.

Figure 3-14 shows wastewater from a dyeing process which was treated in membrane systems.

Results

- Water recycling: 80 to 90 per cent
- Heat recovery: 70 per cent



## Figure 3-14: Bulk results from membrane filtration: left: washing liquor from CPB dyeing, right: after filtration [27, p. 3]

### Wastewater from printing operations

The wastewater generated in textile printing processes has a high chemical oxygen demand (COD) value, heavy coloration and a high content of electrolytes, thus a combination of ultrafiltration and reverse osmosis is required to process the water. Additionally, residual printing pastes are discharged, which makes the membrane difficult to treat. Pilot testing is therefore recommended prior to any investment decisions. Pigment dyes and printing pastes are on no account suitable for membrane filtration systems.

### **Results**

• Not predictable (pilot testing required)

|                                       | Wastewater type   |   |   |
|---------------------------------------|---|---|---|
|                                       | Desizing and pre-<br>treatment  | Dyeing  | Printing  |
| Temperature                           | 80-90°C   | 40/60/95°C  | 60/95°C   |
| Chemical<br>oxygen<br>demand<br>(COD) | 5,000-25,000 mg O <sub>2</sub> /l   | 1,000-3,000mg O <sub>2</sub> /l   | 2,000-15,000mg O <sub>2</sub> /l  |
|                                       | <ul> <li>Size</li> <li>Caustic soda</li> <li>Washing and<br/>wetting agents</li> <li>Salts of alkaline<br/>earth metals</li> <li>Organic<br/>contamination</li> </ul> | <ul> <li>Dissolved dyestuffs<br/>(reactive, direct, acid)</li> <li>Dye pigments (vat dyes,<br/>disperse dyes, pigment<br/>dyes)</li> <li>Salts</li> <li>Washing and wetting<br/>agents</li> </ul> | <ul> <li>Dissolved dyestuffs<br/>(reactive, direct, acid)</li> <li>Dye pigments (vat dyes,<br/>disperse dyes, pigment<br/>dyes)</li> <li>Thickeners</li> <li>Salts</li> <li>Washing and wetting agents</li> </ul> |

### Table 3-3: Typology of textile wastewater [based on 26]

### **3.1.10** Caustic soda recovery

The mercerizing process generates washing water with a high caustic soda concentration of around 60 g/l. The diluted caustic soda is concentrated to 35 to 42 Bé° by evaporation methods, allowing for

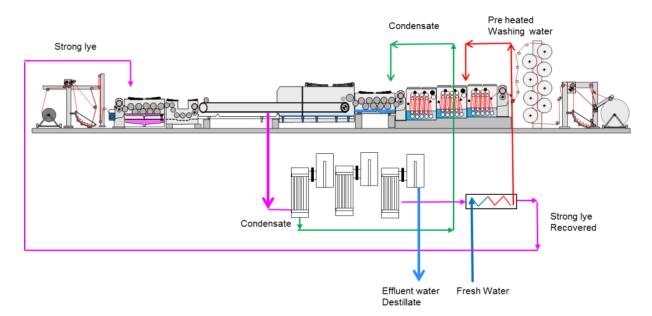
the caustic soda to be reused in the mercerizing plant. Figure 3-15 describes the principle of caustic soda recycling.

After the removal of lint, fluff and other particles (using self-cleaning rotary filters or pressure microfiltration), the weak lye is first concentrated, for instance in a three-stage evaporation process. In many cases, purification of the lye is required after evaporation. The purification technique depends on the degree of lye contamination and can be simple sedimentation or oxidation/flotation with injection of hydrogen peroxide [29, p. 298 ff].

Results

- Recycling of caustic soda: 75 to 80 per cent
- Water recycling: 80 to 85 per cent
- Heat recovery: 70 per cent
- Alkaline load of wastewater significantly reduced and acid required for wastewater neutralization minimized [29, p. 298 ff]

### Operating principle of the Caustic recovery system





#### *Operating principle*

The concentration of sodium hydroxide (NaOH) is increased by evaporation, simply said by boiling off water. To save energy, multiple effect evaporation is applied. Steam is used to heat the first stage. Water evaporates out of the solution. These vapours of the first stage are used to heat the second stage, and so on for the subsequent stages. The more stages there are, the more often the heat is reused and the lower are the steam consumption and consequently the running costs.

The driving force is a temperature and pressure drop over the stages of the evaporation, with the highest temperature and pressure in the first stages and the lowest temperature and pressure in the last stage. To use the vapours of one stage to heat the next stage, the boiling point in the next stage must obviously be lower. This is achieved, despite the higher concentration, by lower pressure in the next stage. The concentration increases over the stages, the temperature decreases.

The vapours of the last stage are not used for heating another stage, but to preheat the weak lye feed, and are then condensed to liquid in a condenser by heating up cold water for process use. The heating energy entering the caustic soda recovery plant in form of steam is not lost, but used for the production of clean hot process water for the finishing mill, usable as washing water, etc., and for other purposes [28, p. 2].

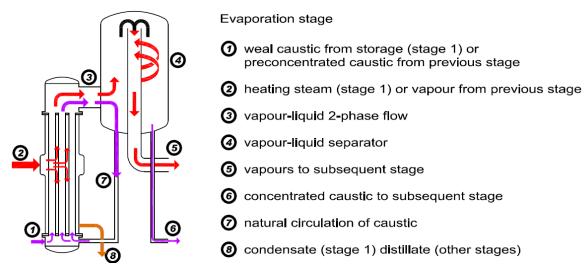


Figure 3-16: Principle of an evaporation plant [28, p. 2]

### **3.2 Substitution of hazardous chemicals**

### 3.2.1 Introduction

Under the pressure of non-governmental organizations and end-users, retailers and brands are increasingly being forced to supply textiles that are sustainably produced and free of hazardous chemicals. It is an improvement that large brands and retailers are auditing their suppliers to establish whether their textile production is sustainable. For this purpose, restricted substance lists (RSLs) indicating prohibited chemicals and/or their limit values are used. In addition to RSLs that describe the chemicals to be avoided, so-called positive lists are published, specifying chemical substances that can be used. The Swiss company Bluesign, for instance, has established a positive list including dyestuffs and chemicals which is available to the company's partners.

### **3.2.2 Overview of most hazardous chemicals**

The list of hazardous chemicals includes products with the following properties:

- Carcinogenic
- Non bio-degradable
- Mutagenic

In general, there are two levels of restriction [30]:

- Restricted use in certain end-user products with specified limit values (for example mg/kg) or limited to certain end-use purposes. For example, the use of a substance is prohibited if the item comes into contact with the skin but may be used in curtains.
- The use of the substance is banned completely.

REACH (Registration, Evaluation, Authorization and Restriction of Chemicals), a regulation released by the European Union, has been in force since 2007. It includes more than 1,000 registered substances and is subdivided into 59 categories. It is a guideline for all textile manufacturers.

In addition, Greenpeace published a list of the 11 most hazardous chemicals used in the textile industry, which are summarized in Table [4, p. 58 ff]. For a complete description of all categories, refer to the brochure "Schmutzige Wäsche" [4].

|    | Description  | Application in textile finishing |
|----|--|----------------------------------|
| 1  | Alkylphenols (APEO)                                    | Wetting, washing agents          |
| 2  | Phthalates   | Certain dyes                     |
| 3  | Brominated and chlorinated flame retardants            | Flame retardants                 |
| 4  | Azo dyes   | Dyeing                           |
| 5  | Organotin compounds                                    | Anti-odour, antifungal           |
| 6  | Perfluorinated chemicals                               | Repellence effects               |
| 7  | Chlorobenzenes   | Solvents for intermediates       |
| 8  | Chlorinated solvents                                   | Solvents                         |
| 9  | Chlorophenols  | Biocides and pesticides          |
| 10 | Short-chain chlorinated paraffins                      | Flame retardants                 |
| 11 | Heavy metals: cadmium, lead, mercury and chromium (VI) | Dyestuffs                        |

### Table 3-4: Most hazardous chemicals

### **3.2.3** Usage of hazardous chemicals

Hazardous chemicals are subject to several restrictions. Most retailers have set up their own definitions and limits. However, most of the globally acting companies have similar descriptions. As an example, the chemical restrictions defined by H&M are described below [31, p. 8].

**Concentration limit:** The substance must not be present in the product at concentrations above this limit.

**Not detected:** The substance must not be present in the finished product at concentrations above the analytic reporting limit.

Usage ban: The substance must be not used in production and it must not be added to the product.

**Exposure limit:** The substance must not be present in the finished product at the concentrations which will result in customer exposure above the limit, at normal and reasonable foreseeable use of the product.

The following chapters describe methods to substitute hazardous chemicals in dyeing and finishing mills and present case studies.

### **3.2.4** Substitution of sodium hypochlorite

For a long time, sodium hypochlorite was one of the most widely used bleaching agents in the textile finishing industry. It is still in use, not only as a bleaching agent but also for the cleaning of dyeing machines or as a stripping agent for the recovery of faulty dyed goods [29, p. 293ff].

Organic impurities on the natural cellulosic fibre act as precursors in the haloform reaction and form the carcinogenic trichloromethane. Trichloromethane is detectable under the sum parameter of adsorbable organic halogens (AOX). Such halogens can hardly be eliminated in sewage treatment plants and consequently become available to humans and animals through drinking water. Hydrogen peroxide is now the preferred bleaching agent for cotton and cotton blends as a substitute for sodium hypochlorite.

### Table 3-5: Comparison of oxidative bleaching options

|               | Comparison of oxidative bleaching options  |   |  |
|---------------|--|---|--|
|               | Peroxide bleach  | Sodium hypochlorite   |  |
| Advantages    | <ul> <li>Ecological friendly</li> <li>Good removal of husks</li> <li>Good scouring effect – resulting into good<br/>absorbency</li> <li>Non corrosive</li> </ul> | <ul> <li>Bluish whiteness</li> <li>Cheap</li> <li>Low energy consumption<br/>(since operation is at room<br/>temperature)</li> </ul>  |  |
| Disadvantages | <ul> <li>Yellowish whiteness</li> <li>Limited whiteness for Linen/flax</li> </ul>  | <ul> <li>APOX load in effluent</li> <li>Poor whiteness</li> <li>No scouring effect (poor<br/>absorbency)</li> <li>Double bleach required</li> <li>Very corrosive against metal</li> </ul> |  |

### **3.2.5** Chlorine-free anti-felt treatment of wool

Wool offers unique properties and enjoys a worldwide revival as multifunctional fibre in sports and functional wear. The scaly surface structure of wool and the swelling of the wet fibres in combination with mechanical action cause a strong felting tendency and unacceptable dimensional change of wool products during washing. Therefore, anti-felt finishing is required [32]. The most common method is the Chlorine-Hercosett process, an oxidative treatment with products containing chlorine. However, although this treatment provides good results in both technical as well as economic terms, the generation of adsorbable organic halogens (AOX) is the main disadvantage. Alternative processes have been developed in recent years (Figure 3-17).

### **ANTIFELT TREATMENTS**

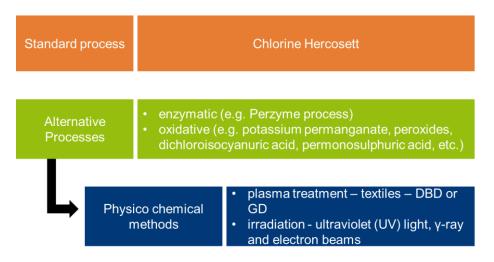
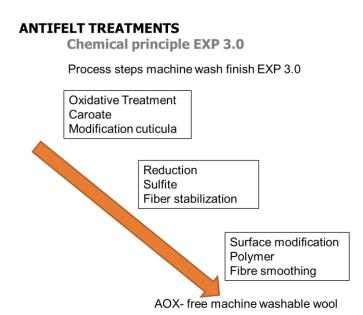


Figure 3-17: Anti-felt treatment processes [33]

The Austrian company Schoeller developed the EXP 3.0 and EXP 4.0 processes, which are chloridefree methods using oxidative and reductive detergents in combination with an organic, environmentally friendly polymer (Figure 3-18). Schoeller Yarn issues worldwide licences upon request. Alternatively, the plasma treatment of wool delivers acceptable results as well.





### 3.2.6 Azo dyes

Azo dyes are widely used for reactive, disperse, direct, acid, naphthol or leuco vat ether dyes and for other applications. Some azo dyes may break down into carcinogenic aromatic amines and are therefore strictly prohibited. Leuco vat ether and naphthol dyes have been completely substituted. In the other dyestuff classes, positive lists exist from which dyeing companies can chose azo dyes that do not form toxic amines.

# **3.2.7** C<sub>8</sub> fluorocarbon chemistry

Perfluorinated chemicals (PFCs) are man-made chemicals widely used by industry for their non-stick and water-repellent properties. In the textile industry, they are used to make textile and leather products both water and stain-proof.

There is evidence that many PFCs persist in the environment and can accumulate in body tissue and biomagnify (increase at successively higher levels in a food chain). Once in the body, some have been shown to affect the liver as well as acting as hormone disruptors, altering levels of growth and reproductive hormones [4, p. 61].

Most critical are the so-called  $C_8$ -based fluorocarbons (Figure 3-19) such as perfluoroctylsulphonate (PFOS), perfluoroctanoicacid (PFOA) and fluorotelomeralcohol (8:2 FTOH).

The C<sub>8</sub>-based fluorocarbon chemistry is still applied in the production of protective clothes for fire fighters, first aiders, surgeon garments, etc. These are areas where oil, blood and soil repellence is essential. But in the much bigger outdoor apparel textile industry, the C<sub>8</sub> technology has been replaced by innovative solutions such as C<sub>6</sub> chemistry with or without combinative plasma treatment [34] or by FC-free solutions such as the Bionic-Finish Eco technology developed by Rudolf Group or others [35]. They are highly resistant to chemical, biological and thermal degradation.

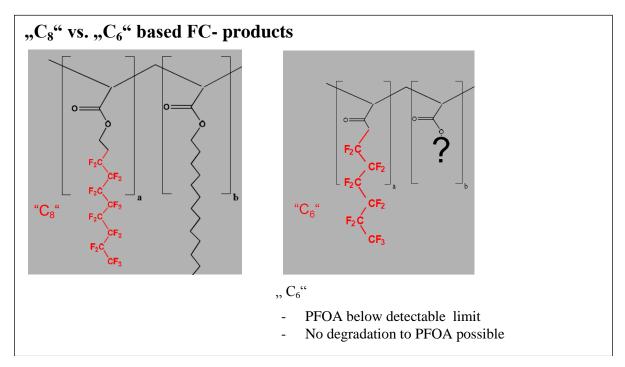


Figure 3-19: C<sub>8</sub> chemistry vs. C<sub>6</sub> chemistry [35, p. 5]

| Table 3-6: Compariso | n of repellence effects vs. | sustainability [based on 35] |
|----------------------|-----------------------------|------------------------------|
|----------------------|-----------------------------|------------------------------|

| Performance      | $C_8^{}$ chemistry | $\mathbf{C}_{_{6}}$ chemistry             | Bionic-Finishing Eco<br>(Rudolf Group) |
|------------------|--------------------|---|--|
| Water repellence | Very good          | Very good                                 | Very good                              |
| Oil repellence   |                    | Equivalent to C <sub>8</sub><br>chemistry | No                                     |

| Performance                        | C <sub>8</sub> chemistry | C <sub>6</sub> chemistry | Bionic-Finishing Eco<br>(Rudolf Group) |
|------------------------------------|--------------------------|--------------------------|--|
| Washing durability                 | Very high                | High                     | High                                   |
| Low temperature curing <b>Poor</b> |                          | Good                     | Excellent                              |
| Abrasion resistance                | Poor                     | Poor                     | Good                                   |
| Touching                           | Moderate                 | Slightly softer          | Very soft                              |
| Price                              | Normal                   | Higher                   | Very competitive                       |
| Chemical base Fluorocarbon         |                          | Fluorocarbon             | Fluorine-free                          |

# 3.2.8 Formaldehyde-free non-iron applications

For many years, the textile industry has been using resins that usually contained formaldehyde to prevent the wrinkling of fabrics. Fabrics are impregnated with urea-formaldehyde resins to give them easy care properties such as:

- Wrinkle-free aspect
- High dimensional stability after household washing
- Hydrophobic effect
- Soil resistance
- Perspiration-proof effect
- Moth-proof protection
- Mildew resistance [36]

Formaldehyde may cause severe irritations to humans. The most common means of exposure is by breathing air containing off-gassed formaldehyde fumes, but the substance is also easily absorbed through the skin. High temperatures (hot days, ironing of coated textiles) and humidity both increase the release of formaldehyde from treated textiles.

Besides being associated with watery eyes, burning sensations in the eyes and throat, nausea, difficulty in breathing, coughing, some pulmonary oedema (fluid in the lungs), asthma attacks, chest tightness, headaches and general fatigue, as well as rashes and other conditions, formaldehyde is also linked to more severe health issues.

Most suppliers of textile chemicals and additives have launched formaldehyde-free easy-care systems in recent years. For example, BASF's formaldehyde-free easy-care finishing product line can help customers meet the latest formaldehyde standards [37, p. 2]. The advertising terms "wrinkle-free" or "non-iron" are replaced by "easy care". Features like high dimensional stability and easy ironing can still be achieved.

# 4 **Cross-cutting innovative approaches**

This section contains an introduction to cross-cutting innovative approaches for the sound management of chemicals and chemical waste that are valid for all sectors in the chemical product's value chain and not only in the sector which is the focus of this document.

The cross-cutting approaches and technologies include:

- How to use chemical leasing and other innovative business models to improve resource efficiency and safety in the value chain while also increasing competitiveness and enabling differentiation in a competitive market place
- How to understand the basic elements of a safety management system in order to reduce the risk of major accidents in facilities manufacturing or handling chemicals
- How to understand and use the Globally Harmonized System of Classification and Labelling of Chemicals to handle chemicals safely and responsibly
- How to safely store chemicals according to their hazard categories and minimize the risk of accidents
- How to develop a fire protection system, classify chemicals and implement technical risk reduction measures
- How to classify and manage hazardous waste effectively and remain in compliance with relevant regulations
- How to improve energy efficiency at facilities manufacturing or handling chemicals

# 4.1 Chemical leasing and other innovative business models

Chemical businesses are dependent on innovation and a continuous pipeline of innovative products and applications. This chapter provides an overview of known and successful chemical management business models.

#### 4.1.1 Introduction to innovative business models

Greater spread and application of innovation in business models that reduce resource use has the potential to create multi-billion euro markets in the EU and overseas and achieve very substantial environmental and economic benefits. The actual spread of innovative business models currently covers a very broad range of sectors including industrial production of solid goods, fluids and ingredients as well as transportation, construction and maintenance, agriculture and public services. [38, p. 1]

#### 4.1.2 Innovative chemical management business models

The chemical industry and the many companies that use its products have developed over time a linear business model in which raw materials are used to create valuable substances which are then, in turn, used to produce other products further down the value chain(s). Traditionally, chemicals are sold to customers, who become owners of substances and therefore responsible for their use and disposal. Their suppliers have a clear economic interest in increasing the amount of chemicals sold, which is usually related to negative releases to the environment. However, this is in opposition to the drive for resource efficiency and sustainability where the aim is to minimize resource use whilst maximizing added value.

Innovative service-based business models have the potential to resolve this problem. They aim to optimize the use of chemicals, save energy and encourage the recovery and recycling of chemicals. They also represent a better use of technical expertise and create an alignment of aims and business models and a stronger relationship between the manufacturers of chemicals and those who use them. Besides, they appear able to deliver benefits throughout the supply chain as well as wider benefits for society. [38, p. 3]

#### Chemical leasing

Chemical leasing (ChL) is a preventive and service-oriented business model that shifts away from high sales volumes of chemicals towards an integrated approach and extended producer responsibility throughout the entire life cycle of a chemical. Compared to conventional approaches, the concept of chemical leasing is much more service-oriented. In this business model, the customer pays for the benefits obtained from the chemical, not for the substance itself. Consequently, the economic success of the supplier is not linked to product turnover anymore. The chemical consumption becomes a cost rather than a revenue factor for the chemicals supplier. Companies will try to optimize the use of chemicals and improve the conditions for recycling in order to reduce the amount consumed, which, in turn, reduces the environmental pollution.

Without the ChL model, the appropriate (safe) use and disposal of chemicals would be the responsibility of the user of the chemicals. In the ChL business model, however, this "classical" role allocation is shifted towards the producer and provider of chemicals and the function performed by these chemicals, respectively. The responsibility of the producer and service provider is extended and may include the management of the entire life cycle.

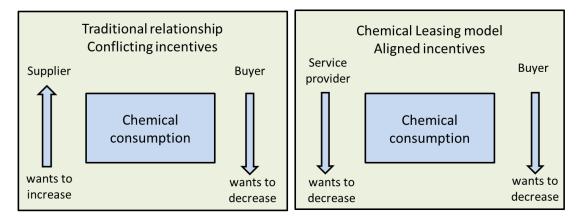


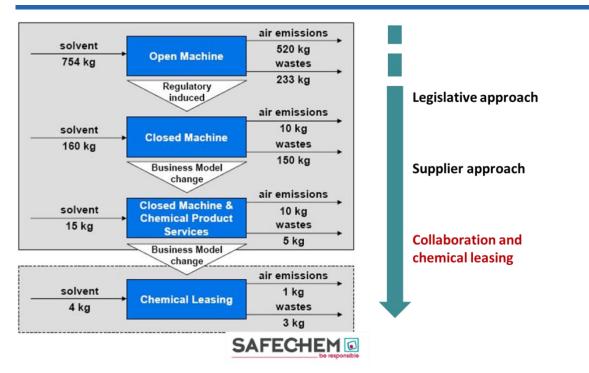
Figure 4-1: Traditional approach vs. chemical leasing model [based on 38, p. 9]

In Europe, the REACH regulation<sup>1</sup> has given a new legislative frame to the production, marketing and usage of chemicals. For certain hazardous chemicals (for example trichloroethylene), it requires authorization processes as a precondition of continued use. In this context, chemical leasing will play an increasingly important role in authorization processes because the business model requires the manufacturers to extend their responsibility and commitment to the safe and optimized use of chemicals. It is expected that in the near future certain chemicals requiring authorization will only be sold under a chemical leasing business model.

The following figure shows how technology and process improvements resulting from intensified collaboration can significantly reduce the consumption of chemicals [40]:

<sup>&</sup>lt;sup>1</sup> More information about REACH:

http://ec.europa.eu/enterprise/sectors/chemicals/reach/index\_en.htm



# Figure 4-2: Example of consumption and emission reduction by technology and process improvements resulting from intensified collaboration [83 and SAFECHEM Europe GmbH]

The application of ChL models achieves economic advantages for all partners involved, provides specific solutions for efficient chemicals management and ways to reduce negative impacts on the environment. Since chemical products provide a broad variety of services such as "cleaning", "coating", "colouring" and "greasing", the ChL model is applicable in a multitude of industry sectors [41].

#### Chemical Management Services (CMS)

Chemical Management Services (CMS) is a business model in which a customer purchases chemical services rather than just chemicals. These services can encompass all aspects of the chemical management lifecycle including procurement, delivery/distribution, inventory, use (including chemical substitute research), collection, monitoring/reporting, training, treatment, disposal, information technology and even process efficiency improvements. Each of these services poses its own costs and risks. Under CMS, the service provider is compensated based on the quality and quantity of services provided that reduce lifecycle costs, risks and environmental impacts of a chemical substance, and not on the volume of chemicals sold. Therefore, the service provider has the same objective as the customer: to reduce chemical use and costs. Both partners achieve bottom-line benefits through reduced chemical use, cost and waste. This model is now widely used in the automotive, aerospace and microelectronics sectors, where environmental benefits observed include reduced chemical use. reduced emissions and reduced waste generation, as well as substantial cost savings. A total average cost reduction of 30 per cent has been achieved in the first 5 years [38]. This model differs from ChL in that the unit of payment in ChL is the service provided by the chemical, which will always result in its efficient use, while in CMS the unit of payment is the whole service of chemicals management. This approach depends on the good management of the chemicals by the service supplier.

#### Closed-loop models

These models take a life cycle approach to materials used in goods and services and furthermore strive to keep materials within the economic system rather than letting them become waste. In the closed loop system, there is effectively no such thing as waste. The application of this approach starts by focusing on what is being delivered to the customer and how it can be achieved more efficiently.

40

More and more sectors and major businesses are moving towards closed-loop approaches in order to internalize major risks, protect against resource supply disruption, reduce environmental impacts and develop a better value proposition for customers. The benefits of this model are therefore broad and not only environmental in character.

For chemistry-using industries, this approach means not only taking responsibility for minimizing the impacts of the substances produced and sold from raw material sourcing right through to the end of product life, but also taking back the product at the end of its life and restoring it to a condition where it can be reused.

The approach ranges from extending the lifespan of a product (repair and remanufacture) to providing a service based on the effect a substance delivers rather than the substance itself. The latter is typically achieved by full recycling of the material with ownership retained by the provider.

Experience has shown that closed loop models work very well business-to-business but can be harder to implement along complicated supply chains or in business-to-consumer industries [39].

#### Feedstock foundation

This model focuses on petrochemicals, and typically consists of three to five business units. Feedstock foundation companies produce the essential building blocks for downstream players in the chemical industry and end markets, and concentrate on adding value to feedstock primarily through "smart" locations (advantaged feedstock, growth markets), large-scale facilities and leading process technology [41, p. 4]. Thus, this innovative business model is suitable for limited, large-scale businesses.

#### Chemicals platform

Chemicals platform companies typically consist of five to ten business units that span the entire chemical value chain. The platform of this model is a sort of "portfolio management company" that concentrates on the businesses, capabilities, markets and products loosely targeted at some of today's mega trends such as health, energy, transportation, housing and construction. These companies consist of a portfolio of business units operating more or less independently according to the companies' governance structure and actively managed for growth and synergy [41, p. 4].

#### Market maker

Market makers typically consist of one to three business units. This model focuses not on chemical end markets, but rather on selected end markets such as life science, agrochemicals, paints and coatings, and related technologies. Market makers focus on driving innovation based on the understanding of product performance and act on pervasive end-market trends, not simply customer input. These players make a significant investment in brand and distribution. They tend to have high growth with products that represent a limited share of customer cost and value chain [41, p. 4].

# 4.1.3 Additional sources of information

#### Websites

**Chemical leasing** website: a one-stop site to learn everything about this business model and to find helpful guidelines and recommendations for its implementation: http://www.chemicalleasing.org/index.htm

Material on chemical leasing provided by UNIDO: http://www.unido.org/chemical-leasing.html

**Chemical Strategies Partnership** (**CSP**) website (USA): provides information on CMS and guidelines for its implementation: <u>http://www.chemicalstrategies.org/implement\_manualstools.php</u>

41

#### Documents

**DEFRA, UK**: "A guide to chemical services" (2013); provides an easily accessible introduction to the chemical services model.

**EU** – **DG Environment**: "Promoting Innovative Business Models with Environmental Benefits" (2008); describes a selection of innovative business models that are economically profitable and also have positive environmental effects.

# 4.2 **Prevention of major accidents**

This chapter provides an overview of the state of the art in the prevention of major accidents, relevant for small and medium enterprises.

### 4.2.1 Importance of preventing major accidents

The advantages of reducing the likelihood and consequences of major accidents – including better protection of human health, the environment and economic resources – are well known [43, p. 6-7]. An example of legislative measures supporting the prevention of major accidents is the Seveso Directive which obliges Member States of the European Union to ensure that operators have a policy in place to safeguard against major accidents [42].

EC Directive 96/82/EC (Seveso  $II^2$ ) definitions [42, article 3]:

**Major accident:** a major emission, fire or explosion, leading to serious danger to human health and/or the environment, immediate or delayed, inside or outside an establishment, involving one or more dangerous substances

Hazard: an intrinsic property of a dangerous substance, with a potential for harm

**Dangerous substances:** named substances or substances with certain generic hazardous properties, for example flammability

#### Community

Major accidents can cause death and serious injury to workers and the local population as well as significant long-term health effects. They can harm livestock, crops and water supplies, and cause considerable environmental damage. They may also result in major economic losses for the enterprise involved and the entire community.

#### Health and environment

Major accidents can have devastating impacts on human health and the environment. For instance, they can cause direct, immediate harm to workers and other persons in the vicinity who are exposed to the harmful chemicals or who are injured by an explosion or fire. Acute exposure to dangerous substances can also cause long-term health effects including chronic diseases and cancer. Additionally, people may suffer harm indirectly through their diet as a result of ingesting contaminated drinking water, agricultural products, fish, livestock and other food items spoiled by polluted air, surface water and soil.

The release of dangerous substances into the air, water and soil can have serious environmental impacts, killing animals and vegetation, poisoning water supplies used for drinking, fishing and irrigation, and rendering soil unfit for agriculture.

 $<sup>^2</sup>$  The Seveso Directive (currently the Seveso II Directive) will be replaced by the Seveso III Directive on 1 June 2015.

#### Economic impact

In addition to the potential impact on human health, accidents can cause significant economic harm, both to the enterprise as well as to the community. The costs associated with response, clean-up and recovery, including health services provided such as medical treatment, can be quite significant.

It is obvious that the enterprise where the accident occurred may suffer significant economic losses (from, for instance, property damage, loss of jobs, having to stop operations for an extended period or even bankruptcy). What is less evident are the costs incurred by other industries in the vicinity of the accident. For example, an accident may pollute local water bodies increasing the costs of water used for drinking and agriculture, and causing significant damage to the fishing industry. In addition, suppliers and customers of the enterprise will be impacted.

# 4.2.2 Main cause of major accidents

The potential for major accidents has become more significant with the increasing production, storage and use of dangerous substances. Inadequate management is often recognized as the main cause of major accidents, specifically:

- Inadequate design;
- Inadequate maintenance and operation procedures;
- Inadequate assessment of the existing hazards and the associated risks in the facility;
- Inadequate staffing or training.

A detailed analysis of an accident will normally reveal three cause levels: basic, indirect and direct (Figure 4-3).

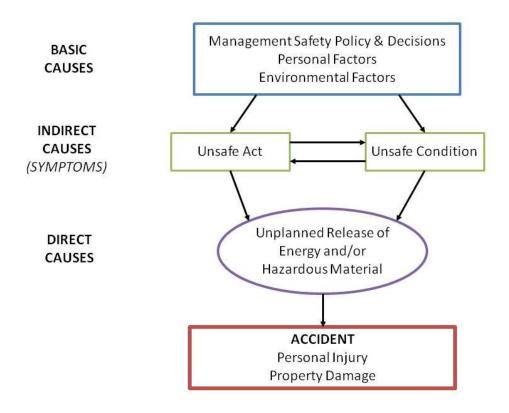


Figure 4-3: The three cause levels of an accident [based on 46, p. 350]

# 4.2.3 Motivation of SMEs and prevention of major accidents

Measures to prevent major accidents could lead to improved efficiency and lower production costs, as well as to improvements in the general health, safety and environmental performance of enterprises. Safe operations also protect the good will and reputation of industry, and foster improved relationships with members of the local communities.

At the local level, creating an effective major accident prevention plan might result in significant political implications. This could provide a platform for improving communication and trust between local leaders, the public and other stakeholders. Furthermore, communities typically blame local leaders for accidents if there has not been adequate warning or appropriate response.

## 4.2.4 **Prevention of major accidents**

Facilities that handle chemicals are actively engaged in dealing with risks to ensure the safety of their workers and their community. Most of their efforts focus on ensuring that the facility is designed and operated safely on a daily basis, using well-designed equipment, preventive maintenance, up-to-date operating procedures and well-trained staff [46, p. 343].

It is recognized that the safe functioning of an enterprise depends on its overall management. Within this overall management system, the safe operation of an enterprise requires the implementation of a system of structures, responsibilities and procedures with the appropriate resources and technological solutions available [43, p. 6-7].

Each enterprise should establish and implement a major accident prevention policy, which provides a basis for major accident prevention in order to minimize the likelihood of an accident and to protect human health, the environment and property. The elements of the safety management system (SMS) should be appropriate to the nature and extent of risks posed by hazardous installations and take the available resources into account [43, p. 92-95].

A safety management system should address<sup>3</sup> the organizational structure, practices, procedures and resources for implementing the major accident prevention policy and should include at a minimum the following items:

- Organizational structure (including roles, responsibilities, training, education, qualifications and inter-relationship of individuals involved in work affecting safety)
- Identification and evaluation of hazards (developing and implementing formal procedures to systematically identify and evaluate hazards including their likelihood and severity arising from normal and abnormal operations, and including the hazards arising from handling, production, transportation, storage or disposal of dangerous substances)
- Facilities and operational control (addressing design and construction as well as the procedures for safe operation, including maintenance of plants, processes, equipment and temporary stops)
- Management of change (planning and controlling changes in various areas such as organization, personnel, plant, processes including prestart-up reviews, maintenance and decommissioning, materials, equipment, procedures, software, design and external circumstances that might affect safety)
- Planning for emergencies (related to developing, adopting, implementing, reviewing, testing and, if appropriate, revising and updating emergency plans)

<sup>&</sup>lt;sup>3</sup> Based on the OECD Guiding Principles for Chemical Accident Prevention, Preparedness and Response (second edition, 2003).

- Monitoring performance (concerning the ongoing assessment of compliance with the safety policy and safety management system, and mechanisms for taking corrective action in the event of non-compliance)
- Audits and reviews (addressing the periodic, systematic assessment of the major accident prevention policy as well as effectiveness and suitability of the SMS)

#### Guidance for SMEs on specific safety management system elements

Small and medium enterprises (SMEs) are a very important part of the global economy, since they are the source of most growth in employment. They are flexible, adaptable and quick to respond to changes in the marketplace and new opportunities.

But if SMEs are to grow and become sustainable, enterprises must learn to consolidate and improve practices, to become more productive, to manage and mitigate risks more effectively and to understand their value chain and business environment more fully. This is why codes, standards, guidelines and frameworks that bring the experience of major companies to small companies in a useable way are so valuable.

UNEP's Responsible Production (RP) Framework for Chemical Hazard Management provides guidelines for small and medium enterprises. It provides a systematic, continuous improvement approach to chemical safety along the value chain. Moreover, the approach provides technical materials and tools to help SMEs understand hazards, control chemical exposure, reduce the risk of accidents and engage stakeholders [44].

The "Guidelines on a Major Accident Prevention Policy and Safety Management System" published in cooperation with the Major Accidents Hazards Bureau of the European Union provide very good advice on safety management systems. The publication provides guidance and descriptions on what is required by the Seveso II Directive [42].

#### **Guidance on safety management systems**

#### Development of a major accident prevention policy

The development of a major accident prevention document/policy is recommended as best practice. This document is intended to give an overview of how the company ensures a high level of protection for humans and the environment. Furthermore, it should clearly indicate the arrangements, structures and management systems required for each of the seven areas described in more detail further below [45, p. 2].

The safety management strategy defines how safety and health are organized, measured and monitored. The development of a safety policy and safety plan is a key point to ensure that the strategies and procedures are implemented at all levels. All seven elements have to be incorporated into the system, including monitoring, audit and review processes which are essential components of the system [47, p. 5].

#### Organization and personnel

The safety management system should reflect the top-down commitment and the safety culture of the company's organization, translated into the necessary resources and direct responsibilities of personnel involved in the management of major accidents at all levels in the organization. Furthermore, it is helpful to identify the skills and abilities needed by such personnel, and ensure their provision [44, p. 2].

The responsible production (RP) approach provides a systematic method of mapping key aspects (inputs, outputs, modes of production, stakeholders) related to reducing the risk of accidents. It often involves a quick on-site assessment of the company and consultation with management in order to gain a better understanding of the company's needs, priorities and potential areas for improvement.

#### Hazard identification and evaluation

Hazard identification and risk assessment are two major elements of the risk management process. They are necessary to be able to make decisions relating to risk, for example in terms of risk avoidance, reduction or transfer, or acceptance of the residual risk.

When undertaking a risk assessment, it is important to carefully consider the various possible approaches and methods available, and choose an approach/method that is appropriate for the particular circumstances, since all approaches/methods have their own strengths and weaknesses and none is perfect.

The methodology used for these processes is known as risk analysis or risk assessment. The spectrum of specific methods is broad and covers various degrees of depth and complexity in the analysis as well as various systems of investigation. Risk assessment methods include hazard mapping, check-lists, hazard and operability study (HAZOP), "What if" analysis and risk matrix<sup>4</sup>.

Techniques that are recommended for the analysis of major hazards include the "Dow Fire and Explosion Index" [48] and the "TNO Purple Book" (guidelines for quantitative risk assessment) [49]. The Responsible Production Toolkit (UNEP) provides tools which can help SMEs undertake hazard identification and risk assessment including prioritization of the identified risks.

#### **Operational control**

The company should prepare, update and keep readily available the information on process hazards, design and operational limits and controls resulting from the hazard identification and risk evaluation procedures. Based on these, documented procedures should be prepared and implemented to ensure the safe design and operation of plants, processes, equipment and storage facilities [44, p. 5].

Straightforward guidelines on how to prepare a company's process flow diagram can be found in the Responsible Production Toolkit. An objective is to clearly map the process flow in order to understand what the activities are and who is involved in them. This will help getting a better understanding of where chemicals are used and located. Process flow means both the sequence of activities that are undertaken in the company and the external activities that the company can influence within its business, ranging from the products and services the company procures to the products and services the company provides [44, p. 14].

#### Management of change (MOC)

According to the International Social Security Association (ISSA), management of change (MOC) is defined as "a systematic process to ensure the transition from an initially safe state to a new – again safe – state, along a safe path. The new state may be permanent or temporary." In 2007, the ISSA published a practical guidance document on maintenance and changes in plants with high safety requirements [50]. This document is a valuable source for helping companies institute MOC.

Maintenance and changes are part of normal plant operation in the chemical industry, yet serious accidents often occur due to changes in processes. Changes frequently leading to unsafe conditions if not properly analyzed include the change of [50]:

- Construction materials
- Process parameters
- Inerting procedures
- Equipment parameters

<sup>&</sup>lt;sup>4</sup> An overview of the listed methods can be found in UNEP's Flexible Framework for Addressing Chemical Accident Prevention and Preparedness, SG-2 Guidance on Risk Assessment (p. 122-125).

Such changes can be temporary or permanent, small or large. Nevertheless, any changes or modifications that result in deviations from the safety protocols (or safety management plan) are subject to a hazard analysis and risk assessment procedure. This is fundamental to all MOC activities.

According to the ISSA, typical items on a plant change form include:

- Administration (sequential number, date, plant, piping and instrumentation diagram)
- Description of the change (What will be changed? Why? What are the objectives?)
- Additional information (deadlines, cost)
- Schedule including the sequence of work (planning, preparation, main work, auxiliary work, termination) designed so that the work flow clearly appears from the entries
- Document update (P&I sheets, permits, explosion protection documents, safety checks and hazard analyses)
- Checks before start-up (process control system (PCS), pipes, pressure vessels, unloading points and filling stations)
- Approvals (with signature and date)

Further practical information relating to planning changes and accounting for safety in the various phases of changes (i.e. preliminary planning, basic design, detailed design, construction, commissioning and production) are found in the ISSA publication.

The following table provides an overview of MOC requirements according to the US Environmental Protection Agency (US EPA) and can be a useful guideline for implementing a company's MOC policy.

| MOC procedures<br>must address:                          | Employees affected by the change must:    | Update process safety information if:                           | Update operating procedure if:                                  |
|--|---|---|---|
| Technical basis for the change                           | Be informed of the change before start-up | A change covered by<br>MOC procedures<br>results in a change in | A change covered by<br>MOC procedures<br>results in a change in |
| Impact on safety and health                              | Trained in the change before start-up     | any process safety information                                  | any operating<br>procedure                                      |
| Modifications to operating procedures                    |   |   |   |
| Necessary time period for the change                     |   |   |   |
| Authorization<br>requirements for the<br>proposed change |   |   |   |

# Table 4-1: Management of change requirements, Chapter 7.8 (2004) of the EPA General Risk Management Program Guidance [based on 51]

#### **Emergency planning**

The safety management system should include the procedures necessary to ensure that an adequate emergency plan is developed, adopted, implemented, reviewed, tested, and, where necessary, revised and updated. The company should develop and maintain procedures to identify foreseeable emergencies arising from its activities, identified through hazard and risk assessment, and to record this analysis and keep it up-to-date. Plans to respond to such potential emergencies should be prepared,

and arrangements for testing and review on a regular basis should be included within the SMS. The procedures should also cover the necessary arrangements for communicating the plans to all those likely to be affected by an emergency [45, p. 6].

Proper assessments can only be made by undertaking a detailed safety and risk assessment audit of the operations, worker practices, company policies and the workplace environment [46, p. 418]. Section 3 of the Responsible Production Toolkit gives recommendations on how to respond to the hazards and risks identified through reviewing the company's processes and activities. Furthermore, it provides guidelines on how to develop an appropriate response to chemical hazard issues and the associated impacts and how to communicate them to the concerned community. There are also a number of international publications that provide guidance on emergency planning related to major accidents, some of them being listed in the following paragraph.

# 4.2.5 Additional sources of information

#### Websites

Health and Safety Executive (**HSE**), UK website: provides a wealth of information and advice on work-related health and safety and the prevention of accidents: http://www.hse.gov.uk/

**UNEP** Safer Production website: provides a list of additional resources related to safer production: http://www.unep.org/resourceefficiency/Business/CleanerSaferProduction/SaferProduction/Additional Resources/tabid/101149/Default.aspx

#### Documents

European Commission, Major Accidents Hazards Bureau (MAHB): "Guidelines on a Major Accident Prevention Policy and Safety Management System"

**OECD**: "Guiding Principles for Chemical Accident Prevention, Preparedness and Response" (second edition, 2003)

GTZ: "Chemical Management Guide for Small and Medium-Sized Enterprises" (2007).

**UNEP**: "Responsible Production Booklet; A Framework for Chemical Hazard Management for Small and Medium-Sized Enterprises" (2009).

European Process Safety Centre (EPSC): "HAZOP: Guide to Best Practice" (second edition, 2008)

# 4.3 Safe handling of chemicals

This section provides a brief overview of:

- Hazards associated with the use and handling of chemicals
- Hazard communication in the form of labels and SDSs
- Performing a basic risk analysis
- Developing workplace operating instructions based on SDSs
- Preventive measures including:
  - Hierarchy: elimination, substitution, control: TOP hierarchy
  - o COSHH Essentials Toolkit or ILO Toolkit (focus on essentials)

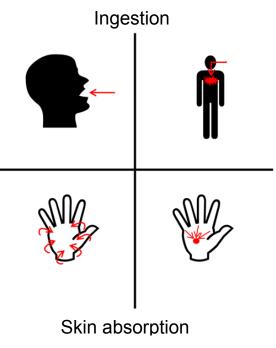
Chemicals are used in virtually all work activities, thus presenting certain chemical risks in a large number of workplaces all over the world. Many thousands of chemicals are used in substantial quantities, and many new chemicals are also introduced on the market every year. Hence, there is an urgent need to establish a systematic approach to safety in the use of chemicals at work.

An effective control of chemical risks at the workplace requires an efficient flow of information on potential hazards and the safety precautions to be taken from the manufacturers or importers of chemicals to the users. Employers should follow up on this information and ensure on a day-to-day basis that the necessary measures are taken to protect workers, and consequently the public and the environment.

Chemicals can be corrosive, reactive, flammable, explosive, oxidizing and inert, and contribute to serious health effects such as burns, rashes, kidney damage, lung damage, heart conditions, cancer, damage of the central nervous system, etc.

Routes of occupational exposure include:

- Inhalation: Nearly all materials that are airborne can be inhaled. This is the most common route. Gases and vapours can pass into the blood whereas solid particles are inhaled into the lungs.
- Dermal absorption: Skin contact with a substance can result in a possible reaction and many solids, liquids, vapours and gases can be absorbed through the skin.
- Ingestion/swallowing: Workers do not deliberately swallow materials they handle, however, the failure to wash hands, or eating in the presence of chemicals can lead to ingestion.
- Injection: Though uncommon, accidents occurring during the handling of sharp objects can result in the injection of a chemical into the bloodstream.
- Ocular: Chemicals are absorbed through the eyes or cause physical damage.





The safe use of chemicals involves several building blocks in which the GHS is a key element (see the following sub-chapter).

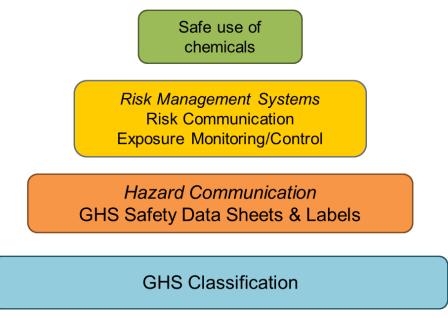


Figure 4-5: Building blocks for the safe use of chemicals

# 4.3.1 Globally Harmonized System of Classification and Labelling of Chemicals (GHS)

The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is an internationally agreed-upon system, created by the United Nations. The GHS is a worldwide initiative to promote standard criteria for classifying chemicals according to their health, physical and environmental hazards. It is an international approach to hazard communication, providing agreed criteria for the classification of chemical hazards, and a standardized approach to label elements and safety data sheets (SDSs). The primary goal of the GHS is better protection of human health and the environment by providing chemical users and handlers with enhanced and consistent information on chemical hazards [52, p. 63].

It is important to note that the GHS is currently being implemented in many countries, which means that users of chemicals will still encounter systems currently used in many major chemical producing countries.

The key elements of GHS include:

- Harmonized classification criteria
- Harmonized labelling elements
- Harmonized safety data sheet elements

The GHS uses the **signal words** "Danger" and "Warning", **pictograms<sup>5</sup>**, **hazard statements**, and **precautionary statements** to communicate hazard information on product labels and safety data sheets.

<sup>&</sup>lt;sup>5</sup> Note: Not all categories have a symbol associated with them

#### 51

#### Hazard classification

The GHS distinguishes three major hazard groups:

- Physical hazards
- Health hazards
- Environmental hazards

Each hazard group consists of classes and categories (sub-sections of classes). For example, the hazard class "self-reactive substances and mixtures" has seven hazard categories (A-G). In general, the hazard categories are either in numerical or alphabetical order with "1" or "A" representing the most hazardous category.

#### Table 4-2: Hazard classification [based on 60]

| Classes in the group "Physical Hazards"  |   |  |  |
|--|---|--|--|
| <ul> <li>Explosives</li> <li>Flammable gases</li> <li>Aerosols</li> <li>Oxidizing gases</li> <li>Gases under pressure</li> <li>Flammable liquids</li> <li>Flammable solids</li> </ul>                                | <ul> <li>Self-reactive substances and mixtures</li> <li>Pyrophoric liquids</li> <li>Pyrophoric solids</li> <li>Self-heating substances and mixtures</li> <li>Substances and mixtures which, in contact with water, emit flammable gases</li> <li>Oxidizing liquids</li> </ul> |  |  |
| Classes in the group   | p "Health Hazards"  |  |  |
| <ul> <li>Acute toxicity</li> <li>Skin corrosion/irritation</li> <li>Serious eye damage/eye irritation</li> <li>Respiratory or skin sensitization</li> <li>Germ cell mutagenicity</li> <li>Carcinogenicity</li> </ul> | <ul> <li>Reproductive toxicity</li> <li>Specific target organ toxicity – single exposure</li> <li>Specific target organ toxicity – repeated exposure</li> <li>Aspiration hazard</li> <li>"Health Hazards"</li> </ul>  |  |  |
| Hazardous to the aquatic environment<br>(acute and chronic)  | Hazardous to the ozone layer  |  |  |

The following figure presents an overview of the pictograms used in the GHS and the UN Model Regulations on the Transport of Dangerous Goods (UNTDG) and their meanings.

# Table 4-3: Pictograms used in the GHS and the UN Model Regulations on the Transport of Dangerous Goods (UNTDG) [based on 61]

| Hazard<br>pictogram | GHS hazard   | Dangerous class labels (pictograms)  | Dangerous good<br>classes |
|---------------------|--|--|---------------------------|
|                     | Explosive<br>Self-reactive<br>Organic<br>peroxides | EXPLOSIVE<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1 | Explosive                 |

| Hazard<br>pictogram | GHS hazard   | Dangerous class labels (pictograms)   | Dangerous good<br>classes  |
|---------------------|--|---|--|
|                     | Flammable<br>Self-reactive<br>Pyrophoric<br>Self-heating<br>Emits<br>flammable<br>gas in contact<br>with water<br>Organic<br>peroxides | RAMARE<br>LQUD<br>3<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMARE<br>1000<br>RAMA | <ul> <li>Flammability<br/>(liquid, solid<br/>or gas)</li> <li>Pyrophoric</li> <li>Emits<br/>flammable gas</li> <li>Organic<br/>peroxide</li> </ul> |
|                     | Oxidizers  | OXIDIZING<br>AGENT<br>5.1<br>2  | <ul><li>Oxidizer</li><li>Oxidizing gas</li></ul>   |
|                     | Gases under<br>pressure  | DN:PLAAMBABLE<br>2000<br>DN:DTCXC<br>22<br>DX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DZ:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:DIG<br>CX:D   | <ul> <li>Non-toxic<br/>non-<br/>flammable gas</li> <li>Flammable<br/>gas</li> <li>Oxidizing gas</li> <li>Toxic gas</li> </ul>                      |
|                     | Acute toxicity   | Page 6  | <ul> <li>Acute toxicity</li> <li>Acute toxic gas</li> </ul>  |
|                     | Acute toxicity<br>Skin irritant<br>Eye irritant<br>Skin<br>sensitizer  | No equivalent   |  |
|                     | Carcinogen<br>Respiratory<br>sensitizer<br>Reproductive<br>toxicant<br>Germ cell<br>mutagen  | No equivalent   |  |

52

| Hazard<br>pictogram | GHS hazard   | Dangerous class labels (pictograms)       | Dangerous good<br>classes |
|---------------------|--|---|---------------------------|
| A CONTRACTOR        | Eye corrosion<br>Skin<br>corrosion<br>Corrosive to<br>metal  | CORROSIVE                                 | Corrosive to<br>metals    |
|                     | Aquatic<br>toxicity<br>Not covered<br>within the<br>scope of<br>workplace<br>hazardous<br>chemical<br>requirements | Y AND | Environmental<br>hazard   |

### Labelling

A label is the key to organizing chemical products for storage. Tanks, containers and bulk stores should be identified and marked with signs indicating the name/identity of the chemical product. The labels must be comprehensive and easily understandable to provide full information about each class and category of hazards according to the GHS.

Containers (including cylinders of compressed gases) must not be accepted without the following identifying labels:

- Identification of contents (for example chemical name)
- Description of principal hazards (for example flammable liquid)
- Precautions to minimize hazards and prevent accidents
- Appropriate first aid procedures
- Appropriate procedures for cleaning up spills
- Special instructions to medical personnel in case of an accident

Below, a model label is shown as adopted by the EU Classification, Labelling and Packaging Regulation (CLP Regulation), which aligns EU legislation to the GHS.

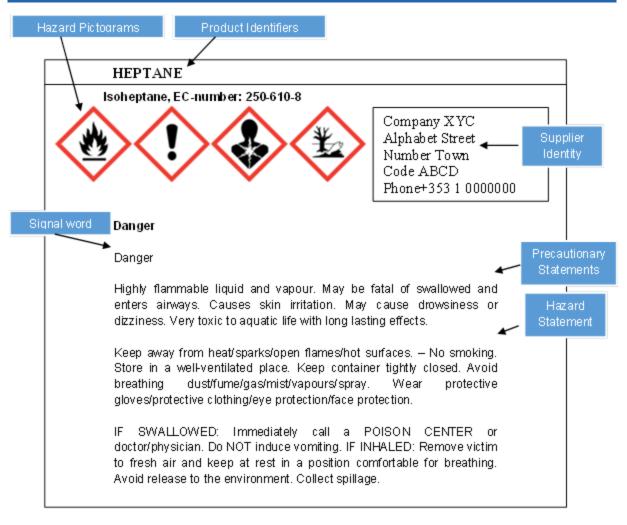


Figure 4-6: Model label according to the EU CLP (harmonized with GHS) [based on 60]

Additionally, a label for combining transport pictograms and GHS requirements is shown.

54

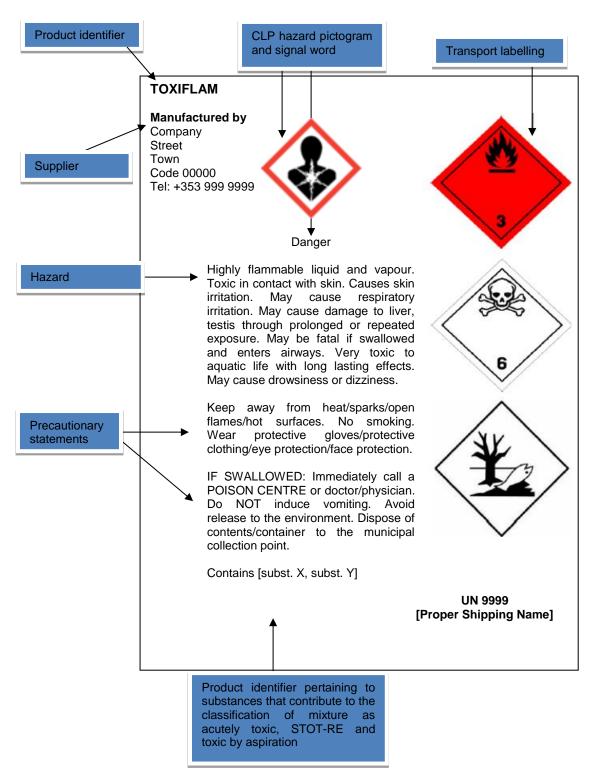


Figure 4-7: Label for combining transport pictograms and GHS requirements [based on 60 and 61]

#### GHS safety data sheets

The GHS safety data sheets are key documents in the safe supply, handling and use of chemicals. They should provide comprehensive information about a chemical product that allows employers and workers to obtain concise, relevant and accurate information on the hazards, uses and risk management associated with the substance in the workplace.

55

An SDS provides the following information:

- Substance properties
- Health, environmental and physical-chemical hazards
- Storage, handling, transportation and final disposal
- Safety instructions for workers and measures to be taken in the event of a fire or accidental release as well as first aid procedures.

Based on this information, a hazard analysis is drawn up and workplace operating instructions are provided.

The SDS should contain 16 sections: [53, p. 5-9, p. 39]

- Identification
- Hazard(s) identification
- Composition/information on ingredients
- First-aid measures
- Fire-fighting measures
- Accidental release measures
- Handling and storage
- Exposure control/personal protection

- Physical and chemical properties
- Stability and reactivity
- Toxicological information
- Ecological information
- Disposal considerations
- Transport information
- Regulatory information
- Other information

In many countries, the chemical producer is under legal obligation to provide an SDS. If the SDS is not delivered together with the chemical or provided electronically, the downstream user should request the SDS from the supplier (always the latest version).

Further information on the preparation of SDSs in compliance with the GHS was developed by the European Chemicals Agency (ECHA) and can be found in the section "Additional sources of information" further below. An example of an SDS complying with the EU CLP legislation is provided on the website indicated below<sup>6</sup>.

# 4.3.2 Hazard identification and risk analysis

The following section is based on UNEP's Responsible Production Approach [54].

#### Understanding your operational processes

"Hot spots" are defined as:

- Places where you can observe inefficient handling or use of chemicals
- Particularly hazardous situations where chemicals are being stored or used and where the potential harm could be reduced or prevented by implementing appropriate control measures

To identify hot spots, you need to look at your operations in a different way. Rather than focusing on the end product, you need to look in a detailed way at the storage, handling and use of chemicals in the production process. Look specifically at how chemicals are being treated in steps involving their purchase, storage, handling and processing with the aim of spotting inefficiencies, waste, losses and risks. [55, p. 20]

The hazard analysis should not only focus on production but include cleaning operations (cleaning of reactors and equipment), maintenance activities (preventive and corrective) and start-up/shut-down procedures.

<sup>&</sup>lt;sup>6</sup> http://reachteam.eu/english/compliance/SDS/docs/CLP\_REACH\_Compliant\_SDS.html

#### Drawing up a chemical process flow diagram

The objective is to clearly map the process flow of chemicals in order to understand what the activities are and who is involved in them. This will help you to understand where chemicals are used and located (chemical streams). [54, p. 14-15]

The basic strategy for a block flow diagram preparation is:

- 1. List all the steps and activities in the process.
- 2. Arrange the activities in sequence.
- 3. Discuss the sequence of activities with the relevant people in your company.
- 4. Review the flowchart with your workers and your business partners.
- 5. Check to see if they agree that the process has been drawn accurately.

#### Identification of chemicals, their quantities and the hazards involved in the process

The next step is to identify chemicals, their quantities and the hazards associated with their use at the company. It is important to identify the hazards for all chemicals involved in the process [54, p. 14-15].

The objective is to systematically identify all chemical substances that are stored, handled and used at your business, along with information on their quantities and type of storage, and to classify them according to chemical product information, labels and GHS safety data sheets. Check this against the process flows to make sure you have not missed anything. Establish what information already exists within the company regarding chemicals (for example, purchasing records, stock control cards, inventories, suppliers' product information, GHS SDSs, etc.). List all chemical substances in an *inventory*. Begin with one department or process and proceed on a step-by-step basis until you have a complete inventory for your whole operation [56, p. 16].

#### Assessing health, environmental and economic risks

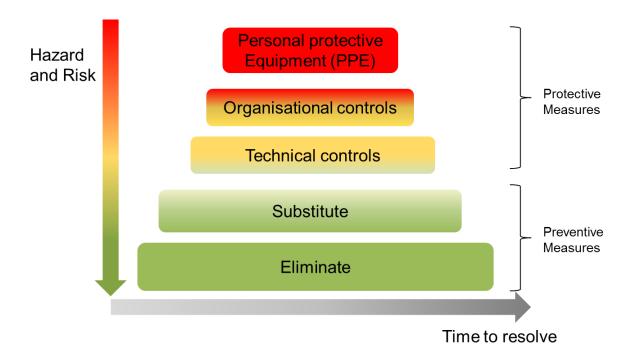
Tool 1.3 of the Responsible Production Toolkit provides a methodology to estimate the impact and likelihood of an accident situation. Note that the assignment of both the severity of impact and the likelihood of occurrence are *subjective* decisions, and therefore a multi-disciplinary team should be involved. The rating of the severity of a hazard should be based on the hazard and precautionary statements outlined in the SDS (hazard and precautionary statements are found in section 2 of the GHS SDS template). Further information on physical and chemical properties, stability and reactivity as well as health effects can be found in sections 9 to 11 of the GHS SDS template.

An essential component to assessing chemical risks is the creation of a compatibility matrix of hazardous substances. This tool can assist in determining the chemical reactivity of substances and mixtures (for example, toxic by-products or extreme heat generation). The Chemical Reactivity Worksheet<sup>7</sup> predicts possible hazards resulting from the mixing of hazardous substances (chemicals) as well as data on whether the substance reacts with air, water or other materials. This hazard information can be entered in the risk matrix of the Responsible Production Toolkit.

### **4.3.3 Preventive and protective measures**

Once you know where the chemicals are, what kind of chemicals you are handling and what their hazards are, you can use a hierarchy of controls to choose the best way of handling the chemicals safely as shown in the figure below.

<sup>&</sup>lt;sup>7</sup> The Chemical Reactivity Worksheet can be downloaded at: http://response.restoration.noaa.gov/oiland-chemical-spills/chemical-spills/response-tools/downloading-chemical-reactivity-worksheet.html



#### Figure 4-8: Hierarchy of steps according to the control strategy [based on 56, p. 22]

#### Preventive measures

Before the materials discarded from a process or a part thereof become waste, there are some measures that can be taken in order to prevent this conversion.

#### Eliminate

If you are not using a hazardous chemical, then there is no risk. Eliminating the hazardous chemical is the best way to control the risk. Consider whether you really need to use a chemical at all. For example, in recent years paint manufacturers have been able to eliminate hazardous solvents such as xylene [57, p. 23]. You could also consider whether it is possible to use a different process which does not require a hazardous chemical.

#### Substitute

It may be possible to replace your hazardous chemical by a less hazardous one. For example, you could replace isocyanate-based paints by water-based paints. You could also use a less hazardous form of the same chemical, For instance, using the chemical in pellet form rather than the powder could have a significant effect on reducing inhalable dust levels [57, p. 23]. It is important that you consider hazards and potential exposure associated with the replacement chemical to ensure that no new hazard is introduced to the workplace.

The CatSub database (www.catsub.eu) provides a publicly accessible catalogue of more than 300 examples of substitution of hazardous chemicals including case studies that describe successful substitutions with less hazardous chemicals or hazard-free products. Furthermore, the European Agency for Safety and Health at Work provides some factsheets to support in the substitution of hazardous chemicals (Factsheet 34 – Elimination and substitution of dangerous substances<sup>8</sup>).

<sup>&</sup>lt;sup>8</sup> See http://osha.europa.eu/en/publications/factsheets/34

The internet portal SUBSPORT<sup>9</sup> (SUBStitution Support PORTal – Moving Towards Safer Alternatives) combines information from several countries (for example, Denmark, Germany, Spain, Sweden and the USA) regarding tools and case studies for the substitution of hazardous substances in products and processes with less hazardous alternatives. The portal is available in English, French, German and Spanish.

#### Protective measures

Protective control measures can be subdivided into the following TOP hierarchy:

- <u>T</u>echnical control measures
- <u>Organizational control measures</u>
- <u>Personal protective equipment</u>

#### **Technical control measures**

Technical control measures are designed to move an air contaminant away from personnel and/or to create a barrier between a hazard and the employee. Some common types of engineering control measures are discussed below [57, p. 2-3].

#### **Chemical fume hoods**

Chemical fume hoods are the primary containment devices used to protect personnel and the laboratory environment from hazardous chemicals that may become airborne through volatilization or aerosol formation.

Use a chemical fume hood when working with

- Flammable liquids
- Particularly hazardous substances that are volatile or that are in powder form
- Other volatile compounds
- Chemicals with a strong odour
- Other materials as indicated by the chemical- or lab-specific standard operating procedure

# Local exhaust ventilation

Local exhaust ventilation is used with a localized source of chemical vapours that can be captured. Examples include snorkel-type exhaust and downdraft sinks. Local exhaust ventilation should only be installed with the involvement of the facility management for your building.

#### Isolation devices

These devices physically separate a contaminant-generating process from the work environment. They will often involve a sealed plexiglass box, and may be combined with local exhaust.

#### Process modification

Process modification involves changing the temperature or pressure at which a process is conducted, or using inert gas, or any other change in the procedure to reduce the likelihood of exposure or incidents.

#### **Organizational control measures**

The use of management and administrative procedures aims to reduce or eliminate exposure [52, p. 24].

Look how the work is done and consider how employees are exposed to the chemical. Think about how the job could be done differently to avoid exposure. Where it is not possible to eliminate or

<sup>&</sup>lt;sup>9</sup> http://www.subsport.eu/

isolate the chemical hazard, you should minimize exposure to it. This can be achieved by introducing written procedures in your workplace to:

- Minimize the number of employees who might be involved in a task, for example by introducing job rotation
- Exclude other employees not involved in the task from the area where the chemical is being used
- Provide training to your employees on the hazards and safe use of the chemicals they work with
- Ensure chemicals with hazardous properties are correctly stored
- Ensure emergency procedures are in place in the event of an accident, for example spillage

These procedures should be known by and available for all organizational levels.

Note: The posting of *operational procedures* highlighting the necessary precautions and methods of handling chemicals for certain tasks can help reduce the risk of accidents. The operational procedures (or working instructions) should contain the following sections: identification of the hazardous substances, hazards to human health and the environment, protective measures and rules of conduct, conduct in the event of danger, first aid and proper disposal. An example of how to obtain working instructions out of an SDS can be found in the annex of the document available at the link indicated below<sup>10</sup>.

#### **Personal protective equipment (PPE)**

The use of personal protective equipment (PPE) should be the last line of defence and not regarded as an alternative to other suitable control measures which are higher up the hierarchy. It should provide adequate protection against the risks arising from the hazardous chemicals to which the wearer is exposed, for the duration of the exposure, taking into account the type of work being carried out. [52, p. 27]

Section 8 of the GHS SDS gives advice on steps needed to reduce exposure, including advice on appropriate PPE. Examples of precautionary pictograms to be included on an operational procedure sign are shown in the figure below:



# Figure 4-9: GHS precautionary pictograms [based on 60]

Personal protective equipment can include:

- Eye/face protection (for example safety glasses, goggles, face shields)
- Skin protection (for example chemical-resistant footwear including shoes, boots and rubber boots, and clothing such as aprons or suits)

<sup>&</sup>lt;sup>10</sup><u>http://www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/TRGS/pdf/TRGS-555.pdf?\_blob=publicationFile&v=2</u>

- Hand protection (for example gloves or gauntlets, disposable or otherwise, that are suitable for the task)
- Respiratory protection (for example respirators, masks or hoods that give adequate protection)
- Thermal protection (employees may need to be protected from excess heat or cold with appropriate clothing)

There are several methods for determining the level of protection for PPE in the workplace. The US agency OSHA defines the four levels A, B, C and D, with A signifying the highest level of protection for skin and respiratory safety in the workplace. The method for determining the level of protection and the following table are provided in chapter 5 of the book "Practical Guide to Industrial Safety" [46].

| Table 4-4: Level of protection and corresponding required personal protective equipment [based | L |
|--|---|
| on 46]   |   |

| Personal protective equipment                                | Level of protection |   |   |   |
|--|---------------------|---|---|---|
| reisonal protective equipment                                | А                   | В | С | D |
| Hard hat   |                     |   |   |   |
| Face shield or safety glasses                                |                     |   |   |   |
| Boots  |                     |   |   |   |
| Inner gloves   |                     |   |   |   |
| Outer gloves   |                     |   |   |   |
| Work coveralls   |                     |   |   |   |
| Chemical-resistant coveralls                                 |                     |   |   |   |
| Chemical-resistant suit                                      |                     |   |   |   |
| Fully encapsulating suit                                     |                     |   |   |   |
| Air purifying respirator                                     |                     |   |   |   |
| SCBA (self-contained breathing apparatus)/airline respirator |                     |   |   |   |
| Two-way radio  |                     |   |   |   |
| Cooling system   |                     |   |   |   |

OSHA provides online tools to help in the selection of appropriate protective equipment, including eye and face protection<sup>11</sup> and respiratory protection<sup>12</sup>. Furthermore, most suppliers provide the ability to search appropriate PPE according to an identified chemical.

# Contractors' and maintenance activities

Two additional sources of accidents that are often neglected are *contractors'* and *maintenance activities* (preventive and corrective). Regular servicing and maintenance work is required due to the high stress placed on equipment in the chemical industry by exposure to very aggressive substances. Three kinds of maintenance work may be identified in the chemical industry: ongoing or daily maintenance work (executed without shutdown of the installation but where the equipment may be isolated), maintenance with a shutdown of the installation, and modification or construction of new units. Subcontractors may be involved in all three kinds of maintenance work. Outsourcing maintenance work is becoming the norm in the chemical industry.

<sup>&</sup>lt;sup>11</sup> https://www.osha.gov/SLTC/etools/eyeandface/index.html

<sup>&</sup>lt;sup>12</sup> https://www.osha.gov/SLTC/etools/respiratory/index.html

In many countries, the company has legal responsibility for the safety of any personnel working within its installations, including contractors and external workers (revise local regulations carefully). Therefore, any occupational safety and health (OSH) management plan should include contractors and maintenance activities. Several fact sheets are available from the European Agency for Safety and Health at Work (EU-OSHA) to assist companies in integrating maintenance activities and any related (sub)-contracting<sup>13</sup>.

# 4.3.4 Online tools for controlling health risks from chemicals: COSHH Essentials

The COSHH Essentials website<sup>14</sup> provided by the UK Health and Safety Executive is similar to the ILO International Chemical Control Toolkit<sup>15</sup>, but it goes a step further and provides direct guidance based on input to an interactive website. After entering data of processes and operations in the online tool<sup>16</sup>, users are given advice on a range of tasks involving chemicals, such as mixing or drying.

Details on relevant control measures such as "drum emptying" or "transferring liquid by pump" are available for download and are valuable tools for protecting workers.

# 4.3.5 Additional sources of information

#### Websites

**UNECE** (United Nations Economic Commission for Europe): provides more information about the GHS and the application of the GHS criteria:

http://www.unece.org/trans/danger/publi/ghs/guidance.html

**HSE** (Health and Safety Executive): UK website providing a wealth of information and advice on work-related health and safety, and guidance on the control of hazardous substances: http://www.hse.gov.uk/

#### Documents

**UNEP:** Responsible Production Handbook. A Framework for Chemical Hazard Management for Small and Medium Sized Enterprises

HAS (Health and Safety Authority), Ireland: Your steps to chemical safety. A guide for small business

GTZ Chemical Management Guide for Small and Medium Sized Enterprises, 2007

# 4.4 Storage of hazardous chemicals

All substances or mixtures presenting one or several hazards that could have adverse effects on humans' and animals' health or life, harm the environment or damage infrastructures are considered as hazardous materials. The presence of these substances in a company requires special rules for handling, processing, disposal and, of course, for storage. The aim of this chapter is to present general

<sup>&</sup>lt;sup>13</sup> https://osha.europa.eu/en/publications/e-facts/e-fact-62-safe-maintenance-working-with-contractorsand-subcontractors/view ; https://osha.europa.eu/en/publications/e-facts/e-fact-66-maintenance-andhazardous-substances/view ; https://osha.europa.eu/en/publications/e-facts/e-fact-67-maintenancechemical-industry/view

<sup>&</sup>lt;sup>14</sup> http://www.hse.gov.uk/coshh/essentials/index.htm

<sup>&</sup>lt;sup>15</sup> http://www.ilo.org/legacy/english/protection/safework/ctrl\_banding/toolkit/icct/

<sup>&</sup>lt;sup>16</sup> http://www.hse.gov.uk/coshh/essentials/coshh-tool.htm

and specific rules for the storage of hazardous substances in order to prevent fires, explosions, the formation of gases and toxic vapours, the pollution of soils, surfaces and groundwater, etc.

The literature is rich with information, and it is not possible to provide here an exhaustive list of the standards regarding the storage of hazardous substances. The objective of this chapter is to present the most relevant rules, applicable in an industrial context, in order to enable the safety manager (or equivalent) to analyze the storage conditions in the company, identify gaps and define where measures need to be taken to ensure compliance with standard storage policies. However, it is important to keep in mind that national regulations and safety values have to be complied with at any time.

# 4.4.1 Storage concept

A storage concept includes all the relevant information needed to ensure the safe storage of hazardous materials and compliance with regulations as well as environmental and safety requirements. It gives an overall view of the local situation and available measures. By drawing up a storage concept, the following objectives can be achieved [58]:

- The local conditions and measures are perfectly adapted to the hazards arising from the stored products.
- As a result of the overall consideration, conflicting measures are identified and may be adjusted.
- Legal requirements are met.

To achieve these goals, a storage concept must include the following information:

- A description of the local environment including storage conditions, physical properties of storage rooms and definitions of the stored substances
- The nature and the quantity of the hazardous substances
- Structural, technical and organizational measures

#### 4.4.2 Classifications/categories

#### Hazards

The hazards associated with chemical substances were presented in the previous chapters of this manual. The various properties need to be described in safety data sheets and other relevant documents, and marked on containers. The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is a standardized system to classify substances and hazards and was covered in Section 4.3.1, where the different hazards and their pictograms were described.

#### Storage classes (SC)

Based on the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR) [62] and the UN Recommendations on the Transport of Dangerous Goods [61], nine material classes (and additional subclasses) were defined, for which specific handling and storage rules were developed. Three of them are not dealt with here as they are too specific (infectious, radioactive and explosive materials). The categories are listed in the following table.

| Storage class | Substance properties   | ADR/UN labelling | GHS labelling |
|---------------|--|------------------|---------------|
| SC 2          | Liquefied gases or gases under pressure  |                  |               |
| SC 3          | Flammable liquids  |                  |               |
| SC 4.1        | Flammable solids   |                  |               |
| SC 4.2        | Substances liable to spontaneous combustion (auto-flammable)   |                  |               |
| SC 4.3        | Substances which, in contact<br>with water, emit flammable<br>gases                                      |                  |               |
| SC 5          | Oxidizing substances/organic peroxides   |                  |               |
| SC 6.1        | Toxic substances   |                  |               |
| SC 8          | Corrosive or caustic substances  | a a              |               |
| SC 9          | Miscellaneous dangerous<br>substances and articles,<br>including environmentally<br>hazardous substances |                  |               |

#### Table 4-5: Storage classes [based on 61 and 62]

#### Examples of hazardous substances and their reactions

As a general rule, the storage of chemicals must be organized in different areas, according to the storage classes defined above. Moreover, possible chemical reactions between substances that can be severe and dangerous have to be considered, for instance:

- When acids react with non-precious metals (aluminium, silicon, zinc or iron) or when alkali metals (sodium or potassium) come into contact with water, or just humidity from ambient air, hydrogen is created. Hydrogen is an extremely flammable gas and can be explosive when mixed with air.
- Powerful oxidants such as hydrogen peroxide can cause fires if they come into contact with organic materials such as wood, paper, cardboard, etc.
- Sulphuric acid mixed with caustic soda creates an important exothermic reaction, which can lead to overflowing or dangerous corrosive projections.

For this reason, the storage of chemical substances requires proper organization, taking into account the hazard of each substance separately as well as the potential reactions between them. The incompatibility rules are presented in chapter 4.4.3, whereas the next table [58] shows most frequently observed dangerous reactions.

| Substance A     | + | Substance B                  | = | Danger                                    |
|-----------------|---|------------------------------|---|---|
| Acids           | + | Metals                       | = | Spontaneous combustion (gaseous hydrogen) |
| Oxidants        | + | Organic substances           | = | Fire, explosion                           |
| Sulphide        | + | Acids                        | = | Toxic gaseous sulphurated hydrogen        |
| Alkali metals   | + | Water                        | = | Spontaneous combustion (gaseous hydrogen) |
| Acids           | + | Bases                        | = | Exothermic reaction (heat emission)       |
| Metal powders   | + | Aqueous solution             | = | Spontaneous combustion (gaseous hydrogen) |
| Metal powders   | + | Air                          | = | Spontaneous combustion                    |
| Nitric acid     | + | Organic substances or metals | = | Toxic nitrous gas                         |
| Chlorine bleach | + | Acids                        | = | Toxic gaseous chlorine                    |

#### Table 4-6: Dangerous reactions

# 4.4.3 Technical solutions

#### General storage rules

The next chapters present the requirements that must always be met, for the storage of any hazardous material, including the waste generated by the use of these materials.

#### Marking and labelling

The hazardous substances must be stored in a specific place, room or cupboard, clearly identified and separated from the process areas. The hazard must be indicated and the access restricted.

Every container, from the smallest bottle to the largest tank, must be labelled, in order to provide immediate information on the substance contained and the related hazard. For more information about labelling according to the GHS, refer to Section 4.3.1.

#### Inventory and safety data sheets (SDS)

In order to have a complete overview of the situation and of the potential hazards in case of an incident (leakage or fire), the company systematically needs to register the stored hazardous substances, including:

- Maximum quantities for every category and updated currently stored quantities
- Storage position(s) on a map

The fire brigade must be informed about the inventory. Furthermore, safety data sheets of every substance must be registered and easily available. Ideally, copies of these SDSs are stored with the substances. They provide information about the hazards, the storage requirements and the expected reactions in case of an accident.

The manufacturers of hazardous materials have to provide safety data sheets with the products they are selling. These SDSs must be regularly updated to comply with national and international standards and requirements. Specific information about SDSs, as specified by the GHS, is provided in Section 4.3.1 in the subsection "GHS safety data sheets".

#### Water protection

Every liquid must be stored on a catch basin in order to manage overflow, leakage or accidental spillage. The objective of containing the liquid and avoiding its dispersion is to prevent:

- Environmental contamination and human exposure
- Dangerous reactions

If the substances stored present a high aquatic toxicity, or if this toxicity is low, but the quantities stored are high (over 1,000 kg), the retention capacity must provide for 100% of the highest volume stored plus the retention of the water that would be used to extinguish a fire.

A flow to the sewage system or to surface water must be prevented. The position of evacuation grids must be checked. They might be covered. In case of a dangerous spillage, they must be covered by appropriate means (for example special bags).

#### Storage incompatibilities

Hazardous substances must be stored separately from any other non-hazardous material, and especially from food or drugs.

This matrix shows a classification of substances that, according to their hazardous properties, must not be stored together (red), can be stored together under certain conditions that have to be verified in the SDS (orange) or can usually be stored together without disadvantages (green).

Acids and bases must not be stored together.

Appendix 3: Storage shows storage incompatibilities for 16 substances commonly used in industry.

#### Other safety and organizational requirements

- The flooring of the storage area must be impermeable. A special coating (sealing) will often be necessary, as concrete is permeable to many substances. This coating must be incombustible.
- The storage room and the facilities must be made of fire-proof material.
- The separation of the storage areas (or compartments) according to the storage categories must be clearly identified and labelled (flammable, toxic, corrosive, etc.).
- Other non-hazardous materials should not be stored in the same place (wrapping, paper, cardboard, spare parts, etc.).
- A substance must never be stored in a container that is not the original one, unless it has been specifically designed for this use (sufficient mechanic, thermal and chemical resistance).
- The containers must be protected from any mechanical or thermal influence (heat sources, falling objects, pressure through weight, etc.).
- Training must be conducted regarding chemical hazards and behaviour in case of an accident.
- There must be one responsible person (and one deputy) appointed for the storage area(s).

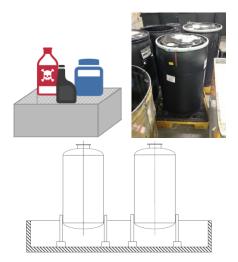


Figure 4-10: Different kinds of catch basins, according to the required volume [87], [88], [64]

|                   |   |   | ٨ | $\diamond$ |   |   |   |   |   |
|-------------------|---|---|---|------------|---|---|---|---|---|
|                   | 0 | - | - | -          | - | - | + | - | - |
|                   | _ | + | - | -          | - | - | + | - | - |
| ٨                 | _ | - | + | 0          | - | - | - | I | - |
| $\diamond$        | - | - | 0 | +          | 0 | - | - | - | - |
| $\diamond$        | - | - | - | 0          | 0 | 0 | 0 | 0 | 0 |
|                   | _ | - | - | -          | 0 | + | + | + | + |
| $\langle \rangle$ | + | + | - | -          | 0 | + | + | + | + |
|                   | - | - | - | -          | 0 | + | + | + | + |
|                   | - | - | - | -          | 0 | + | + | + | + |

Figure 4-11: Storage incompatibilities [based on 66]

- Appropriate personal protective equipment (PPE) must be easily available and properly maintained.
- At least one eye shower must be installed. An emergency shower can be necessary.

#### Specific rules for each storage category

#### Storage category 2: Liquefied gases or gases under pressure

In case of accidental destruction or fire, pressurized containers can turn into dangerous projectiles. Hence, the following safety measures have to be taken:

- Gas bottles must be protected by a fence.
- Use natural or forced ventilation (air renewal 3 to 5 times per hour, extraction near the ceiling or the floor depending on the properties of the gas).
- If the flammable gas is heavier than the air, consider an explosive atmosphere extending from the ground up to 1 metre (Zone Ex 2<sup>17</sup>) [63].
- If the flammable gas is equal in weight or lighter than the air, consider an explosive atmosphere in the whole room (Zone Ex 2).

If the vapours or gases are heavier than the air, the openings should be located near the ground. It they are lighter than the air, the openings should be located near the ceiling.

Ammoniac or gaseous chlorine storage requires very specific storage conditions that are not described here.

#### Storage category 3: Flammable liquids [58], [59]

The vapours of these substances are usually explosive. In exposed rooms, active ignition sources<sup>18</sup> must be avoided. Even the spark of a switch or an electrostatic discharge can set fire to these vapours. Therefore, smoking is strictly forbidden in those areas. In addition, electrical devices must be grounded and used so as to avoid ignition.

Explosive air or gas mixtures are often created in empty containers that have not been cleaned. In a fire situation, flammable substances burn fast or explode. Their flow accelerates the spread of fire.

Flammable liquids are divided into six categories, according to their flashpoint<sup>19</sup>.

- F1 = Liquids with a flash point below  $21^{\circ}C$
- F2 = Liquids with a flash point from 21 to  $55^{\circ}C$
- F3 = Liquids with a flash point from 55 to 100°C



Figure 4-12: Storage of liquefied gases or gases under pressure [84]



Figure 4-13: Fire-proof cabinet [84]

F4 = Liquids with a flash point above  $100^{\circ}C$ 

F5 = Not easily flammable liquids

F6 = Non-flammable liquids

<sup>&</sup>lt;sup>17</sup> According to ATEX regulations

<sup>&</sup>lt;sup>18</sup> Active ignition sources include flames, incandescent materials, hot surfaces or sparks emitted electrically, mechanically or electrostatically.

<sup>&</sup>lt;sup>19</sup> The lowest temperature at which a liquid can vaporize to form a combustible concentration of gas

The storage place shall meet the following requirements, according to the category of the liquid and the quantity stored:

Table 4-7: Storage place depending on the flammable liquid category and the volume (expressed in litres) [based on 59]

| Storage place (small   | Indicative maximum authorized quantity [litres] |                          |  |  |  |
|--|---|--------------------------|--|--|--|
| container/tank)  | Categories F1 and F2                            | Categories F3, F4 and F5 |  |  |  |
| Any type of room   | 5   | 30                       |  |  |  |
| Cabinet made of materials with low flammability                      | 100   | 450                      |  |  |  |
| Premises with specific structural properties designed to resist fire | > 100   | >450                     |  |  |  |

- For quantities over 100 litres (F1, F2) or 450 litres (F3, F4, F5), the flammable liquid must be stored in a specific room built with material showing specific fire-resistant properties and fire compartments. Consider an explosive atmosphere (Zone Ex 2) extending up to 1 metre above the installation that requires earthing.
- For quantities over 1,000 litres, each substance must be isolated in a specific fire compartment<sup>20</sup>. Consider an explosive atmosphere (Zone Ex 2) extending up to 1 metre above the installation that requires earthing. For quantities over 2,000 litres, protection against lightning is required.

The storage area must be naturally or artificially ventilated:

- Natural ventilation is sufficient if the room is situated above the ground and has two openings directly connected to the ambient air. One of them has to be placed at a maximum of 0.1 metres above the ground. Each opening requires at least 20 square centimetres per square metre of floor area.
- Without sufficient natural ventilation, forced ventilation of the storage area is mandatory (3 to 5 air renewals per hour). The opening has also to be placed at a maximum of 0.1 metres above the ground.
- Storage areas in high-rise warehouses where flammable liquids are stored must be artificially ventilated.

Storage rooms (or racks) must be equipped with drip pans capable of collecting at least the volume of the biggest can, drum or intermediate bulk container (IBC).

Non-buried outdoor storage sites must meet the following requirements:

- Access is limited to authorized persons (a fence is mandatory, surveillance might be needed).
- A safety distance of 5 to 25 metres to neighbouring buildings must be observed, depending on the category, the volume of liquids and the risks for the neighbourhood (see Appendix 3: Storage; [59]).
- An adequately dimensioned drip pan providing for at least the volume of the biggest tank must be installed.

#### **Storage category 4.1: Flammable solid**

Dusts can be explosive and therefore dust deposits must be avoided and regularly cleaned.

• For quantities over 1,000 kg, the substances must be isolated in a specific fire compartment.

<sup>&</sup>lt;sup>20</sup> A fire compartment is an area encircled by fire breakers (walls and ceiling must be fire-resistant) in order to prevent fire or smoke from spreading to other areas.

#### **Storage category 4.2: Substances liable to spontaneous combustion (auto-flammable)**

These substances can ignite very fast when in contact with the air, even in very low quantities. Examples include phosphor and freshly prepared metallic powders.

- Auto-flammable substances must never be stored outdoors.
- The storage area must be protected from any heat source. Ambient temperature should be controlled.
- They must not be stored with combustive, explosive or flammable substances.
- For quantities over 100 kg, the substance must be isolated in a specific fire compartment.

#### Storage category 4.3: Substances which, in contact with water, emit flammable gases

The reaction usually releases heat and the gas can ignite spontaneously. Examples include calcium and zinc powder.

- These substances must be stored in a dry place in hermetically closed containers.
- They must not be stored with halogens (fluorine, chlorine, bromine).
- For quantities over 100 kg, the substance must be isolated in a specific fire compartment.
- Specific extinguishers must be available and the sign "Do not extinguish with water" must be visible.

#### Storage category 5: Oxidizing substances/organic peroxides

These substances form highly flammable or explosive mixtures with any combustible material, flammable substance or just paper, sugar or wood. Notably **organic peroxides** must be carefully stored and handled, as they usually burn explosively.

- These substances must not be stored with combustibles (not even non-hazardous materials such as wood or paper) or caustic substances.
- They can be stored in the same room as other substances, but in a separate specific metal box or cupboard. Some organic peroxides must be refrigerated (well below their decomposition point).
- For quantities over 100 kg, the substance must be isolated in a specific fire compartment.

#### **Storage category 6.1: Toxic substances**

Even in very small quantities, these substances can be very harmful, even fatal.

- The storage must be secured and only accessible to authorized persons (key or code).
- For quantities over 1,000 kg, the substance must be isolated in a specific fire compartment.

#### **Storage category 8: Corrosive and caustic substances**

These substances can be very harmful, even fatal, in case of contact with the skin, the eyes or in case of ingestion or inhalation of vapours.

- They must not be stored with substances that form toxic gases with acids, or with combustive and oxidizing substances.
- Containers and catch basins must be resistant to corrosion (special plastics).
- Acids and bases must be physically separated and stored on distinct catch basins.
- For quantities over 1,000 kg, the substance must be isolated in a specific fire compartment.
- Storage rooms (or racks) must be equipped with drip pans capable of collecting at least the volume of the biggest can, drum or intermediate bulk container (IBC).

# Storage category 9: Miscellaneous dangerous substances and articles, including environmentally hazardous substances

This group includes halogenated hydrocarbons such as perchloroethylene, chloroform or methylene chloride. Concrete is permeable to these highly pollutant substances.

- The catch basin must be capable of collecting at least the volume of 100 per cent of liquids utile volume (real volume occupied by the substance) and not only 100 per cent of the biggest container.
- The storage floor must be coated (sealed).

# 4.5 Fire protection

Every company should have a fire protection concept. Industries storing or processing any kind of flammable substances are by nature more exposed to the risk of fire, and developing a fire protection concept is therefore mandatory.

This chapter aims primarily at explaining the procedures and working methods for drawing up a fire protection concept and defining associated measures designed to reduce the fire risk.

Fire protection has the following objectives:

- Prevent fire occurrence and fire/smoke propagation
- In case of a fire, ensure effective response
- Provide health protection to persons, rescue teams and animals through safe escape routes
- Protect property (movable and immovable) and the environment

The organization of fire protection must comply with national and regional legislation. As presented in the figure below, it includes the two main aspects fire prevention and rescue procedures.

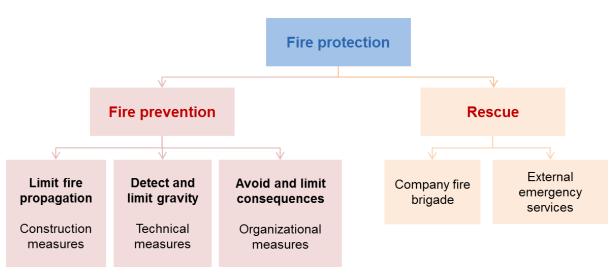


Figure 4-14: Fire protection [87]

Prevention includes structural, technical and organizational measures to limit, detect and avoid the risk of fire. The rescue phase covers support from internal and external emergency services and the fire brigade.

# A fire protection concept should include all essential protection measures in terms of construction, technology, processes and organization likely to achieve the objectives of protection.

A fire protection concept is the result of a methodical procedure, as shown in the Figure 4-15, where a range of essential protection measures (structural, technological, process-based, organizational) are planned, taking into account the current situation, the identified hazards and the protection objectives. The concept should ideally be integrated in the planning of new facilities but can as be included in the conversion or restoration of already existing buildings [70].



Figure 4-15: Fire protection concept [87]

# 4.5.1 Classification/categories

# Hazardous materials (hazard inventory)

The Table A4-1 presents the main hazardous material classes affected by fire or explosion hazards, including GHS pictograms and statement codes for different classes of flammable, explosive and oxidizing materials as well as gases under pressure.

The first step of a fire protection concept is to draw up an inventory of flammable, explosive, gaseous and oxidizing materials used in the company in order to define the concerned materials, their quantities and the conditions of storage, handling, processing and disposal.

# Fire activation risk (hazard inventory)

The probability of accidentally setting fire to a tank of benzene is higher in a production area (where movements, heat sources or physical dangers are likely to be present) than in a secured storage site. The diagram below shows the increase in probability of the fire activation risk depending on the environmental context and the related physical constraints.

The fire activation risk can be defined as the probability of realization of the risk, depending on the environmental context and related physical constraints. It increases as shown in the diagram below:

- Storage
- Storage + process
- Storage + process + distillation/condensation
- Storage + process + distillation/condensation + pressure (storage and/or process)



The evaluation of the fire activation risk is the basic information to be considered in the fire risk assessment, as shown in Table 4-9. In addition, the following internal and external causes can increase the fire activation risk and might be considered in the risk analysis:

Table 4-8: Internal and external hazards [based on 69]

| Internal hazards   | External hazards  |
|--|---|
| <ul> <li>Ignition sources</li> <li>Shortage of facilities and missing or<br/>damaged fire safety equipment</li> <li>Lack of organization</li> <li>Lack of ability to respond to an emergency<br/>(lack of training)</li> </ul> | <ul> <li>Arson</li> <li>Natural disasters</li> <li>Proximity of neighbouring buildings</li> </ul> |

Fire risk evaluation (risk analysis)

Based on the information collected through the hazard inventory, a rough assessment of the fire risk can be performed, considering the "Largest Individual Quantity" (LIQ) and the "Total Quantity" (TQ) of material identified in the area and the constraints on these materials. The figure below shows how this information can be used for the allocation to one of the three risk categories in order to define the level of protection measures required. The matrix presented here applies to solvents with a boiling point of up to  $150^{\circ}C$  [67].

|  | Larges   | t Individ  | lual Qua  | ntity, LI  | Q (t), To  | otal Qua    | ntity, T(  | <b>)</b> (t) |
|--|--|--|-----------|------------|------------|-------------|------------|--------------|
| Constraints  | <0.5<br>LIQ                                    | <1<br>TQ   | <1<br>LIQ | 1-10<br>TQ | <5<br>LIQ  | 10-30<br>TQ | <10<br>LIQ | >30<br>TQ    |
| Stored in tanks, receptacles, bulk containers, drums |  |  |           |            |            |             |            |              |
| The above and processed in reactors                  |  |  |           |            |            |             |            |              |
| The above and distilling, condensing                 |  |  |           |            |            |             |            |              |
| The above and/or processing under pressure           |  |  |           |            |            |             |            |              |
| Category 1: Basic fire risk                          | Basic fire protection measures are sufficient. |  |           |            |            |             |            |              |
| Category 2: Medium fire risk                         | Additio  | nal fire p   | rotection | n measure  | es are req | uired.      |            |              |
| Category 3: High fire risk                           | Additio  | Additional fire protection measures are mandatory. |           |            |            |             |            |              |

# Table 4-9: Determination of the fire risk category [based on 67]

In order to define specific measures, the fire risk should be assessed separately for each area.

# **4.5.2** Technical solutions (risk reduction measures)

Based on the categories defined by the risk analysis, appropriate measures can be taken in relation to construction, technology and organization in order to reduce the fire risk.

The following sections are inspired by the CFPA Guidelines "Fire protection on chemical manufacturing sites" [67] and "Safety distances between waste containers and buildings" [68].

## Construction measures

The global purpose of applying structural measures is to limit fire propagation. These measures prevent the propagation of a fire by using suitable construction materials and confine the fire through fire compartments.

Table 4-10: Fire protection – Construction measures (non-exhaustive list) [based on 67]

| Construction measures   | Fire  | risk   |      |
|---|-------|--------|------|
|   | Basic | Medium | High |
| Maintain safety distances to other buildings (2.5 metres), especially for premises where hazardous products are stored.   | X     | X      | x    |
| Use non-combustible building materials, especially for supporting structures and exterior walls.                          | Х     | X      | х    |
| Separate different types of activities in separate fire-compartments (administration, storage, production).               | Х     | X      | х    |
| Limit the size of the fire compartments, especially of those with a high fire hazard.                                     | X     | X      | x    |
| Adapt the fire resistance of the compartments to the amount of flammable/explosive products and the fire activation risk. | Х     | Х      | x    |
| Provide enough safe escape routes.  | Х     | X      | X    |
| Install drainage and spill control systems designed to contain leakages and firefighting water.                           | Х     | X      | X    |

In addition, the following information should be observed:

- The minimum horizontal safety distance between combustible objects and buildings is 2.5 metres. Certain situations require a larger safety distance (4, 6 or 8 metres) depending on the content, number and volume of the containers. Other parameters can affect this safety distance. Interested readers can find more detailed information in the corresponding guideline published by CFPA Europe [68].
- Buildings where flammable products are stored and handled must be made of non-combustible materials, including the insulation in roofs and walls. Floors of multi-level buildings, open structures and load-bearing structures should preferably be made of concrete.
- The maximum size of a fire compartment is about 3,200 square metres.
- The drainage and spill control systems must be designed for simultaneous flow of flammable liquids and fire-fighting water away from the building.
- It is essential that there is enough retention capacity for the firefighting water, especially if the products stored are dangerous to the aquatic environment or the soil.

# Technical measures

Technical measures are implemented to detect the fire risk by using alarms and fire or gas detection devices, and to limit the impact by using water, fire extinguishers or a sprinkler system. Specific installations and devices are needed to protect an object from fire risk [67].

| Technical measures   | Fire  | risk   |      |
|--|-------|--------|------|
|  | Basic | Medium | High |
| Provide air handling and smoke exhausting systems (automatic + manual)   | Х     | Х      | Х    |
| Provide manual firefighting equipment in adequate quantity (internal fire hydrants, fire extinguishers, etc.)    | X     | X      | Х    |
| Provide manual alarm points  | Х     | X      | Х    |
| Provide an automatic fire detection system   |       | X      | Х    |
| Provide an automatic fire extinction system (with adequate extinguishing agents)                                 |       |        | Х    |
| Provide a gas detection system   |       |        | Х    |
| Install a lightning rod for all production buildings with significant amounts of flammable or explosive products | Х     | Х      | Х    |
| Install a safety lighting system   | Х     | X      | Х    |
| Provide sufficient fire water capacity   | Х     | Х      | Х    |

# Table 4-11: Fire protection – Technical measures (non-exhaustive list) [based on 67]

Furthermore, the following items have to be considered:

- The maximum distance between internal fire hydrants should be around 75 metres.
- Manual fire alarm points must be strategically located throughout the site and production units. Alarm points need to be provided at 60 metre intervals.
- Fire detection systems are mandatory in areas with low manning levels (automated plants). The system has to be strategically positioned in order to detect fires starting inside processing equipment.
- Gas detection systems should be provided where potential leak sources could occur (pumps, compressors, tank cars, control rooms, etc.) in order to be used for emergency functions like shutdown of processes and/or activation of emergency ventilation.
- According to evaluations of firefighting statistics, fire water volumes of 8,000 l/min up to 12,000 l/min are required without fixed extinguishing systems. The water supply should provide fire water for a minimum of two hours and preferably 3 to 4 hours. The water retention capacity must be designed accordingly.



Figure 4-17: Gas detector [87]

# Organizational measures

Organizational measures are implemented to avoid and control the impact of a fire and include the training of employees, the maintenance of equipment and the provision of safe escape routes.

74



Figure 4-16:

Fire alarm [87]

| Organizational measures   | Fire risk |        |      |  |
|---|-----------|--------|------|--|
|   | Basic     | Medium | High |  |
| Establish a preventive maintenance programme for all equipment, including fire protection equipment | Х         | X      | х    |  |
| Appoint an adequately trained person responsible for fire protection                                | Х         | X      | X    |  |
| Organize an employee training programme   |           | Х      | Х    |  |
| Organize a training programme for visitors  |           |        | X    |  |
| Develop an escape and emergency plan  |           | Х      | X    |  |
| Organize evacuation exercises with local emergency services   |           | Х      | X    |  |

# Table 4-12: Fire protection – Organizational measures (non-exhaustive list) [based on 67]

Responsibilities include the coordination and implementation of the fire protection measures, focusing in particular on the following points:

- An internal inspection system should be implemented to ensure the periodical checks of installations and organizational measures that are relevant to fire protection.
- A person responsible for fire protection must be appointed and given practical training.
- All employees must receive periodical training on fire safety and emergency procedures.
- The fire protection documentation such as escape and emergency plans has to be continually updated and made available in every building in case of an emergency. An example is provided in Appendix 4: Fire protection)

# 4.6 Management of chemical waste

Out of 5 to 7 million known chemical substances, more than 80,000 are used by companies in their production processes and operations. Numerous new chemicals are developed and produced every year. Today, almost every company uses some type of chemicals and generates chemical waste. Those enterprises which effectively manage chemicals and chemical waste can gain concrete benefits.

In general, hazardous waste is any waste or combination of waste which may have detrimental effects on the environment or human health because of its specific nature. These wastes not only pose risks and hazards because of their nature but also have the potential to contaminate large quantities of otherwise non-hazardous wastes if allowed to mix. [55, p. 9]

# Benefit by reducing costs and environmental impact

Chemicals can represent a major part of the production cost for companies. Any measures that can be taken to reduce the loss, waste, contamination and expiry of these substances will bring cost savings to companies and, at the same time, reduce their environmental impact.

# Benefit by becoming more competitive

By improving the management of chemicals and chemical waste, companies that are striving to achieve certification under management system standards such as ISO 9000 (quality) and 14000 (environment) will gain synergies. Many of the activities required for Environmental Management Systems (EMS) certification are aimed at reducing the use of hazardous substances, protecting the health of workers and reducing negative effects on the environment.

# Benefit by improving workers health and safety

Reducing health and safety risks for employees improves their motivation and productivity and reduces absenteeism due to injury and illness.

# 4.6.1 Waste management options

In Europe, waste producers have a statutory duty to consider the **waste hierarchy** when deciding how to deal with waste.

# Hazardous waste hierarchy

The waste hierarchy is a concept at European level that provides a preferred order of priorities for selecting, ranking and deciding upon waste management options with the aim to conserve resources and to minimize environmental damage. It gives top priority to preventing waste in the first place. When waste is created, it gives priority to preparing it for re-use, then recycling, then recovery, and last of all disposal (for example landfill).

In the European Union Waste Framework Directive (2008), the waste hierarchy has five steps: prevention, preparing for re-use, recycling, other recovery (for example energy recovery) and disposal. [71, p. 3]

**Prevention** means measures taken before a substance, material or product has become waste in order to reduce:

- The quantity of waste, also through the re-use of products or the extension of the life span of products
- The adverse impacts of the generated waste on the environment and human health
- The content of harmful substances in materials and products

**Re-use** means any operation by which products or components that are not waste are used again for the same purpose for which they were conceived.

**Preparing for re-use** means checking, cleaning or repairing operations, by which products or components of products that have become waste are prepared so that they can be re-used without any other pre-processing.

**Recycling** means any recovery operation by which waste materials are reprocessed into products, materials or substances, whether for the original or other purposes. It includes the reprocessing of organic material but not energy recovery or the reprocessing into materials that are to be used as fuels or for backfilling operations.

**Recovery** means any operation the principal result of which is waste serving a useful purpose by replacing other materials which would otherwise have been used to fulfil a particular function, or waste being prepared to fulfil that function, in the plant or in the wider economy.

**Disposal** means any operation which is not recovery even where the operation has a secondary consequence, the reclamation of substances or energy.

**Other recovery** is not specifically defined in the revised Waste Framework Directive, although 'energy recovery' is referenced as an example. Since the term 'other recovery' is explicitly excluded from the definition of recycling, 'other recovery' can be considered the processing of wastes into materials to be used as fuels or for backfilling.

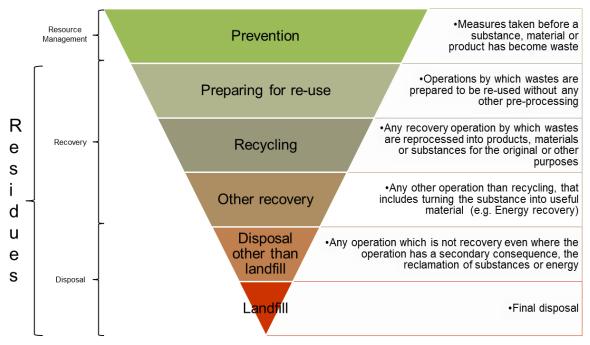


Figure 4-18: Hazardous waste hierarchy [based on 71]

# 4.6.2 Good practices in hazardous waste management

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal defines the **environmentally sound management of hazardous wastes** as "taking all practicable steps to ensure that hazardous wastes or other wastes are managed in a manner which will protect human health and the environment against the adverse effects which may result from such wastes" [75, p. 17].

Therefore an overarching objective of the sound management of hazardous waste is to minimize the negative effects of the generation and management of hazardous waste on human health and the environment.

A very useful flow diagram to start a hazardous waste management plan, is shown in the document "Guidance on applying the waste hierarchy to hazardous waste" by DEFRA [71, p. 15].

# Handling of hazardous waste

Adequate handling of hazardous waste is an integral part of the waste management system. The list below provides an overview of good management practices that help avoiding accidents:

- Train personnel on safe procedures to transfer chemicals to waste containers.
- Ensure that waste containers are in good condition.
- Check whether waste containers are compatible with the waste type they are expected to contain.
- Keep an adequate spill control kit nearby. The kit should be big enough to control the release of the largest type of container in the storage area. Clean up spills quickly.
- When handling waste containers, use mechanical aids such as drum lifts, drum hand trucks and drum dollies. Do not roll drums on their side or edge.
- Make sure container caps are secure.
- Train personnel on spill clean-up procedures.
- Maintain good general housekeeping. Keep aisles and walkways clear [76].

77

# Identification, classification and labelling of hazardous waste

The hazardous waste identification and classification process is the crucial first step in the hazardous waste management system.

## **Identification and classification**

The waste producers usually possess the best knowledge of the generated waste, as they are aware of the raw materials<sup>21</sup> used in the production process and the technologies applied. They should be in charge of the proper classification and registration of their waste. If already available, the national classification system should be used. In any case, a basic characterization with the indication of the main physical and chemical properties is necessary. Further information on other hazardous properties such as explosivity, corrosivity, etc. should be provided. If possible, indications for the appropriate waste treatment could already be given (for example methods of stabilization) [72, p. 234].

Two of the main systems for hazardous waste identification are that of the European Union (EU) and that of the US Environmental Protection Agency (US EPA). These systems determine whether a waste is recognized as hazardous or non-hazardous and are based on defining threshold concentrations for the hazardous characteristics. If the waste exhibits hazardous characteristics at a quantity above such thresholds, it is then considered to be hazardous [73, p. 9].

## Labelling

As a generator of hazardous waste, you are responsible for assuring that any container used to accumulate hazardous waste is properly labelled in order to meet regulatory requirements and assure the safety of those around you. During storage and transport, it is important that your waste can be easily identified and that containers are labelled with the following information:

- Indication that it is waste
- Contents of the container (where it is a chemical you should use the chemical identity rather than a trade name)
- Data of the waste generator
- State of the substance (solid, liquid or gas)
- Hazard(s) where applicable
- Emergency contact details [74, p. 4]

## Hazardous waste management components

In principle, waste management comprises any step of handling waste from the moment of its generation up to the moment of its final disposal or its re-entering into the product status by means of recycling or recovery. Accordingly, the EU Waste Framework Directive defines waste management as "the collection, transport, recovery and disposal of waste, including the supervision of such operations and the after-care of disposal sites, and including actions taken as a dealer or broker".

# Segregation

It is important that hazardous waste is segregated properly because of the effects it may have on human health or the environment if it is not properly controlled.

You must keep separate:

- Hazardous waste from non-hazardous waste
- Different types of hazardous waste from each other, and
- Hazardous waste from other materials [74, p. 3].

<sup>&</sup>lt;sup>21</sup> Safety data sheets (SDSs) are an important information source to determine whether the waste you produce is hazardous.

## Storage

Hazardous waste should be properly stored on-site. The storage areas should be away from public places in order to prevent any harm to the public or those persons exposed to the waste, and should be adequately dimensioned for the waste quantities to be stored.

The key factors which a company needs to ensure are that waste is:

- Secure
- Contained so that it cannot escape
- Protected from the weather, vehicles (including fork lift trucks), and scavengers and pests [74, p. 4].

It is important to ensure that any container used for waste meets certain minimum requirements. First and foremost, the container and its closure need to be compatible with the contained waste.

For certain wastes, there are additional storage requirements, for example chemicals which can have different properties and have the potential to react dangerously if not properly stored. The Health and Safety Executive, UK, have produced guidance on dealing with chemical storage (HSG 71)<sup>22</sup> and the storage of flammable chemicals (HSG 51)<sup>23</sup>.

In small and medium enterprises, often only small quantities of hazardous wastes are generated. Therefore, on-site collection and temporary storage is necessary until quantities are large enough for shipment by a licensed hazardous waste transporter.

Hazardous waste should be stored so as to prevent or control accidental releases to air, soil and water resources in a location where [75, p. 48-49]:

- Waste is stored in a manner that prevents the commingling or contact between incompatible wastes, and allows for inspection between containers to monitor leaks or spills. Examples include sufficient space between incompatibles or physical separation such as walls or containment curbs.
- Waste is stored in closed containers away from direct sunlight, wind and rain.
- Secondary containment systems should be constructed with materials appropriate for the wastes being contained and adequate to prevent loss to the environment.
- Secondary containment is included wherever liquid wastes are stored in volumes greater than 220 litres. The available volume of secondary containment should be at least 110 per cent of the largest storage container, or 25 per cent of the total storage capacity (whichever is greater), in that specific location.
- Adequate ventilation is provided where volatile wastes are stored.

Hazardous waste storage activities should also be subject to special management actions, conducted by employees who have received specific training in handling and storage of hazardous wastes. These activities include [75, p. 49]:

- Providing readily available information on chemical compatibility to employees, including labelling each container to identify its contents
- Limiting access to hazardous waste storage areas to employees who have received proper training
- Clearly identifying (label) and demarcating the area, including documentation of its location on a facility map or site plan
- Conducting periodic inspections of waste storage areas and documenting the findings
- Preparing and implementing spill response and emergency plans to address their accidental release
- Avoiding underground storage tanks and underground piping of hazardous waste

<sup>&</sup>lt;sup>22</sup> Health and Safety Executive, 2009. Chemical warehousing: The storage of packaged dangerous substances. HSG 71

<sup>&</sup>lt;sup>23</sup> Health and Safety Executive, 1998. The storage of flammable liquids in containers. HSG 51

## **Collection and transportation**

On-site and off-site transportation of waste should be conducted so as to prevent or minimize spills, releases and exposures of employees and the public. A licensed waste transporter<sup>24</sup> must ensure that hazardous waste is packaged, documented and labelled in compliance with the method of transport used (road, rail, air or sea) [75, p. 49].

Moreover, the transporter must ensure that the emergency response information contained on the manifest is immediately accessible to emergency responders. The transporter regulations do not apply to the on-site transportation of hazardous waste by generators who have their own treatment or disposal facilities, nor to TSD facilities transporting wastes within a facility.

All waste containers designated for off-site shipment should be secured and labelled with the contents and associated hazards, properly loaded on the transport vehicles before leaving the site, and accompanied by a shipping paper (i.e., EU consignment note <sup>25</sup> or US hazardous waste manifest<sup>26</sup>) that describes the load and its associated hazards [75, p. 49]). Completion of the documentation together with proper marking and labelling of containers and vehicles enables police, ambulance, fire and other first responders to react effectively and safely in the event of a spill or other accident involving hazardous waste while in transit.

Information required for consignment notes in the UK including an example can be found in the Guide to Hazardous Waste Regulations for small businesses published by the UK Environment Agency [74, p. 6]. However, local regulations and requirements must be observed.

## Treatment and disposal of hazardous wastes

The purpose of treating hazardous waste is to convert it into non-hazardous substances or to stabilize or encapsulate the waste so that it will not migrate and present a hazard when released to the environment. Treatment methods can be generally classified as chemical, physical, thermal and/or biological.

Some types of waste may be managed properly and legally at company premises (for example in case of reuse). Other types require particular handling and shipment to businesses that are specialized and licensed in storage, recycling, treatment and disposal technologies. It is the responsibility of an enterprise to decide which method of management is best for the facility in terms of future liability, potential adverse environmental impact and cost [75, p. 48].

Selected management approaches should be consistent with the characteristics of the waste and local regulations, and may include one or more of the following [75, p. 48]:

- On-site or off-site biological, chemical or physical treatment of the waste material to render it nonhazardous prior to final disposal
- Treatment or disposal at authorized facilities specially designed to receive the waste. Examples include composting operations for organic non-hazardous wastes, properly designed, licensed and operated landfills or incinerators designed for the respective type of waste, or other methods known to be effective in the safe, final disposal of waste materials such as bioremediation.

In the absence of qualified commercial or government-owned waste disposal operators (taking into consideration proximity and transportation requirements), companies should consider [75, p. 50]:

• Installing on-site waste treatment or recycling processes

EU DIRECTIVE 2008/68/EC on the inland transport of dangerous goods: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:260:0013:0059:en:PDF

<sup>&</sup>lt;sup>24</sup> US EPA regulations governing hazardous waste transporters: http://www.epa.gov/osw/inforesources/pubs/orientat/rom34.pdf

<sup>&</sup>lt;sup>25</sup> EC detailed description of consignment note data: <u>http://ec.europa.eu/transport/rail/interoperability/doc/aeif-annex-a3-en.pdf</u>

<sup>&</sup>lt;sup>26</sup> US EPA hazardous waste manifest system: http://www.epa.gov/waste/hazard/transportation/manifest/index.htm

• As a final option, constructing facilities that will provide for the environmentally sound, long-term storage of wastes on-site or at an alternative appropriate location until external commercial options become available

The following table shows the main processes for waste treatment and disposal:

82

| Table 4-13: | Waste disposal | l technologies | [based on 77, | p. 147] |
|-------------|----------------|----------------|---------------|---------|
|-------------|----------------|----------------|---------------|---------|

| 1. P                                 | Physical treatment p            | processes                               | 2. Chemical treatment processes            | 3. Biological treatment processes | 4. Thermal treatment processes | 5. Disposal<br>processes  |
|--------------------------------------|---------------------------------|---|--|-----------------------------------|--------------------------------|---------------------------|
| a. Gas<br>cleaning                   | b. Liquids-solids<br>separation | c. Removal of<br>specific<br>components | a. Absorption                              | a. Aerobic systems                | a. Incineration                | a. Deep-well<br>disposal  |
| i. Mechanical collection             | i. Centrifugation               | i. Adsorption                           | b. Chemical oxidation                      | b. Anaerobic systems              | b. Pyrolysis                   | b. Dilution and dispersal |
| ii. Electrostatic precipitation      | ii. Clarification               | ii. Crystallization                     | c. Chemical<br>precipitation               | c. Activated sludge               | c. Vitrification               | c. Ocean dumping          |
| iii. Fabric filter                   | iii. Coagulation                | iii. Dialysis                           | d. Chemical reduction                      | d. Spray irrigation               |                                | d. Sanitary landfill      |
| iv. Wet<br>scrubbing                 | iv. Filtration                  | iv. Distillation                        | e. Wet oxidation                           | e. Tricking filters               |                                | e. Land burial            |
| v. Activated<br>carbon<br>adsorption | v. Flocculation                 | v. Electrodialysis                      | f. Ion exchange                            | f. Waste stabilization ponds      |                                |                           |
| vi. Adsorption                       | vi. Flotation                   | vi. Evaporation                         | g. Neutralization                          | g. Rotating bio<br>contactors     |                                |                           |
|                                      | vii. Foaming                    | vii. Leaching                           | h. Chemical fixation<br>and solidification |                                   |                                |                           |
|                                      | viii. Sedimentation             | viii. Reverse osmosis                   | i. Dehalogenation                          |                                   |                                |                           |
|                                      | ix. Thickening                  | ix. Solvent extraction                  |  |                                   |                                |                           |
|                                      |                                 | x. Stripping                            |  |                                   |                                |                           |

# Monitoring

Monitoring activities associated with the management of hazardous and non-hazardous waste should include:

- Regular visual inspection of all waste storage and collection areas for evidence of accidental releases and verification that wastes are properly labelled and stored. When significant quantities of hazardous wastes are generated and stored on site, monitoring activities should include:
  - o Inspection of vessels for leaks, drips or other indications of loss
  - o Identification of cracks, corrosion or damage to tanks, protective equipment or floors
  - Verification of locks, emergency valves and other safety devices for easy operation (lubricating if required and keeping locks and safety equipment in standby position when the area is not occupied)
  - Checking the operability of emergency systems
  - Documenting results of testing for integrity, emissions or monitoring stations (air, soil vapour or groundwater)
  - Documenting any changes to the storage facility and any significant changes in the quantity of materials in storage
- Regular audits of waste segregation and collection practices including tracking of waste generation trends by type and amount of waste generated, preferably by facility departments
- Characterizing waste at the beginning of the generation of a new waste stream, and periodically documenting the characteristics and proper management of the waste, especially hazardous wastes
- Keeping manifests or other records that document the amount of waste generated and its destination
- Periodic auditing of third-party treatment and disposal services including re-use and recycling facilities when significant quantities of hazardous wastes are managed by third parties. Whenever possible, audits should include site visits to the treatment storage and disposal location.

# 4.6.3 Additional sources of information

# Websites

**UNEP**-Global Partnership on Waste Management (**GPWM**): provides a guideline platform that deals with different aspects of waste management, including hazardous waste: http://www.unep. org/gpwm/InformationPlatform/WasteManagementGuidelines/tabid/104478/Default.aspx

**UK** Environment Agency: provides information and guidelines that will help you classify your waste (using the List of Waste), identify if it is hazardous waste, and understand the controls that apply to hazardous waste: http://www.environment-agency.gov.uk/business/topics/waste/32180.aspx

Website of the **European Commission**: provides information on EU hazardous waste legislation: http://ec.europa.eu/environment/waste/hazardous\_index.htm

# Documents

**DEFRA** (Department for the Environment, Food and Rural Affairs, UK): "Guidance on Applying the Waste Hierarchy to Hazardous Waste" (2011). This guidance is for any business or public body which generates, handles or treats hazardous waste.

**GIZ** (Deutsche Gesellschaft für Internationale Zusammenarbeit) "Manual on industrial hazardous waste management for authorities in low and middle income economies" (2012): gives an overview of key issues related to legal requirements and practical procedures pertaining to the environmentally sound management of hazardous waste, taking into account requirements, recommendations and guidelines supplied by the Basel Convention and OECD, where relevant, and providing provisions and procedures, in particular from the European Union, as model examples.

**IFC** (International Finance Corporation, World Bank Group): "General EHS Guidelines: Environmental Waste Management" (2007): provides general guidelines for the management of non-hazardous and hazardous waste

**EU**: "Reference Document on Best Available Techniques for the Waste Treatments Industries" (2006): provides BAT in the waste treatment sector, including generic BAT and BAT for specific types of waste treatments

Environment Agency UK: "Guide to the Hazardous Waste Regulations for Small Businesses" (2013): explains how to determine if your waste is hazardous and what your responsibilities are as a producer of hazardous waste

Blackman, William C. "Basic hazardous waste management", third edition (2001), Lewis Publishers, CRC Press LLC.

# 4.7 Energy efficiency and chemicals

Industrial boiler design and operating conditions can have a significant impact on the production of persistent organic pollutants (POPs). Boilers are used for heating water for industrial processing or for domestic and industrial heating but also for producing steam. They can unintentionally form or release dioxins and furans (PCDD/F) or hexachlorobenzene (HCB). It has been demonstrated that it is possible for these compounds to be unintentionally formed during the combustion of fossil fuels. The volumetric concentrations of these pollutants in the emissions from boilers are generally very low. However, the total mass emissions from the boiler sector may be significant because of the scale of fossil fuel combustion in terms of tonnage and distribution. Besides the emission of POPs, the combustion of fossil fuels also forms other types of pollutants like SO<sub>2</sub>, NOx, CO and particulate matter that may have a significant effect on the environment [78].

The unintentional production of POPs compounds during the combustion process follows three general pathways:

- Undestroyed compounds originally present in the fuel
- Gas-phase formation from precursors (for example polyhalogenated phenols, chlorinated aromatic compounds) at temperatures higher than 500°C
- Re-formation of POPs in the cooling of flue gases

Modern industrial boilers are normally identified by the methods of heat transfer utilized.

# 4.7.1 Heat transfer systems

- Water-tube boilers: Heat transfer tubes containing water are directly contacted by hot combustion gases. Commonly used in coal fired boilers but can accommodate almost any combustible fuel including oil, gas, biomass and refuse-derived fuel (RDF).
- Fire-tube boilers: Water surrounds tubes through which hot combustion gases are circulated. The application is more common for pulverized coal, gas and oil fired boilers but various types can also burn biomass and RDF. They are generally used for lower pressure applications.
- Cast-iron boilers: Cast sections of the boiler contain passages for both water and combustion gas, used for low-pressure steam and hot water production. They are generally oil or gas fired with a smaller number of coal-fired units.



Figure 4-19: Fire-tube boiler (opened) [87]

# 4.7.2 Fuel type

Various types of fuels such as coal, oil, gas and biomass are used either individually or in combination with energycontaining waste products from other processes for steam and hot water generation in boilers. The type of fuel used depends on fuel availability and process economics.

**Heavy fuel oil** is still combusted for steam generation and is usually burned in specially designed burners incorporated in the boiler walls. The formation of PCDD/PCDF is favoured during co-combustion when liquid or sludge wastes such as waste oil or used solvents are added to the fuel mix, possibly due to lowered combustion efficiency.



Figure 4-20: Fuel oil operated boilers [87]

**Light fuel oil and natural gas** are always fired in specially designed burners and are generally unlikely to generate large amounts of PCDD/PCDFs, since both are very high calorific, clean-burning fuels with little ash.

Coal use in less efficient sectors could be a significant source of local emissions. It is acknowledged that the reduction techniques for dusts, SO2 and NOx on a flue gas can also reduce or remove PCDD/PCDF. This reduction is inconstant.

The use of **biomass** energy derived from renewable animal and plant sources can contribute to the energy requirements of industrial boilers. Usually the combustion of renewable biomass is less efficient than conventional fossil fuels and it is mostly burnt as a supplement along with feed from a conventional fossil fuel energy source. Potential for POPs emission may be increased by co-firing biomass if the boiler efficiency is not maintained by appropriate system redesign or control.

# 4.7.3 Emission reduction measures

In order to reduce the emission of POPs from fossil fuel-fired industrial boilers, the three pathways mentioned above must be minimized in the design and operation of the process. This will be effectively achieved by addressing:

- Energy conservation
- Fuel quality
- Combustion conditions
- Installation of most appropriate air pollution control devices

While the low level of precursors necessary to promote the unintentional formation of POPs via gas formation above  $500^{\circ}$ C occurs in most fuels, attention must be paid to reduce, as much as possible, the unintentional introduction of contaminated fuels, which may promote the formation of POPs. This is especially valid when co-firing fossil fuels with waste material. Other types of pollutants like SO<sub>2</sub> can also excessively occur due to low fuel quality.

The table below shows the scale of the potential firing technique savings achieved by the designated remedial actions. This is only a rough calculation. The actual savings would have to be calculated based on the actual plant and using the current operating profile. The designated values depend on the plant's condition.

| Loss            | Remedy  | Energy savings |
|-----------------|---|----------------|
| Flue gas losses | Economizer                                    | 3-15%          |
|                 | Air pre-heater                                |                |
|                 | Condensing technology                         |                |
| Surface losses  | Appropriate insulation                        | 0.3-1%         |
|                 | Lower boiler pressure                         |                |
|                 | Combustion air from top of boiler house       |                |
| Purging losses  | Optimize control circuits                     | 0.2-5%         |
|                 | Hot standby                                   |                |
|                 | Set wider turndown ratio of burner            |                |
| Boiler scale    | Correct feedwater preparation                 | Up to 10%      |
|                 | Clean boiler                                  |                |
|                 | Optimize flue gas temperature                 |                |
| Water losses    | Replace pipes                                 | 0.2-1%         |
|                 | Renew seals                                   |                |
|                 | Change valves and cocks                       |                |
| Blowdown losses | Retrofit continuously regulated blowdown      | 0.5-5%         |
|                 | Fit blowdown heat exchanger                   |                |
|                 | Correctly adjust blowdown valve               |                |
| Excess air      | Retrofit electronic compound regulator        | 0.5-1.5%       |
|                 | Retrofit O <sub>2</sub> and CO control system |                |
| Plumes of steam | Retrofit vent condenser                       | 0.3-4%         |
|                 | Retrofit deaerator control unit               |                |
|                 | Retrofit magnetic shut-off valve              |                |

## Table 4-14: Energy saving potential in different areas of an industrial combustion plant

# Combustion conditions

To achieve the complete combustion of POPs contained in the fuel, special attention has to be paid to the four cornerstones of high destruction efficiency: **temperature**, **time**, **turbulence** and **excess oxygen**. In this way, precursors are destroyed and soot formation is reduced, allowing fewer possible sites for solid catalysis in the cooling gas effluent. It is generally accepted that a temperature over 900°C and a gas residence time of 2 seconds are sufficient to achieve the complete oxidation of dioxins as long as the gas flow is sufficiently turbulent and excess oxygen is present.

The air-fuel ratio for every firing has to be precisely calculated and adjusted accordingly to obtain the required output. Each level of output or quantity of fuel requires an exact amount of air. A regulator is required to calculate how much air is needed for which quantity of oil and gas. Mechanical regulators are robust, easy to use and have an air curve for all fuels but the mechanical tolerance could result in excess amounts of air being used and might not compensate temperature variations [79].

With electronic compound regulation, a microcontroller adjusts all firing functions individually. For this purpose, each valve and trap has its own actuator which is individually programmed at each load point. This means that different programmes can be used for different fuels. By using precisely adjusted valves and traps, the fuel consumption can be drastically reduced, whilst allowing  $O_2$  and CO regulation.

The different densities of the hot and cold induction air have an effect on the oxygen transfer and may change fuel consumption significantly. Fixed regulation means that a burner set up in winter with little excess air may be operated in summer with an air deficit if the supply is not manually adjusted. A combined  $O_2/CO$  regulation always prevents an excess of air within a defined, lower range and equalizes the constant variations between temperature and pressure in the ambient air. It includes a broad regulation range for the  $O_2$  content. In addition, CO occurs as a stop signal. Gases are measured by a lambda wave in the waste gas stream and the measurement signals are used to regulate the amount of air. A lower quantity of excess  $O_2$  therefore results in fuel savings of up to 2 per cent.

# Heat recovery

Usually, the waste gas temperature is slightly above the medium temperature when heat is generated at 30-50 K, which represents the lowest threshold at which the waste gas can be cooled inside the boiler. Waste gas temperatures of 250° C or even 400° C downstream of thermal oil heaters therefore occur inside the plant. The residual heat contained in the exhaust gas can be partially recovered through heat exchange by using so-called economizers that preheat the feed water, or through air-to-air heat exchangers that heat the fresh air. Regardless of the type of heat exchanger, a retrofit achieves significant savings if the plant discharges large quantities of waste gas. As a rule of thumb, a 100 K reduction of the waste gas temperature saves 4 per cent of fuel, whatever the operating method.

An **economizer** passes boiler feed water through the waste gas stream at a temperature of  $103^{\circ}$  C, before it returns to the boiler, causing the temperature to increase from  $125^{\circ}$  C to  $135^{\circ}$  C while the waste gas is cooled down. This temperature should not be exceeded in order to avoid the condensation of the waste gas in the chimney, which may cause construction damage or corrosion. If the sulphur concentration in the waste gas is elevated, the temperature must be even higher. In addition, if the waste gases contain dust, the heat exchanger's geometry will have to be adjusted to prevent blockage. Using an economizer has been tested worldwide and it works: the higher the waste gas temperature the longer the full-load operation and the quicker the amortization.

Economizers must not be used, if the boiler contains high-pressure condensates or if thermal oil is used instead of water. In this case, **air-to-air heat exchangers (air pre-heaters)** are used. This type of heat exchanger uses the residual energy of the waste gas to heat the burner's combustion air and can reduce energy costs by over 5 per cent. Usually, however, the burner control has to be reconfigured, if the fuel-air ratio is altered.

If the waste gas is cooled again downstream of the economizer, condensate is formed. In this case, the so-called **condensing technology** can be used to recover condensation heat. It involves a heat exchanger in the waste gas with sufficiently cold surfaces, on which water vapour can condense. The heat exchanger must be made of stainless steel and is connected to a condensate removal system in order to avoid corrosion by the acidic condensate. The waste gas is cooled down to a temperature of 45 to 50°C and fresh water can be heated to approximately 60°C. A 50-per cent condensation of the waste gas may result in 5.5 per cent fuel savings.

Depending on the heat generator, it is also possible to combine all three heat recovery technologies, specifically economizers, condensing technology and air pre-heaters. The table below summarizes the potential energy savings achieved by these three technologies.

| Technology               | Medium   | Operational area   | Potential saving                            |
|--------------------------|--|--|---|
| Economizer               | Waste gases/water<br>Boiler supply water<br>pre-heated           | Downstream of heat<br>exchanger; for supply water  | 4-7%  |
| Air-to-air heat          | Waste gas/air  | Downstream of heat   | 4-10%                                       |
| exchanger                | Combustion air pre-<br>heated                                    | exchanger at high<br>temperatures (water tube<br>boilers, thermal oil heaters) or<br>recidual heat final phase | (water tube boilers,<br>thermal oil heater) |
|                          |  | residual heat final phase  | 0.5-4%                                      |
|                          |  |  | (final phase)                               |
| Condensing<br>technology | Waste gas/water<br>Prepared<br>water/process water<br>pre-heated | As second heat exchanger<br>downstream of an economizer<br>or air-to-air heat exchanger                        | 4-7%  |

# Table 4-15: Potential energy savings of different heat recovery technologies

# Blowdown

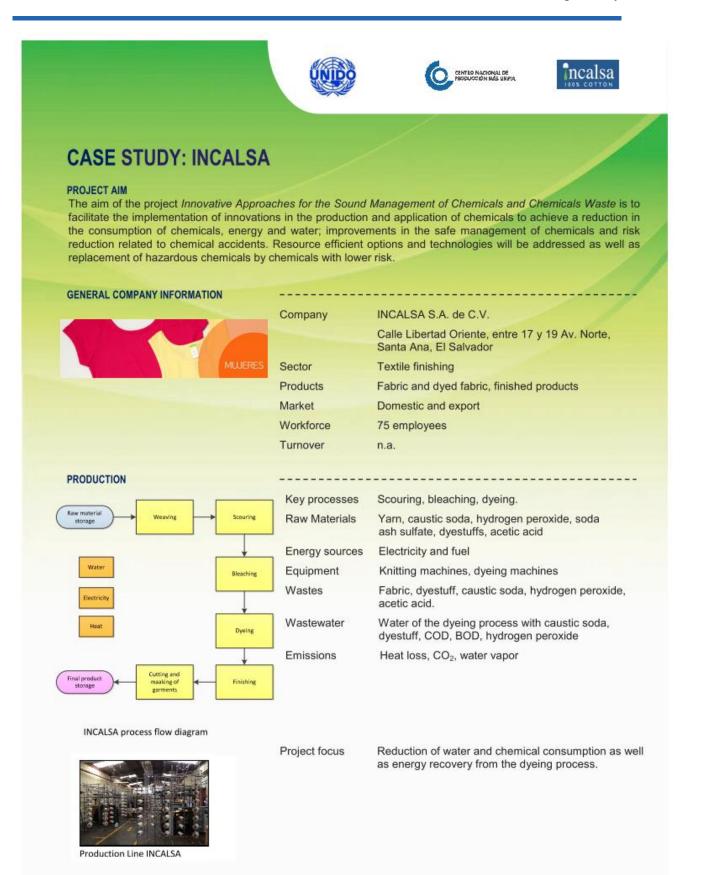
When vapour is removed from the boiler, salts are concentrated as water is continually added to the boiler. The amount of salt and additives depends greatly on the way the water was previously processed and is lowest in de-ionized supply water. The dissolved salts, particularly sodium hydrogen carbonate, are expelled from the boiler using the blowdown valve, with hot water being discharged along with the accumulated salt. The manual operation of the blowdown valve often results in unwanted water and energy losses, since the salt concentration is not always visible in the water. By continuously measuring the electrical conductance, an undesired high carbonate content of the water can be determined. Coupled with a regulator and an automatic blowdown valve, the conductance, and therefore the salt content in the boiler water, may be kept exactly below a set threshold level and no more water than necessary is discharged.

Using a blowdown cooler, the residual water may then serve to heat up additional water, which then flows from the water processor into the degasser.

These measures discharge cool salt water while heat and expensive supply water remain in circulation and can achieve energy savings of up to 5 per cent.

# 5 Case studies

The selected case studies with findings of assessments in the textile finishing industry which are presented below were elaborated in the project *Innovative Approaches for the Sound Management of Chemicals and Chemical Waste*.



Fact sheet Incalsa, February 2014, NCPC El Salvador, CSD/ISSPPRO

90

#### INNOVATION ASSESSMENT



Obsolete dyeing equipment PROCESS IMPROVEMENTS



Dyeing process improved: dyeing jet

#### BENEFITS



Steam system measures

INCALSA was approached to conduct an innovation assessment to determine the three basic technical components of increasing material and energy efficiency to produce more products with correspondingly less waste and pollutants, a reduction in toxicity of materials used and safety and risk reduction. Particular focus lied on the innovative solutions in these areas which were generated, implemented, monitored and documented together with the company representative.

The company implemented a condensate return system to raise the temperature of the water used in the boiler, induced insulation and repair of leaking pipes in order to make the process more energy efficient.

The company also replaced two existing dyeing machines by a jet dyeing machine with a capacity of 250 kg of fabric. This jet has a consumption of 6.5 kg of steam per kg of dyed fabric which makes the process more energy efficient vis-à-vis the existing dyeing machines with a consumption of 8.02 kg of steam per kg of dyed fabric.

The measures at the condensate system required a total investment of US\$ 6,057 with savings of US\$ 2,817 resulting in reductions of 1,055 gallons of fuel per year (46,720 kWh/year) which represents a reduction in emissions of 12 ton  $CO_2$  per year.

The implementation of the dyeing jet increased production output by 45% full load and reduced the dyeing time by 21%. and Further reductions of 170 kg of chemicals (Dispercol SNL, Secuestrante FA, Lubritex, Caustic Soda, Surfactol CC) were recorded and fuel reduction of 2,489 gallons per year (110 MWh/year) equivalent to 30 ton/a of CO<sub>2</sub>. This measure entailed an investment of US\$ 35,000 with annual savings of US\$ 7,100.

|                            | Environmental/Safety benefits |                              |                    |             |                           | Economic savings    |                 |  |  |
|----------------------------|-------------------------------|------------------------------|--------------------|-------------|---------------------------|---------------------|-----------------|--|--|
|                            | Chemical consumption          |                              | Energy consumption |             |                           |                     | Simple          |  |  |
| Clean Technology           | chemicals/year                | % reduction                  | kWh/year           | % reduction | Total Savings<br>[USD/yr] | Investment<br>[USD] | payback<br>[yr] |  |  |
| Steam system<br>measures   | 1,055 gal of<br>fuel/year     | 5.27% of fuel<br>consumption | 46,720             | 4.7         | 2,817                     | 6,057               | 2.2             |  |  |
| Dyeing Jet<br>Installation | 170 kg/year                   | 2.08                         | 110,225            | 11.0        | 7,100                     | 35,000              | 4.9             |  |  |

#### COMPANY STATEMENT

"INCALSA constantly develops new projects aimed at protecting the environment and develops garments with organic raw materials and natural colors, with energy and resource efficiency in order to satisfy customers with eco-friendly products."

### Owner: Mr. Mauricio Saade

FURTHER INFORMATION

El Salvador NCPC Calle El Lirio #19, Colonia Maquilishuat, San Salvador, El Salvador Tel: +503 22643210, Fax +503 22643210 Email: cnpml@cnpml.org.sv www.cnmpl.org.sv

Fact sheet Protecno, February 2014, NCPC El Salvador, CSD/ISSPPRO



# BENNINGER

# CASE STUDY: BENNINGER AG

### **PROJECT AIM**

The aim of the project *Innovative Approaches for the Sound Management of Chemicals and Chemicals Waste* is to facilitate the implementation of innovations in the production and application of chemicals to achieve a reduction in the consumption of chemicals, energy and water; improvements in the safe management of chemicals and risk reduction related to chemical accidents. Resource efficient options and technologies will be addressed as well as replacement of hazardous chemicals by chemicals with lower risk.

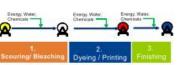
**GENERAL COMPANY INFORMATION** 



| Company   | BENNINGER AG   |  |
|-----------|--|--|
|           | Fabrikstrasse, CH-9240 Uzwil, Switzerland                                  |  |
| Sector    | Manufacturing of textile finishing machines                                |  |
| Products  | Bleaching, Mercerizing, Dyeing, Washing and Waste water recycling machines |  |
| Market    | Export 95%, Domestic 5%  |  |
| Workforce | 300 worldwide  |  |
| Turnover  | n.a.   |  |
|           |  |  |

#### PRODUCTION







Workflow processing knitwear



Benninger production line

| Continuous open width processing knitwear   |
|---|
| Cotton, viscose knitted fabric, chemicals and dyestuffs   |
| Steam, electricity  |
| Slitting, Singeing, Scouring/bleaching, Cold Pad Batch<br>dyeing (CPB), Washing machine, Drying and<br>Compacting machine |
| Dyestuff, chemicals, salt   |
| Hot water discharged at 40°C,<br>COD (approx. 4800 mg/l), BOD <sub>5</sub> (approx. 1600mg/l)<br>cooling water            |
| CO <sub>2</sub> , smoke, dust, wastewater, noise < 80dB   |
|   |

Project focus Replace obsolete exhaust (discontinuous) dyeing and finishing process by continuous open width process

Fact sheet BENNINGER AG, 12/09/2014, CSD/ISSPPRO

#### INNOVATION ASSESSMENT



Obsolete exhaust dyeing machine (Jet, Softflow machine)

BENNINGER AG was approached to conduct an innovation assessment to determine the three basic technical components of increasing material and energy efficiency to produce more products with correspondingly less waste and pollutants, a reduction in toxicity of materials used and safety and risk reduction. Particular focus lied on the innovative solutions in these areas which were generated, implemented, monitored and documented together with the company representative.



Instead of processing by batch method the continuous production method is much gentler to the fabric and quality aspects such as less hairiness, smoother surface etc. are improved. The workflow is optimized and productivity and efficiency can be increased from 70% to approx. 90%.

Workflow of continuous open width processing

#### BENEFITS

Processing knitwear by continuous open width method leads to big savings in regards to water, salt and steam. This method can replace dyeing on discontinuous softflow or jet dyeing machines. The process is suitable for all cellulosic fibres.

|                     | EXHAUST DYEING<br>vs. Continuous   |                            | 8                          | 8                          |
|---------------------|--|----------------------------|----------------------------|----------------------------|
|                     | Production : 10 tons per day   |                            | (LR 1:8)                   | (LR 1:5)                   |
|                     | Total Water<br>Total Energy (Steam)  | 220 m <sup>3</sup><br>19 t | 850 m <sup>3</sup><br>71 t | 610 m <sup>3</sup><br>52 t |
|                     |  |                            |                            |                            |
|                     | Total Salt   | 0.0 t                      | 4.0 t                      | 2.5 t                      |
|                     | Saving on 10 ton/d production  | Water<br>Steam<br>Salt     | 630 m3<br>52 l<br>4.0 t    | 390 m3<br>33 l<br>2.5 t    |
| COMPANY STATEMENT   | Processing knitwear by contin<br>savings in water, energy and (  |                            |                            |                            |
|                     | reduced water availability can   | still expand th            | eir production             |                            |
| FURTHER INFORMATION | reduced water availability can<br>BENNINGER AG   | still expand th            | eir production             |                            |
| FURTHER INFORMATION | reduced water availability can<br>BENNINGER AG<br>Mr. Jürgen Ströhle (CTO)   | still expand th            | eir production             |                            |
| FURTHER INFORMATION | reduced water availability can<br>BENNINGER AG   | still expand th            | eir production             |                            |
| FURTHER INFORMATION | reduced water availability can<br>BENNINGER AG<br>Mr. Jürgen Ströhle (CTO)<br>Fabrikstrasse                              |                            | eir production             |                            |
| FURTHER INFORMATION | reduced water availability can<br>BENNINGER AG<br>Mr. Jürgen Ströhle (CTO)<br>Fabrikstrasse<br>CH-9240 Uzwil/Switzerland | 71 955 85 47               |                            |                            |

Fact sheet BENNINGER AG, 12/09/14, CSD/ISSPPRO

KASAG

BENNINGER

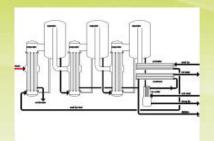


# CASE STUDY: BENNINGER AG

### **PROJECT AIM**

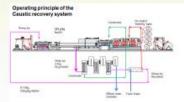
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**GENERAL COMPANY INFORMATION** 



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| Market    | Export 95%, Domestic 5%  |
| Workforce | 300 worldwide  |
| Turnover  | n.a.   |

## PRODUCTION



Flowchart caustic soda recovery station



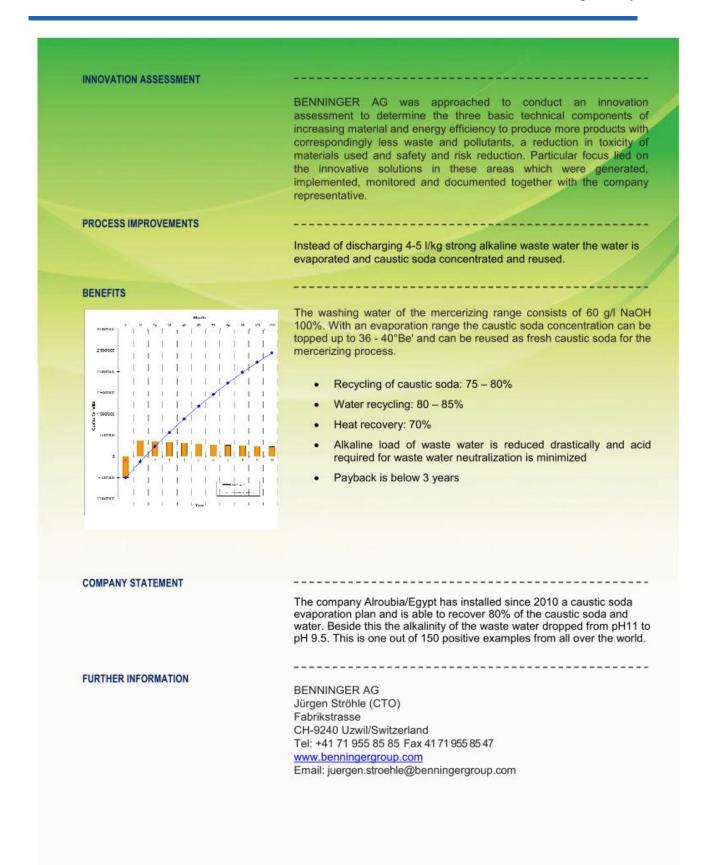
3-stage caustic soda recovery plant

| Caustic soda recovery station                     |  |
|---|--|
| Weak lye of 60 g/l NaOH 100%                      |  |
| Steam, electricity                                |  |
| Evaporation plant, tanks, filter, pumps           |  |
| Organic waste, short fibres                       |  |
| Hot water 40°C, condensate 90°C,<br>cooling water |  |
| Wastewater, noise <80dB                           |  |
| Recycling of caustic soda from the mercerizing    |  |
|   |  |

process

very plant

Fact sheet BENNINGER AG, 11.09.2014, CSD/ISSPPRO



Fact sheet BENNINGER AG, 12.09.14, CSD/ISSPPRO

95

# **6** Supporting policies

The implementation of innovative solutions for the sound management of chemicals and chemicals waste in the private sector is frequently hindered due to technical, financial, organizational and also political reasons. Thus, the creation of an enabling environment with stimulating policies helping overcome barriers is essential for enterprises.

The supplementation of national policy instruments at regional level considering local circumstances might be advantageous. For example, a national support programme for energy-efficient manufacturing processes might be linked with cantonal subsidies for renewable energy use and information-based instruments. In general, the following instruments facilitating the implementation of innovative process optimization measures in industry can be differentiated. A mix of these instruments has proved to be beneficial:

**Market-based instruments:** They internalize the environmental cost, i.e. the polluter pays, and take into account the "hidden" cost of production and consumption. For instance, a VOC tax compensates for the environmental cost of ozone formation. Market-based instruments also lead to technology innovation such as VOC-free products (paints, varnishes etc.) or waste gas burners.

**Regulatory instruments:** Command and control instruments typically form the basis of environmental policy frameworks and should be flexible. In Switzerland for instance, the handling of synthetic refrigerants (HFC) is restricted to trained personnel and the re-use of greenhouse gas (GHG) refrigerants is promoted. However, the substitution of HFC with environmentally sound and harmless natural refrigerants based on modern technologies is not facilitated at all, showing the one-sided approach of this instrument.

**Voluntary agreements:** They encourage businesses to improve their resource and energy efficiency beyond regulatory measures. The use of voluntary agreements in parallel with regulations, for instance  $CO_2$  legislation, is most useful. In some countries, an agreement between businesses and the government for the reduction of GHG emissions through energy efficiency is possible. This might lead to a more proactive behaviour and a shift from end-of-pipe thinking to increased efficiency.

**Monitoring:** Compliance monitoring with relevant indicators is crucial to detect violations and provide evidence to support enforcement actions. Second monitoring allows for assessing whether policies have been effective over the long term. In some European countries, regular monitoring inspections by parties contracted by the government are conducted for wastewater pollution and GHG emissions in industries.

**Education:** Training and outreach are relevant for the replication of resource efficiency in industry. For instance, through UNIDO's Resource-Efficient and Cleaner Production (RECP) Programme<sup>27</sup>, hundreds of workers were trained on the basics of industrial process optimization, and subsequent train-the-trainers programmes on RECP created the basis for further outreach in the countries involved.

**Overlapping instruments:** Some types of instruments overlap and can hamper each other. The enforcement of a  $CO_2$  regulation, for instance, can lead to a switch from fossil fuel to electricity consumption for heating. Electricity, however, is to be reduced as well and regulated too (for example through a national energy law). A coordinated approach is needed to ensure policy coherence.

In the following sections, supporting policies and instruments are summarized for the countries involved in the UNIDO initiative Innovative Approaches for the Sound Management of Chemicals and Chemical Waste.

<sup>&</sup>lt;sup>27</sup> UNIDO's Resource-Efficient and Cleaner Production (RECP) Programme: http://www.unido.org/cp. html

# 6.1 Market-based instruments to promote efficient technologies and preventive environmental practices

Market-based instruments aim at addressing the market failure linked to environmental externalities by changing the economic conditions. Incentives or disincentives are created to encourage or discourage specific behaviours. For instance, prompting businesses to internalize costs induced by their polluting activities (for example taxation, non-compliance fines, etc.) or creating property rights (for example tradable pollution permits) are two economic instruments. Other market-based instruments can be used to stimulate the use of efficient technologies and preventive environmental practices, including [80]:

- Grants, subsidies and financial assistance (for example the National Environmental Fund in Colombia, Subsidy for Technological Conversion to avoid the use of CFCs in Chile)
- Marketable permits
- Deposits and product charges
- Harmful subsidy removal
- Reduction in taxes, duties and fees
- Targeted technical assistance
- Liability rules (Enterprises are held responsible for the environmental damage they cause which often leads them to minimizing their risks and take preventive measures.)

Because market-based instruments act as cost-effective pollution control measures, they have shown to be more economically efficient in reaching pollution reduction goals than just regulatory instruments. They allow a greater flexibility in the choice of technology and prevention strategy and may also provide the government with a source of revenue. The latter can, for instance, be used to support other environmental initiatives enhancing the sustainable development of the country. Before introducing economic instruments, the government should carefully analyze the impact of each instrument on the society and the economy. Indeed, subsidies can be used to make local industries more competitive, which may lead to reduced energy prices and therefore increases in energy consumption, shortages and pollution.

# El Salvador - Market-based instruments

El Salvador has set a market incentive, known as the "Green Seal", to foster the sustainable and efficient use of natural resources and to promote processes and activities preventing the contamination of the environment. The seal was conceived as an instrument of differentiation for the goods and services produced in an eco-efficient way, as well as for those exported to international markets.

El Salvador also has a **tax incentive law** for the promotion of renewable energies in electricity generation. This law promotes the realization of investment projects based on the use of renewable energy through the use of hydraulic, geothermal, wind and solar resources, as well as the biomass for power generation.

The benefits and tax incentives of this law on electricity generation projects are:

- Projects up to 10 MW: exemption from income tax for a period of 10 years
- Projects between 10 and 20 (MW): exemption from income tax for a period of 5 years
- Projects up to 20 MW: exemption from the payment of customs duties on the import of machinery, equipment, materials and supplies for the first 10 years
- Total exemption from payment of all tax revenues directly from the sale of "Certified Emission Reductions" (CERs) under the Clean Development Mechanism (CDM) or similar carbon markets

# Colombian water quality policy and impacts on water quality

The Colombian water quality regulation is composed of five key elements [82]:

- **Registration and permitting**: Any discharger of liquid waste is required to obtain a discharge permit from the appropriate authority.
- **Discharge standards:** Discharge standards regulate the discharges of liquid waste in terms of location and quantity. None of these standards are industry-specific and firms may be inspected at any time to sample effluents and inspect equipment.
- **Licensing:** Prior to construction, facilities that intend to discharge liquid effluents are required to conduct an environmental impact assessment and hold a public hearing in order to obtain a licence from the environmental authorities.
- **Discharge fees:** Between 1997 and 2002, all water users discharging liquid effluents in lakes and rivers had to pay a monthly fee per unit of biochemical oxygen demand (BOD) and total suspended solids (TSS) discharged. Annual targets were set for the total quantity of BOD and TSS discharged into the same water basin by all the sources. If these targets were not met, the fees paid by the individual facilities were increased, every six months, by a factor of 0.5.
- **Quality standards:** They specify in considerable detail the maximum permissible levels of pollutants for each type of use.

Colombia's water quality regulation strategy, and especially the discharge fee programme, showed a significant and positive impact on the water quality, as pollution loads dropped dramatically. Indeed, according to a quality evaluation realized in 2002, the implementation of discharge fees reduced the total BOD discharge by 27 per cent and total TSS discharges by 45 per cent between 1997 and 2002.

# 6.2 Optimization of the use of natural resources and raw materials, minimization of emissions

The optimization of the use of natural resources and raw materials protects the environment, but provides also sustainable economic and business practices. One way of optimizing the use of resources is, for instance, by minimizing waste production. By setting objectives, defining and implementing resource optimization and waste reduction strategies, companies are able to:

- Gain efficiency in production practices by achieving greater output of product per unit input of natural resources and raw materials
- Improve the financial performance of the firm by using more efficient processes to reduce the raw material and natural resource input and, as a result, the related costs
- Enhance the firm's public image, as the environmental impact of a company and its willingness to protect the environment are important factors in its overall reputation
- Improve the quality of products manufactured by introducing new innovation and technological practices
- Meet targets set by environmental regulations, policies and standards. An environmentally responsible firm reduces its harmful emissions and impacts.

In general, governments and international organizations (for example ISO, the International Organization for Standardization) provide regulatory frameworks and guidelines to drive companies towards a more sustainable development. Below, examples of how different countries promote a more sustainable development country-wide are presented.

# Egypt

The Government of Egypt has set a strategy to implement a number of policies by 2022 to diversify energy resources and rationalize the energy needs of different activities without hindering the development plans. On 10 April 2007, the Supreme Energy Council in Egypt adopted a resolution on an ambitious plan aiming at increasing the contribution of renewable energy to reach 20 per cent of the total energy generated in 2020 (8 per cent hydro power and 12 per cent wind power). This target will be achieved by private-sector participation in financing, building, owning and operating wind farms in Egypt. By 2020, a total installed wind energy capacity of 7,200 MW producing about 31 billion kWh yearly should be reached. The latter should result in annual fuel savings of about 7 million tons of oil equivalent and 17 million tons of  $CO_2$  emissions.

## Colombia

Rates of water use, as well as rates for the use of other natural resources, are indirect signals to producers to promote the rational use of these resources. Pollution fees are also a strong signal to firms that an improvement in the firm's pollutant release should be considered. Other voluntary mechanisms contribute to reaching these goals, especially in Colombian firms:

- Environmental management systems in firms
- Clean production programmes
- Eco-labels
- Sustainable procurement
- Efficiency programmes for the use and conservation of water
- Clean energy programmes
- Post-consumer and chemicals management (SAICM/OECD programmes)

## Morocco

To reduce the emissions of greenhouse gases, the Moroccan energy programme will invest an estimated \$18.95 billion by 2020 and will create about 50,000 jobs. It predicts that, by 2020, electrical power produced by renewable energy (solar, wind and hydro power) will account for 42 per cent of the total power produced. The main objectives of this strategy are to:

- Decrease energy dependence
- Preserve the environment
- Limit greenhouse gas emissions
- Combat climate change

# 6.3 Reward for good environmental performance and practices

Rewards for good environmental performance and practices are an innovative way to raise awareness of cleaner production at company, industry and national levels.

### El Salvador award programmes

El Salvador has set up the National Environmental Award which is one of the incentives of the state to promote environmental management. For this award, the ministry has defined several categories. The Award for Business Efforts was established for private-sector companies which have carried out environmental restructuring in their processes. The winners receive a medal and/or an honourable mention. According to information provided by the ministry, during the period 1999-2007, 163 awards and honourable mentions were given for each of the existing categories. For the category "Business Efforts", 12 awards were granted for the same period.

The Cleaner Production Award is a strategy that the El Salvador Ministry of Environment and Natural Resources (MARN), the National Cleaner Production Centre (NCPC) El Salvador and the Central American Commission on Environment and Development (CCAD) have been promoting to the private sector to encourage and reward the companies implementing cleaner production as a tool for improving environmental performance and increase competitiveness.

The Energy Efficiency Award is a strategy that the National Energy Council and 21 organizations, including the NCPC, have been promoting to the private sector to encourage and reward the companies implementing energy efficiency as a tool for increasing competitiveness. This award was created by the programme "El Salvador is Saving Energy".

# 6.4 Minimization of practices leading to the exclusive use of end-ofpipe technologies

Environmental quality has often been built on regulation and authority control with specific targets and demands imposed by authorities on industries with very little flexibility with regard to reaching these requirements [81]. Such governmental control has improved the environmental conditions but also has some drawbacks such as encouraging the use of end-of-pipe technologies. Several environmental policy instruments, such as tax write-offs or financial support for environmental measures, also tend to sometimes support end-of-pipe measures and therefore work against the environmental preventive and cleaner production approach [80].

End-of-pipe technologies are generally used to control pollution rather than to prevent the pollution from happening. This approach most often comes down to fulfilling legal prescriptions and typically includes solutions like the reduction of waste and emissions through treatment units and filters. They generally also lead to higher additional costs compared to preventive and integrated solutions.

Pollution prevention and cleaner production approaches tackle the environmental problems at all levels and fields. Prevention of waste and emissions takes place at the source, and environmental protection is an integral part of process engineering. Environmental innovations are developed within the company and make environmental protection a permanent challenge. Moreover, prevention measures often help reduce costs by optimizing the material and resource consumption.

More recently, many authorities have developed a negotiated compliance approach to build cooperation strategies between the regulators and the regulated (companies, industries, etc.) to, for instance, set and enforce standards and promote an open exchange of information [81]. For example, the authorities might define the targets, but the means of reaching these targets are left to the hands of the companies [81]. This more flexible approach enables the adoption of innovative and preventive technologies.

In Colombia, for example, environmental preventive strategies are promoted in the productive general sectors through the Colombian policy of sustainable production and consumption.

# Morocco – National Programme for the Prevention of Industrial Pollution (PNPPI)

In Morocco, the PNPPI allows harmonization and planning of actions that the Administration and the private sector must achieve in order to prevent pollution. It promotes and implements prevention methods by focusing on the reduction of emissions and waste as well as on the compliance with environmental laws and regulations.

The specific objectives of the program are:

- Diagnosis of the current status and the technical, institutional and regulatory framework for the prevention and fight against various forms of industrial pollution
- Identification of priority actions to be undertaken
- Development of terms of reference for studies to be carried out

# 6.5 **Industry-lead initiatives**

The various industry sectors in the economy have very different environmental impacts. The System of Environmental and Economic Accounts (SEEA), an international standard developed within the UN system, is used to assess the environmental impact of the different industries in a country and helps in identifying the domains the environmental policies should be focused on.

In Peru, illegal gold mining has been identified as a major issue in terms of environmental impact and pollution. Indeed, illegal gold mining has led to high mercury and lead contamination in the Peruvian rainforest. The Peruvian Ministry of Environment has formalized a programme to address this environmental issue.

# **Peru** – Chemical industry-lead initiatives

In the chemical industry, different projects and technical committees aim to improve and develop the sustainable formulation, production and use of chemical substances. The following programmes and committees are managed by the Peruvian Ministry of Environment:

## SAICM (Strategic Approach to International Chemicals Management)

The objective of SAICM is to strengthen the institutional capacities, regulations and techniques for managing chemicals in Peru. One output of this project was a toolkit on chemical management. The project was implemented by the Centro de Ecoeficiencia y Responsabilidad Social (CER) and the Ministry of Health with support of UNIDO from 2009 to 2011.

# "Technical Group for Chemicals" (Grupo Tecnico de Sustancias Quimicas)

In 2002, the Technical Group for Chemicals (GTSQ) was formed. It is responsible for coordinating integrated actions on chemicals and implementing the Stockholm Convention on Persistent Organic Pollutants, the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade and the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal.

# 6.6 Regulatory instruments: command and control for environmental protection and safety

Regulatory instruments are used to set a legal framework in order to control the environmental impacts of industries by defining prohibited or permitted conduct and to establish procedures for certain environmentally risky activities. Public authorities usually set environmental standards and goals, and then inspect, monitor and punish transgressions with legal sanctions. A sound legal framework promoting environmental protection and safety is generally achieved in the following cases [82]:

- The public and private sector cooperate in the elaboration of environmental policies and regulations.
- The regulatory framework promotes continuous innovation by not specifying any particular technology.
- The decisions on innovations generated to comply with the regulation are taken by industry and not the regulatory entity.
- Environmental regulations do not promote end-of-pipe solutions but innovations designed to reduce resource consumption
- Low levels of compliance with the standards are not accepted.
- Incentives are created for the private sector, etc.

Examples of regulatory instruments for environmental protection and safety include [80]:

- Environmental standards and regulations
- Product bans and trade restrictions (for example cadmium, pesticides, CFCs)
- Quotas for raw material depletion (for example a forestry law in Costa Rica prohibiting exports of unprocessed timber)
- Facility operation standards and permits
- Liability assignment

# El Salvador – Environmental regulatory instruments

El Salvador has a Cleaner Production Policy whose main objective is to incorporate ecological efficiency and effectiveness in the environmental performance and competitiveness of companies, minimizing pollution by the implementation of preventive actions in services, technologies and production processes.

During the governmental programme "País Seguro" (2004-2009), an environmental strategy was established that consisted in the establishment of voluntary agreements for cleaner production between companies and the Ministry of Environment and Natural Resources (MARN) to gradually restructure production processes into cleaner processes.

Voluntary Agreements for Cleaner Production (AVPL) are instruments of the environmental policy, based on an agreement between the private sector and the competent public administration. They are legally binding and seek to achieve specific environmental objectives and competitiveness.

# Egypt – Environmental policy framework

The environmental policy of the Government of Egypt seeks to achieve environmental protection through the establishment of proper institutional, economic, legislative and technical frameworks at the local, regional, national and international levels. This is expressed through the seven directives of the policy statement of the Minister of State for Environmental Affairs (MSEA):

- 1. Strengthening partnerships at the national level
- 2. Supporting bilateral and international partnerships in the environmental fields
- 3. Enforcing Law 4 of 1994 and Law 9 of 2009 for the protection of the environment, and Law 102 of 1983 for natural protectorates as well as all other environmental legislation
- 4. Supporting institutional strengthening and capacity building for the Egyptian Environmental Affairs Agency (EEAA) and Environmental Management Units (EMUs) of the governorates
- 5. Supporting integrated environmental management systems
- 6. Integrating the use of market-based instruments in the field of environmental protection
- 7. Transferring and adapting environmentally friendly technologies

Within the national environmental policy framework, an Egyptian Environmental Policy Programme was initiated in 1999 with the support of the United States Agency for International Development. Based on this programme, the Government of Egypt implemented its priority environmental policy objectives and measures, through institutional and regulatory reforms, with a focus on a number of areas. These included economic and institutional constraints, cleaner and more efficient energy use, reduced air pollution, improved solid waste management, sustainable tourism as well as nature conservation.

Within this policy framework, institutional and regulatory reforms are carried out, aiming at the implementation of national environmental policy objectives and measures. The implementation of the environmental policies of the Government of Egypt, as expressed by the policy framework and directives of the MSEA, is undertaken with regard to four main principles underlying environmental management and protection initiatives:

- 1. Strengthening the integrative capacity of central and local government
- 2. Strengthening of public-private partnerships
- 3. Partnerships with environmental non-governmental organization
- 4. Integration of gender issues in environmental policies and programmes

# 7 **Funding of innovations**

In many countries, the lack of attractive financial conditions is a barrier to comprehensive investments in new technologies in companies, thus also limiting the success of clean, innovative and environmentally sound technologies. That is why numerous alternative finance instruments were developed in the past to facilitate industrial investments. In the following section, selected instruments are presented as examples in countries within the scope of the present UNIDO project.

# 7.1 Funding in Peru

# 7.1.1 Green Credit Trust Fund

The Green Credit Trust Fund (GCTF) was initiated in Peru in 2004 by the State Secretariat for Economic Affairs (SECO). It is oriented towards supporting sustainable industrial production initiatives in small and medium enterprises. The GCTF supports projects related to eco-efficiency and technological reconversion up to a maximum amount of \$1 million worth of credit. To benefit from the fund, the enterprise must seek to improve its processes through green technologies. Projects that only aim to fulfil legal requirements are not supported by the credit fund.

To qualify for the GCTF, the enterprise must be registered in Peru, have a maximum of 25 per cent of foreign capital and be legally independent from any international organization. The GCTF is available to manufacturing companies but SMEs in this sector must not own more than \$8.5 million worth of fixed assets and must not have more than 500 employees.

The company first applies for the credit through one of three different intermediary financing institutions (Banco de Crédito del Perú, Interbank and Scotiabank del Perú). Then, the enterprise selects environmental indicators, in consultation with the Peruvian NCPC. Next, an evaluation of whether the new technology will improve the production and reduce the environmental impact of the company is undertaken. Once the new technology is installed, the indicators are monitored and a report based on the improvements is sent to SECO.

SECO can also provide a guarantee of 50 per cent if required. If the report shows significant improvements of the enterprise's environmental performance, the company receives a reimbursement from SECO.

The reimbursement levels are based on the credit amount or the investment amount, whichever the smaller of the two. The levels are the following:

- 15 per cent reimbursement for 30 per cent worth of environmental improvement
- 25 per cent reimbursement for 50 per cent worth of environmental improvement

There are no intermediate levels for the reimbursement.

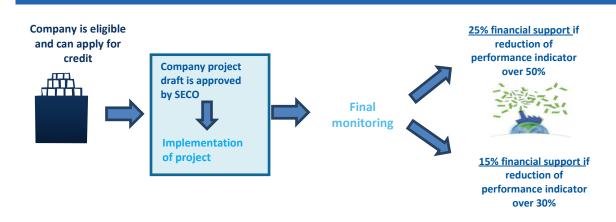


Figure 7-1 : The Green Credit Trust Fund [87]

Since the beginning of the initiative, 17 projects have been approved, with a total amount of more than \$4.3 million.

The GCTF concept has proven to be operational. The success is embedded in combining a financial instrument with Sustainable Enterprise Development (SED) centres which have extensive environmental know-how (for example in Peru Centro de Ecoeficiencia y Responsabilidad Social (CER)). With the GCTF, no direct interferences in finance markets occur, which allows banks to assume their role as agents to analyze the creditworthiness of investments.

Most of the investments prove to be win-win solutions improving the economic aspects as well as reducing the environmental impacts of the companies. Some projects even improve social aspects, thus clearly demonstrating the potential of environmentally sound technologies (ESTs). With the GCTF, SED centres get access to clients who potentially have projects related to cleaner production.

# 7.2 Funding in El Salvador

# 7.2.1 FONDEPRO

The Productive Development Fund (Fondo de Desarallo Productivo, FONDEPRO) is an incentive created to promote the development of quality, productivity and innovation, and to support the adoption and implementation of technological improvements leading to cleaner production processes. The fund supports the competitive strengthening of small and medium enterprises by co-financing up to 60 per cent of the total cost of a project or timely initiative.

The fund has two co-financing models:

- Fast track model: support of up to \$15,000 for a project focused on a specific activity
- Support of up to \$100,000 for a project combining multiple activities

Annual sales must not exceed \$7 million and the enterprise must be located in El Salvador.

From 2002 to 2008, 718 projects were supported through the fast track model, which represents a placement of more than \$1.3 million.

# 7.2.2 BANDESAL-KfW Environmental Conversion Line

El Salvador's bank for development BANDESAL (Banco de Desarollo de El Salvador) contracted with the German development bank KfW a three-phase credit line for the environmental conversion of companies. For the first phase from 2007 to 2010, \$10 million were released, with \$500,000 non-refundable and allocated for technical assistance in environmental projects. For the second phase from 2011 to 2013 and the third phase, respectively \$27 million and \$50 million were released.

105

The main objectives of the programme are to contribute to the reduction of environmental pollution, to promote the efficient use of natural resources by small and medium enterprises and to deepen the financial system by establishing long-term instruments for environmental investments for companies located in El Salvador. This programme supports entrepreneurs willing to invest in more efficient and environmentally friendly production processes. For an environmental project, the credit limit is set to \$500,000. For a project concerning renewable energies, a credit of a maximum of \$4 million can be provided (projects of more than \$500,000 require an authorization by KfW). The credit finances up to 80 per cent of the value of the investment and has a fixed yearly interest rate of 3.6 per cent for the life of the loan.

With the technical support of the NCPC, the credit line has assisted 28 small and medium enterprises since 2010.

The benefits obtained in these 28 companies are, in average, the following:

- Energy consumption reduced by 6.7 per cent
- Fuel oil consumption reduced by 8.4 per cent
- Savings of \$1.1 million achieved per year
- Investments of \$1.3 million
- 2,300 tons of CO<sub>2</sub> emissions avoided per year

# 7.3 Funding in Egypt

# 7.3.1 Private Public Sector Industry Project

The Private Public Sector Industry (PPSI) Project aims to protect the environment by contributing to the reduction of industrial pollution. PPSI focused on private and public industrial establishments in Upper Egypt and the Delta, and operated from 2008 to 2012. PPSI was implemented by the Egyptian Environmental Affairs Agency and supported by KfW under the German financial cooperation with Egypt.

Grants covering 20 to 30 per cent of the pollution abatement investment costs, with a maximum of \$1 million, were provided for eligible sub-projects. Preferential treatment was applied to SMEs (companies with a turnover of less than \$2.8 million) and at least 30 per cent of the investment funds were allocated for SMEs. The second phase of PPSI ended in 2012. The third phase has not yet started.

# 7.3.2 Environmental Compliance Office Revolving Fund Programme

The Environmental Compliance Office (ECO) was set up in 2002 by the Egyptian Government and the Danish International Development Agency (DANIDA) to assist in achieving compliance in industry. A cooperation agreement was signed in February 2005 between the Egyptian Environmental Affairs Agency (EEAA), the Federation of Egyptian Industries (FEI) and the National Bank of Egypt (NBE) for the purpose of operating the ECO Revolving Fund to invest in new equipment.

DANIDA provided funds equivalent to more than \$11 million to be allocated within the industrial sector to support initiatives aiming at abating pollution, encouraging safe working conditions and ensuring environmental legislative compliance. The revolving fund provided enterprises with the opportunity to make economic benefits and ensure proper compliance with environmental laws.

Small and medium enterprises being members of the FEI are eligible to apply. Loans can reach up to \$420,000 per enterprise with a 2.5 per cent interest rate per year. Loans are repaid over 5 years and funds are reused for financing new cleaner production initiatives in other enterprises.

## 107

# 7.4 Funding in Morocco

# 7.4.1 National Fund for the Environment (FNE)

The National Fund for the Environment is a financial incentive instrument established in 2004 for the protection and valorization of the environment. This fund aims at:

- Funding programmes for domestic and industrial water treatment
- Financing solid waste management programmes
- Financing pilot projects for the environment

# **7.4.2** Fund for Industrial Depollution (FODEP)

FODEP promotes the environmental upgrading through technical and financial support of industrial companies. The subsidy covers up to 40 per cent of the investment, with a maximum of \$625,000.

# 7.4.3 Voluntary Mechanism of Industrial Wastewater Treatment

This programme is funded by the Moroccan state and aims at encouraging industrial companies to invest in wastewater treatment processes. Industrial volunteers can benefit from a subsidy covering up to 40 per cent of the investment cost, with a maximum amount of \$625,000 for individual projects and \$1.25 million for collective projects.

# 7.4.4 Business Advisory Service Programme

Launched by the European Bank for Reconstruction and Development (EBRD), this programme aims at developing the expertise and local consultancy through technical and financial support to consulting assignments. The financial support covers 50 to 75 per cent of the mission's expenses. Moroccan companies with a turnover of less than \$68.2 million can benefit from this programme. Beneficiaries can be supported for the realization of:

- Technical studies: planning/architectural design, space optimization, IT infrastructure design, selection of machinery and equipment, installation, training
- Quality management system and certification: ISO 9000, Hazard Analysis and Critical Control Points (HACCP)
- Energy efficiency and environmental impact reduction: energy audit, mechanism for clean growth, renewable energy, environmental impact assessment, ISO 14000 implementation

# 8 Where do I find support?

The identification and implementation of innovative solutions and alternatives for chemicals and chemical waste management require extensive know-how of logistic processes, technical requirements, optimization techniques, standards and legal requirements. If a thorough analysis of possible innovations cannot be completely undertaken by a competent and experienced team within the company, the participation of external experts is highly recommended.

For assistance on innovative chemical solutions, the National Cleaner Production Centre (NCPC) Programme offers services such as RECP assessments on energy and resource efficiency, technology gap assessments and generation of process optimization measures.

NCPC representatives in the five countries involved in the project *Innovative Approaches for the Sound Management of Chemicals and Chemical Waste* can be reached at:

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Further information and contacts please refer to the UNIDO NCPC website at www.unido.org.

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# Appendices

# **Appendix 1: Important auxiliaries and basic chemicals used in textile production**

Table A1-1: Auxiliaries and basic chemicals in textile production [based on 10]

| Process   | Auxiliary  | Effect  | Chemical composition  |
|---|--|---|---|
| Manufacturing of<br>man-made fibres,<br>coning, texturizing,<br>spinning, twisting,<br>winding, warping,<br>weaving, knitting | Preparation<br>agents<br>(preparation<br>agents for<br>primary spinning,<br>lubricants,<br>conditioning<br>agents, coning<br>oils, warping<br>oils, twisting oils,<br>knitting oils) | Increasing processability,<br>protection of fibres/yarns;<br>adjusting of friction<br>properties; imparting anti-<br>electrostatic properties;<br>improvement of coning,<br>texturizing, etc. | Mineral oils, common fatty<br>acid esters, ethylene oxide-<br>propylene oxide adducts,<br>hindered fatty acid esters,<br>polyolester, polyester-<br>polyethercarbonates,<br>silicones, additives<br>(emulsifiers, antistatic<br>agents, corrosion<br>inhibitors, anionic/non-<br>ionic surfactants) |
| Sizing  | Sizing agents<br>Sizing additives  | Protection of warp yarns<br>during weaving (applied in<br>weaving mills)  | Macro-molecular natural<br>or synthetic products<br>(starch, modified starch,<br>modified celluloses,<br>polyvinyl alcohol,<br>polyacrylates, polyesters)<br>Additives (oils, waxes,<br>starch solubilizing agents<br>(peroxides))  |
| Pre-treatment   |  |   |   |
| All pre-treatment steps   | Fibre protecting agents  | Protection of the fibre and<br>reduced strain on he fibre<br>during pre-treatment<br>processes  | Protein fatty acid<br>condensates and<br>Guanidinium derivatives  |
| Desizing  | Desizing agents  | Removal of sizing agents  | Enzymes (amylases) for<br>enzymatic desizing; mono-<br>and di-persulphates for<br>oxidative desizing;<br>surfactants, complexing<br>agents  |
| Scouring<br>(kierboiling)   | Scouring<br>auxiliaries  | Removal of fibre by-<br>products (fats, waxes,<br>pectins, inorganics, etc.)<br>from cellulose fibres in<br>cellulose materials or<br>blends of cellulose fibres<br>with synthetic fibres     | Strong alkali; alkaline-<br>resistant and electrolyte-<br>resistant surfactants (fatty<br>alcohol ethoxylates, alkane<br>sulphonates), complexing<br>agents   |
| Bleaching   | Bleaching<br>auxiliaries   | Bleaching, whitening  | Peroxide, sodium chlorite,<br>sodium hydroxide,<br>dithionite and dithionite  |

| Process                              | Auxiliary   | Effect  | Chemical composition  |
|--------------------------------------|---|---|---|
|                                      |   |   | derivatives, complexing<br>agents, surfactants stable in<br>acidic or alkali conditions,<br>silicates, polycarboxylic<br>acids, sugar polymers as<br>peroxide stabilizers,<br>nitrates (anti-corrosion),<br>polyacrylamide (crease-<br>preventing) sodium<br>sulphite, enzymes<br>(catalases) to remove<br>peroxide surplus |
| Mercerizing                          | Mercerizing<br>auxiliaries                            | Increase in dyestuff uptake<br>and tensile strength of<br>textiles by means of alkali<br>treatment under tension                                | Strong alkali (sodium<br>hydroxide; ammonia);<br>wetting agents, stable in<br>highly concentrated lyes<br>(low molecular weight<br>alkyl sulphates, alkane<br>sulphonates), antifoaming<br>agents as shorter-chain<br>alkyl phosphates,<br>complexing agents  |
| Causticizing                         | Causticizing auxiliaries                              | See mercerizing (no tension applied to textile)   | See mercerizing   |
| Carbonizing                          | Carbonizing<br>auxiliaries                            | Removal of vegetable<br>impurities with acid or<br>acid salts   | Strong sulphuric acid, acid-<br>stable wetting agents (alkyl<br>arylsulphates, alkane<br>sulphonates, fatty alcohol<br>ethoxylates)   |
| Optical bleaching                    | Fluorescent<br>brighteners                            | Whitening   | Stilbene, pyrazoline or benzeneazole derivatives  |
| Dyeing/Printing                      |   |   |   |
| Dissolving of<br>dyestuffs           | Dyestuff<br>solubilizing and<br>hydrotropic<br>agents | Promotion of the<br>dissolution of dyestuffs in<br>water  | Alcohols, polyols, fatty alcohol ethoxylates, esters  |
| Dissolving of<br>dyestuffs           | Dispersing agents<br>Protective<br>colloids           | Promotion of the<br>formation and stability of<br>dyestuff and pigment<br>dispersions   | Naphthalene sulphonic acid<br>formaldehyde condensates,<br>naphthalene sulphonates,<br>lignosulphonates, fatty<br>alcohol ethoxylates, alkyl<br>sulphonates, alkylaryl<br>sulphonates, polyacrylates  |
| Exhaust dyeing,<br>padding processes | Wetting agents<br>De-aeration<br>agents               | Increase of wetting<br>capacity of the dye liquors;<br>improvement of dye<br>penetration in padding<br>processes; increase of dye<br>absorption | Alkyl sulphates, alkane<br>sulphonates, alkylaryl<br>sulphonates, salts of<br>sulphosuccinic acid esters,<br>fatty alcohol ethoxylates,<br>alcohols of higher valence,<br>phosphoric acid esters,   |

| Process   | Auxiliary   | Effect   | Chemical composition  |
|---|---|--|---|
|   |   |  | hydrocarbons, sequestering agents   |
| Levelling Retarding agents<br>Migration agents<br>Compensating<br>agents<br>Penetrating<br>agents |   | Promotion of an even<br>distribution of dyestuffs in<br>the textiles   | Alkyl-, alkyl aryl-, alkyl<br>amine- and alkyl aryl<br>amine ethoxylates, fatty<br>acid esters and amides,<br>fatty acid ethoxylates, fatty<br>acid condensates,<br>sulphonated PES<br>derivatives, polyvinyl<br>pyrrolidone, quaternary<br>ammonium salts, alkyl<br>sulphates, alkyl aryl<br>sulphonates |
| Exhaust dyeing<br>(esp. PES,<br>PES/WO)   | Carriers  | Acceleration of dye<br>absorption, dye diffusion<br>esp. for PES and PES/WO<br>dyeing  | Aromatic hydrocarbons,<br>chlorinated aromatic<br>compounds, benzoic acid<br>esters (benzyl benzoate)<br>phthalic acid esters, alkyl<br>phthalimides, alkylphenol<br>ethoxylates  |
| Skein dyeing of piece goods   | Crease<br>preventing agents   | Crease preventing esp.<br>during skein-dyeing of<br>piece goods  | Polyglykolethers,<br>polyamide, polyacrylates,<br>fatty alcohol ethoxylates,<br>phosphoric acid esters,<br>fatty acid esters  |
| Exhaust dyeing  | Dyestuff<br>protecting agents,<br>boildown<br>protecting agents             | Protection of dyestuffs<br>during application from<br>destruction by foreign<br>matters with a reducing<br>effect                          | Buffers and/or oxidizing<br>substances (nitrobenzene<br>sulphonate), urea, alkylaryl<br>sulphonates   |
| Padding   | Padding<br>auxiliaries<br>Antimigration<br>agents<br>Antifrosting<br>agents | Prevention of undesired<br>migration of dyestuffs in<br>or onto the textile<br>Prevention of frosting<br>effects in pad-steam<br>processes | Polyacrylates,<br>polyacrylamides, EO/PO-<br>adducts, alkyl phosphates,<br>alkyl aryl ether sulphates,<br>alginates, polyacrylates,<br>EO/PO-adducts, guar<br>derivatives, polyacrylamide<br>polymers and copolymers,<br>foaming surfactants as<br>ethylene oxide adducts                                 |
|   | Wet pick-up<br>increasing<br>substances                                     | Increase of dye yield in<br>reactive pad batch<br>processes  | Polyacrylates, EO/PO<br>adducts, alkyl aryl ether<br>sulphates  |
| Continuous dyeing,<br>printing  | Fixing<br>acceleration for<br>continuous<br>dyeing and<br>printing          | Acceleration of dye<br>fixation and diffusion,<br>increase of dyestuff yield   | Aromatic ethers, fatty acid<br>ethoxylates, polyglycols   |

| Process                             | Auxiliary  | Effect   | Chemical composition   |
|-------------------------------------|--|--|--|
| After-treatment                     | After-treatment<br>agents for<br>fastness<br>improvement | Improvement of rubbing<br>fastness, wet fastness and<br>light fastness   | Soaping after-treatment<br>with detergents or dye-<br>affinitive polymers.<br>Cationic fixing agents for<br>direct and reactive dyes<br>(polyquaternary ammonium<br>compounds, cationic<br>formaldehyde condensates.<br>Polysulphonates for<br>improvement of polyamide<br>dyeing with anionic<br>dyestuffs. Reducing agents<br>for PES. Heterocyclic<br>compounds to improve<br>light fastness<br>(benzophenone,<br>benzotriazole, benztriazine<br>derivatives) Organic copper<br>compounds or<br>benzophenones for the<br>improvement of light<br>fastness of PA resp. PES |
| Pigment dyeing,<br>pigment printing | Bonding agents<br>(also for pigment<br>dyeing)           | Fixing of inorganic and<br>organic pigments onto the<br>textiles (pigment printing)  | Film-forming substances<br>(styrene butadiene<br>copolymers, polyacrylates,<br>acrylate copolymers,<br>polyurethane  |
| Printing paste<br>manufacturing     | Thickeners   | Adjusting of viscosity<br>required in printing pastes  | Alginates, galactomannans,<br>modified starch,<br>polyacrylates,<br>polysaccharide<br>combinations, additives,<br>esp. mineral oils  |
| Printing paste<br>manufacturing     | Emulsifier   | Dispersion of the pigments<br>in the printing paste  | Alkylarylethoxylates<br>(APEO), fatty alcohol<br>ethoxylates, isopropanol,<br>N-methylpyrrolidone  |
| Pigment printing                    | Fixation agents  | Cross-linking of bonding agents  | Melamine derivatives, urea formaldehyde condensates  |
| Printing                            | Agents to remove<br>printing<br>thickeners               | Removal of printing thickeners   | Alkylamine ethoxylates,<br>fatty acid ethoxylates, fatty<br>alcohol ethoxylates  |
| Printing                            | Printing and edge<br>adhesives                           | Printing adhesives fasten<br>the goods to be printed<br>onto the printing blanket<br>Edge adhesives (edge<br>stiffening agents) for the<br>hardening of edges, so that<br>they do not role up in case<br>of treatment in broad form<br>(also used in pre-treatment | Water-soluble adhesives<br>(starch, starch derivatives,<br>vegetable gum, polyvinyl<br>alcohol, polyvinyl-<br>caprolactam, polyacrylate<br>etc.). Water-insoluble<br>compounds (polyvinyl<br>acetate, polyacrylic acid<br>esters). Polyvinyl alcohol,  |

| Process                                     | Auxiliary  | Effect  | Chemical composition  |
|---|--|---|---|
|   |  | and dyeing)   | polyvinyl chloride,<br>polyacrylic acid esters,<br>polyvinyl acetate  |
| Dyeing and printing                         | Oxidizing agents                                   | Oxidizing of reduced<br>forms of vat dyes, leuco<br>ester, vat dyes and sulphur<br>dyes<br>Stripping (removal) of<br>dyes and auxiliaries from<br>the fibre   | Peroxo compounds, sodium<br>perborate, sodium<br>persulphate, sodium<br>chromate, salts of m-<br>nitrobenzene sulphonic<br>acid, bromite<br>Sodium chlorite   |
| Dyeing and<br>printing                      | Reducing agents                                    | Reduction of vat and<br>sulphur dyes in order to<br>make them water-soluble<br>Removal of dispersion<br>dyes (reductive after-<br>treatment) Destruction of<br>dyes in case of faulty<br>dyeing (stripping) | Vat dyes: sodium<br>dithionite, sulphinic acid<br>derivatives. Sulphur dyes:<br>sodium sulphide, sodium<br>dithionite, glucose and<br>mixtures thereof.<br>Sodium dithionite, thiourea<br>dioxide.<br>Sodium dithionite, sodium<br>or zinc formaldehyde<br>sulphoxylates, thiourea<br>dioxide |
| Discharge printing                          | Discharging<br>agents<br>Discharging<br>assistants | Discharging agents are<br>printed onto a pre-dyed<br>textile material for the<br>destruction of the dyes and<br>thus cause a pattern  | Reducing and oxidizing<br>agents (see above)<br>Anthraquinone derivatives   |
| Dyeing, resist<br>printing                  | Resist agents                                      | Reduced or complete<br>prevention of<br>dyeing/printing   | Dyeing: inorganic salts,<br>tannins, alkyl aryl -, aryl-,<br>alkane sulphonates,<br>aromatic sulphonates,<br>anionic or polyanionic<br>compounds<br>Printing: aluminium and tin<br>salts, alkali compounds  |
| Dyeing and<br>printing with<br>mordant dyes | Mordants   | Improvement of dye affinity of the fibre  | Quaternary ammonium<br>compounds, Al-, Cr-, Fe-<br>salts  |
| Dyeing, colour<br>correction                | Brightening<br>agents                              | Partial removal of the dye<br>already absorbed and fixed  | Polyvinylpyrrolidone,<br>polyglycol ether, cellulase,<br>alkyl aryl sulphonates,<br>alkyl amine ethoxylates,<br>reducing agents and<br>oxidizing agents   |
| Dyeing, fibre<br>protection                 | Fibre-protective agents                            | Prevention or reduction of<br>damage to the fibre during<br>dyeing, finishing   | Protein hydrolysates,<br>polyglycol ether, protein<br>fatty acid condensates,<br>lignosulphonates,<br>formaldehyde eliminating  |

| Process             | Auxiliary  | Effect   | Chemical composition   |
|---------------------|--|--|--|
|                     |  |  | products (urea derivatives),<br>guanidine derivatives  |
| Dyeing in general   | pH-regulators,<br>acids and alkali<br>dispensers                                 | Adjustment/control of pH values  | Organic acids, esters,<br>buffering salts  |
| Dyeing in general   | Salts  | Increase of substantivity<br>for reactive and direct<br>dyes; levelling effect on<br>acid dyes, etc. | Sodium chloride, sodium sulphate, etc.   |
| Dyeing in general   | Acids/alkalis  | Adjustment of pH value   | Organic acids (mainly<br>acetic acid, formic acid,<br>oxalic acid), inorganic<br>acids (sulphuric acid,<br>hydrochloric acid); sodium<br>hydroxide, ammonia (in<br>water), sodium carbonate  |
| Finishing           |  |  |  |
| Optical brightening | Fluorescent<br>brighteners   | See pre-treatment  |  |
| Easy-care           | Agents for the<br>improvement of<br>crease and shrink<br>resistance<br>Additives | Increase of crease recovery<br>and/or dimensional<br>stability of textile<br>materials               | Dimethylolurea and<br>dimethylolurea-derivatives,<br>1,3-dimethylol-4,5<br>dihydroxy-ethylene urea<br>and derivatives, melamine-<br>derivatives, carbamates,<br>cyclic urea compounds.<br>Polyethylene dispersions,<br>silicone emulsions<br>Metal or ammonium salts |
|                     |  |  | and preparations of acids or alkalis   |
| Handle              | Handle imparting agents  |  |  |
|                     | Weighting agents   | Increase the basic weight of textiles  | Pigments (kaolin, talcum);<br>soluble compounds (urea,<br>glycerine, salts)  |
|                     | Filling and stiffening agents  | Impart of a full handle and<br>increase of stiffness<br>(bending modulus)                            | Polyacrylates, polyvinyl<br>acetate, polyurethane,<br>polyvinyl alcohol,<br>ethylene-vinylacetate-<br>copolymers, starch,<br>modified starch   |
|                     | Softening agents   | Impart of a soft handle  | Fatty acid condensation<br>products, alkanolamides,<br>waxes, paraffines,<br>polysiloxanes,<br>polyethylene, quaternary<br>ammonium compounds  |

| Process                    | Auxiliary                                       | Effect   | Chemical composition  |  |
|----------------------------|---|--|---|--|
| Anti-electrostatic         | Anti-electrostatic<br>agents                    | Prevention of electrostatic charging   | Ethoxylation products of<br>fatty acids, alkane<br>sulphonates, alkyl aryl<br>sulphonates, phosphoric<br>acid esters, quaternary<br>ammonium compounds,<br>alkylamine oxides                    |  |
| Repellents                 | Water repellents                                | Impart of a water-proof finish   | Fluorocarbon resins,<br>polysiloxanes, paraffins<br>together with aluminium,<br>zirconium and chromium<br>compounds   |  |
|                            | Oil repellents                                  | Impart of an oil-repellent finish  | Fluorocarbon resins   |  |
|                            | Soil repellents                                 | Improvement of soil-<br>repellent properties and<br>removal of impurities  | Polysiloxanes,<br>fluorocarbon resins   |  |
|                            | Soil release<br>agents                          | Improvement of soil release from textiles  | Fluorocarbon resins,<br>polyacrylates, fatty acid<br>condensation products,<br>polyurethane   |  |
| Felting                    | Felting agents (animal fibres)                  | Promotion of felting<br>during the milling<br>operation  | Fatty alcohol ethoxylates,<br>alkyl sulphonates, fatty<br>acid condensation products  |  |
| Anti-felting               | Anti-felting<br>agents (animal<br>fibres)       | Reducing of shrinkage<br>during washing  | Reducing or oxidizing<br>agents, chlorocyanurate,<br>polysiloxane, polyurethane,<br>polyamide-epoxide<br>copolymers   |  |
| Lustre                     | Lustring agents                                 | Impart or increase of lustre<br>(with or without<br>connection to a mechanical<br>treatment)   | Emulsions of paraffins,<br>waxes, polyolefins,<br>polyglycols or<br>polysiloxanes   |  |
|                            | Delustring agents                               | Reduction of lustre  | Pigments  |  |
| Non-slip, ladder-<br>proof | Non-slip, ladder-<br>proof, anti-snag<br>agents | Reduction of the slipping<br>of various yarn systems<br>and of ladders in knitwear.<br>Prevention of snags in<br>hosiery and other ready-<br>made goods of continuous-<br>filament yarns | Modified silicic acid,<br>polyvinyl acetate,<br>copolymers, acrylate-styro<br>copolymers  |  |
| Flame resistance           | Flame retardants                                | Reduction of flammability<br>and combustibility  | Inorganics (e.g. ammonium<br>salts), antimony trioxide in<br>combination with<br>halogenated synergists<br>(chloroparaffins,<br>brominated compounds),<br>reactive P-organic<br>compounds (e.g. |  |

| Process   | Auxiliary  | Effect   | Chemical composition  |
|---|--|--|---|
|   |  |  | derivatives of phosphonic<br>acid dimethylester,<br>derivatives of tetrakis-<br>hydroxmethylphosphonium<br>chloride, cyclic phosphonic<br>acid esters)  |
| Antimicrobiotics<br>(rot-proofing,<br>mould prevention) | Antimicrobiotic<br>agents                              | Protection against<br>microorganisms   | Zinc organics,<br>benzimidazole- derivatives,<br>triclosan, isothiazolinone,<br>chlorophene derivatives   |
| Chemical bonding<br>of non-wovens                       | Binder   | Promotion of fibre<br>bonding<br>Additives   | Polymers of acrylic acid<br>esters, acrylonitrile,<br>ethylene, butadiene,<br>styrene, vinyl chloride,<br>vinyl acetate. Latex, starch<br>etc. Polyethers, N-methylol<br>compounds etc.         |
| Coating   | Coating agents   | Production of adhesive<br>layers on textile fabrics  | Polymers of vinyl chloride,<br>acrylic acid esters,<br>acrylonitrile, ethylene,<br>butadiene, styrene,<br>vinylidene chloride, vinyl<br>acetate. Natural latex,<br>additives, filling materials |
| Laminating  | Laminating<br>agents                                   | Bonding of two or more<br>textile fabrics with other<br>fabrics or foils                                   | Natural or synthetic<br>latexes, polyvinyl acetates,<br>polyurethanes,<br>polyacrylates, cellulose<br>esters, polyethylene,<br>polypropylene, polyvinyl<br>chloride, additives                  |
| Textile auxiliaries<br>for multipurpose<br>use          | Wetting agents   | Increasing of wetting<br>power   | Alkyl sulphates, alkane<br>sulphonates, alkyl aryl<br>sulphonates, alkyl ether<br>sulphates, alkyl esters of<br>sulphosuccinic acids,<br>ethoxylation products,<br>phosphoric acid esters       |
|   | Anti-foaming<br>agents                                 | Prevention of foam in<br>sizing, pre-treatment baths,<br>printing pastes, dye baths<br>and finishing baths | Phosphoric acid esters,<br>hydrocarbons, high<br>molecular alcohols, silicon<br>and fluorine derivatives  |
|   | Foaming agents   | Generation and stabilizing<br>of foam if foam<br>application is used                                       | Sodium<br>dioctylsulphosuccinate,<br>ethoxylated tridecylalcohol  |
|   | Detergents,<br>dispersing and<br>emulsifying<br>agents |  | Soaps, alkyl sulphonates,<br>alkyl aryl sulphonates,<br>alkyl ether sulphates, EO-<br>PO adducts, fatty alcohol<br>ethoxylates, alkyl aryl  |

| Process   | Auxiliary            | Effect  | Chemical composition  |
|---|----------------------|---|---|
|   |                      |   | ethoxylates   |
|   | Spotting agents      | Removal of spots  | Surfactants, solvents<br>(hydrocarbons, chlorinated<br>solvents)  |
| After-treatment in<br>yarn and fabric<br>dyeing, raising,<br>emerizing                        | Conditioning agents  | Influencing of frictional<br>behaviour and handle<br>(softening effect) | See also preparation agents<br>and softening agents;<br>quaternary ammonium<br>compounds, ethoxylation<br>products of fatty acid- fatty<br>amines etc. polysiloxanes,<br>waxes, paraffines          |
| Scouring,<br>bleaching,<br>mercerizing,<br>causticizing,<br>desizing, dyeing<br>and printing. | Complexing<br>agents | Complexing of heavy<br>metals   | Polyphosphates,<br>phosphonates,<br>polycarboxylates,<br>(polyacrylates,<br>polyacrylate-maleinic acid<br>copolymers), sugar<br>copolymers, hydroxy-<br>carboxylic acids, amino<br>carboxylic acids |

# **Appendix 2: Chemical resistance selection chart for protective gloves**

The ratings are abbreviated as follows: VG: Very Good; G: Good; F: Fair; P: Poor (not recommended). Chemicals marked with an asterisk (\*) are for limited service.

| Chemical              | Neoprene | Latex/Rubber | Butyl | Nitrile |
|-----------------------|----------|--------------|-------|---------|
| Acetaldehyde*         | VG       | G            | VG    | G       |
| Acetic acid           | VG       | VG           | VG    | VG      |
| Acetone*              | G        | VG           | VG    | Р       |
| Ammonium hydroxide    | VG       | VG           | VG    | VG      |
| Amy acetate*          | F        | Р            | F     | Р       |
| Aniline               | G        | F            | F     | Р       |
| Benzaldehyde*         | F        | F            | G     | G       |
| Benzene*              | Р        | Р            | Р     | F       |
| Butyl acetate         | G        | F            | F     | Р       |
| Butyl alcohol         | VG       | VG           | VG    | VG      |
| Carbon disulphide     | F        | F            | F     | F       |
| Carbon tetrachloride* | F        | Р            | Р     | G       |
| Castor oil            | F        | Р            | F     | VG      |
| Chlorobenzene*        | F        | Р            | F     | Р       |
| Chloroform*           | G        | Р            | Р     | F       |
| Chloronaphthalene     | F        | Р            | F     | F       |
| Chromic acid (50%)    | F        | Р            | F     | F       |
| Citric acid (10%)     | VG       | VG           | VG    | VG      |
| Cyclohexanol          | G        | F            | G     | VG      |
| Dibutyl phthalate*    | G        | Р            | G     | G       |
| Diesel fuel           | G        | Р            | Р     | VG      |
| Diisobutyl ketone     | Р        | F            | G     | Р       |
| Dimethylformamide     | F        | F            | G     | G       |
| Dioctyl phthalate     | G        | Р            | F     | VG      |
| Dioxane               | VG       | G            | G     | G       |
| Epoxy resins, dry     | VG       | VG           | VG    | VG      |
| Ethyl acetate*        | G        | F            | G     | F       |
| Ethyl alcohol         | VG       | VG           | VG    | VG      |
| Ethyl ether*          | VG       | G            | VG    | G       |

Table A2-1: Chemical resistance selection chart [based on 46]

| Chemical                | Neoprene | Latex/Rubber | Butyl | Nitrile |
|-------------------------|----------|--------------|-------|---------|
| Ethylene dichloride*    | F        | Р            | F     | Р       |
| Ethylene glycol         | VG       | VG           | VG    | VG      |
| Formaldehyde            | VG       | VG           | VG    | VG      |
| Formic acid             | VG       | VG           | VG    | VG      |
| Freon 11                | G        | Р            | F     | G       |
| Freon 12                | G        | Р            | F     | G       |
| Freon 21                | G        | Р            | F     | G       |
| Freon 22                | G        | Р            | F     | G       |
| Furfural*               | G        | G            | G     | G       |
| Gasoline, leaded        | G        | Р            | F     | VG      |
| Gasoline, unleaded      | G        | Р            | F     | VG      |
| Glycerin                | VG       | VG           | VG    | VG      |
| Hexane                  | F        | Р            | Р     | G       |
| Hydrazine (65%)         | F        | G            | G     | G       |
| Hydrochloric acid       | VG       | G            | G     | G       |
| Hydrofuoric acid (48%)  | VG       | G            | G     | G       |
| Hydrogen peroxide (30%) | G        | G            | G     | G       |
| Hydroquinone            | G        | G            | G     | F       |
| Isooctane               | F        | Р            | Р     | VG      |
| Kerosene                | VG       | F            | F     | VG      |
| Ketones                 | G        | VG           | VG    | Р       |
| Lacquer thinners        | G        | F            | F     | Р       |
| Lactic acid (85%)       | VG       | VG           | VG    | VG      |
| Lauric acid (36%)       | VG       | F            | VG    | VG      |
| Lineolic acid           | VG       | Р            | F     | G       |
| Linseed oil             | VG       | Р            | F     | VG      |
| Maleic acid             | VG       | VG           | VG    | VG      |
| Methyl alcohol          | VG       | VG           | VG    | VG      |
| Mehylamine              | F        | F            | G     | G       |
| Methyl bromide          | G        | F            | G     | F       |
| Methyl chloride*        | Р        | Р            | Р     | Р       |
| Methyl ethyl ketone*    | G        | G            | VG    | Р       |
| Methyl isobutyl ketone* | F        | F            | VG    | Р       |
| Methyl metharcrylate    | G        | G            | VG    | F       |
| Monoethanolamine        | VG       | G            | VG    | VG      |
| Morpholine              | VG       | VG           | VG    | G       |

| Chemical                           | Neoprene | Latex/Rubber | Butyl | Nitrile |
|------------------------------------|----------|--------------|-------|---------|
| Naphtalene                         | G        | F            | F     | G       |
| Napthas, aliphatic                 | VG       | F            | F     | VG      |
| Napthas, aromatic                  | G        | Р            | Р     | G       |
| Nitric acid*                       | G        | F            | F     | F       |
| Nitric acid, red and white fuming  | Р        | Р            | Р     | Р       |
| Nitromethane (95.5%)*              | F        | Р            | F     | F       |
| Nitroprophane (95.5%)              | F        | Р            | F     | F       |
| Octyl alcohol                      | VG       | VG           | VG    | VG      |
| Oleic acid                         | VG       | F            | G     | VG      |
| Oxalic acid                        | VG       | VG           | VG    | VG      |
| Palmitic acid                      | VG       | VG           | VG    | VG      |
| Perchloric acid (60%)              | VG       | F            | G     | G       |
| Perchloroethylene                  | F        | Р            | Р     | G       |
| Petroleum distillates<br>(naphtha) | G        | Р            | Р     | VG      |
| Phenol                             | VG       | F            | G     | F       |
| Phosphoric acid                    | VG       | G            | VG    | VG      |
| Potassium hydroxide                | VG       | VG           | VG    | VG      |
| Propyl acetate                     | G        | F            | G     | F       |
| Propyl alcohol                     | VG       | VG           | VG    | VG      |
| Propyl alcohol (iso)               | VG       | VG           | VG    | VG      |
| Sodium hydroxide                   | VG       | VG           | VG    | VG      |
| Styrene                            | Р        | Р            | Р     | F       |
| Styrene (100%)                     | Р        | Р            | Р     | F       |
| Sulphuric acid                     | G        | G            | G     | G       |
| Tannic acid (65)                   | VG       | VG           | VG    | VG      |
| Tetrahydrofuran                    | Р        | F            | F     | F       |
| Toluene*                           | F        | Р            | Р     | F       |
| Toluene diisocyanate<br>(TDI)      | F        | G            | G     | F       |
| Trichloroethylene*                 | F        | F            | Р     | G       |
| Triethanolamine (85%)              | VG       | G            | G     | VG      |
| Tung oil                           | VG       | Р            | F     | VG      |
| Turpentine                         | G        | F            | F     | VG      |
| Xylene*                            | Р        | Р            | Р     | F       |

# **Appendix 3: Storage**

## Storage incompatibilities

## Table A3-1: Storage of hazardous substances commonly used in industry [based on 85]

|  |                  | Formic acid | Solution of ammonia | Solution of iron<br>chloride (III) | Solution of iron<br>chloride (III) sulfate | Acetic acid | Hydrofluoric acid | Solution of potas-<br>sium hydroxide | Solution of sodium<br>hydroxide | Solution of sodium<br>hydrogensulfite | Solution of sodium<br>hypochlorite | Peracetic acid | Phosphoric acid | Nitric acid | Hydrochloric acid | Sulphuric acid | Hydrogen peroxide |
|--|------------------|-------------|---------------------|------------------------------------|--|-------------|-------------------|--------------------------------------|---------------------------------|---------------------------------------|------------------------------------|----------------|-----------------|-------------|-------------------|----------------|-------------------|
|  | Storage category | 8           | 8                   | 8                                  | 8  | 3           | 6.1               | 8                                    | 8                               | 10/12                                 | 5                                  | 5              | 8               | 5           | 8                 | 8              | 5                 |
| Formic acid                                | 8                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Solution of ammonia                        | 8                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Solution of iron chloride<br>(III)         | 8                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Solution of iron chloride<br>(III) sulfate | 8                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Acetic acid                                | 3                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Hydrofluoric acid                          | 6.1              |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Solution of potassium hydroxide            | 8                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Solution of sodium hydroxide               | 8                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Solution of sodium hydrogensulfite         | 10/12            |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Solution of sodium hypochlorite            | 5                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Peracetic acid                             | 5                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Phosphoric acid                            | 8                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Nitric acid                                | 5                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Hydrochloric acid                          | 8                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Sulphuric acid                             | 8                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |
| Hydrogen peroxide                          | 5                |             |                     |                                    |  |             |                   |                                      |                                 |                                       |                                    |                |                 |             |                   |                |                   |

### Safety distances

| Type of storage                | Neighbouring building activity |                             |                           |  |  |  |  |
|--------------------------------|--------------------------------|-----------------------------|---------------------------|--|--|--|--|
| building                       | Low danger <sup>28</sup>       | Medium danger <sup>29</sup> | High danger <sup>30</sup> |  |  |  |  |
| Specifically resistant to fire | Low                            | Low                         | Low                       |  |  |  |  |
| Non-flammable<br>(concrete)    | Low                            | Medium                      | High                      |  |  |  |  |
| Flammable (wood)               | Medium                         | High                        | High                      |  |  |  |  |

| Table A3-2: | <b>Evaluation</b> | of the | neighbouring | risk | [based c | on 861 |
|-------------|-------------------|--------|--------------|------|----------|--------|
|             |                   |        |              |      |          |        |

Table A3-3: Safety distance in metres between outside warehouses and buildings, structures and facilities [based on 86]

|                              | Storage in containers (in litres) |                 |                 |                          |                 |                 |  |  |  |
|------------------------------|-----------------------------------|-----------------|-----------------|--------------------------|-----------------|-----------------|--|--|--|
| Neighbouring<br>risks (Table | Cat                               | egories F1 and  | 1 F2            | Categories F3, F4 and F5 |                 |                 |  |  |  |
| A3-2)                        | Up to 5,000                       | Up to<br>50,000 | Above<br>50,000 | Up to 5,000              | Up to<br>50,000 | Above<br>50,000 |  |  |  |
| Low                          | 5                                 | 10              | 15              | -                        | 5               | 8               |  |  |  |
| Medium                       | 10                                | 15              | 20              | 5                        | 8               | 12              |  |  |  |
| High                         | 15                                | 20              | 25              | 8                        | 12              | 15              |  |  |  |

Table A3-4: Safety distance in metres between unburied tanks and buildings, structures and facilities [based on 86]

|              | Storage in tanks (in m <sup>3</sup> ) |                |           |                              |               |              |  |  |  |
|--------------|---------------------------------------|----------------|-----------|------------------------------|---------------|--------------|--|--|--|
| Neighbouring | Cate                                  | egories F1 and | l F2      | Categories F3, F4 and F5     |               |              |  |  |  |
| risks (Table | Tank                                  | Vertic         | al tank   | Tank                         | Vertical tank |              |  |  |  |
| A3-2)        | resistant to<br>overpressure          | Up to 500      | Above 500 | resistant to<br>overpressure | Up to 500     | Above<br>500 |  |  |  |
| Low          | 12                                    | 20             | 30        | 6                            | 10            | 15           |  |  |  |
| Medium       | 16                                    | 25             | 35        | 8                            | 12            | 18           |  |  |  |
| High         | 20                                    | 30             | 40        | 10                           | 15            | 20           |  |  |  |

<sup>&</sup>lt;sup>28</sup> Production, treatment and storage of non-flammable materials

<sup>&</sup>lt;sup>29</sup> Engineering workshops, car repair, offices, apartments

 $<sup>^{30}</sup>$  Storage and treatment of hazardous materials, wood processing, printing, professional accommodation, buildings with space for a large number of occupants

# **Appendix 4: Fire protection**

Table A4-1: Main hazardous product classes associated with fire or explosion hazards

| Hazard class                               | GHS <sup>31</sup><br>pictogram | Hazard statement codes  |
|--|--------------------------------|---|
|  |                                | H200 – Unstable explosive   |
|  |                                | H201 – Explosive; mass explosion hazard   |
| Explosives                                 |                                | H202 – Explosive; severe projection hazard  |
|  |                                | H203 – Explosive; fire, blast or projection hazard                                      |
|  |                                | H204 – Fire or projection hazard  |
| Flammable gases                            | ۲                              | H220 – Extremely flammable gas  |
|  | ^                              | H222 – Extremely flammable aerosol  |
| Aerosols                                   |                                | H223 – Flammable aerosol  |
|  | $\mathbf{v}$                   | H229 – Pressurized container; may burst if heated                                       |
| Oxidizing gases                            | ٢                              | H270 – May cause or intensify fire; oxidizer  |
| Gas under pressure                         | $\diamond$                     | H280 – Contains gas under pressure; may explode if heated                               |
|  | ~                              | H224 – Extremely flammable liquid and vapour  |
| Flammable liquids                          |                                | H225 – Highly flammable liquid and vapour   |
|  | $\sim$                         | H226 – Flammable liquid and vapour  |
| Flammable solids                           | ٢                              | H228 – Flammable solid  |
| Substances and mixtures which in           | ٨                              | H260 – In contact with water releases flammable gases<br>which may ignite spontaneously |
| contact with water emit<br>flammable gases | ~                              | H261 - In  contact with water releases flammable gases                                  |
| Oxidizing liquids or                       |                                | H271 – May cause fire or explosion; strong oxidizer                                     |
| solids                                     | $\checkmark$                   | H272 – May intensify fire; oxidizer   |

<sup>&</sup>lt;sup>31</sup> Globally Harmonized System of Classification and Labelling of Chemicals (GHS)

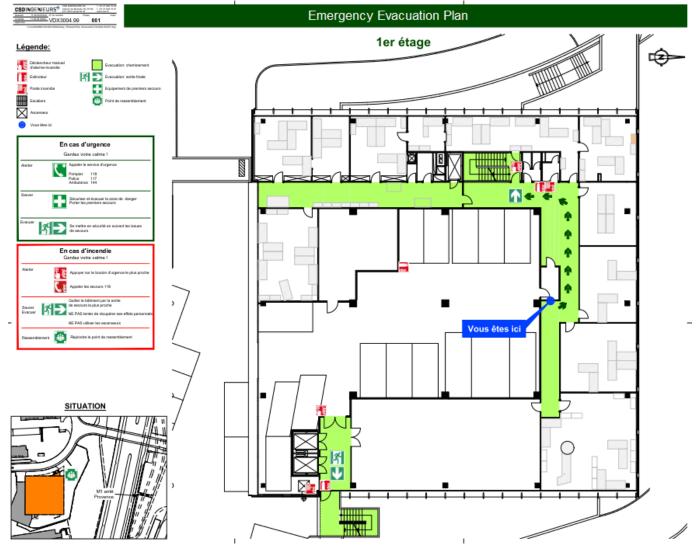


Figure A4-1: Emergency plan [87].