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THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY**

Environmental Exposure Assessment

DRAFT EMISSION SCENARIO ON TEXTILE MANUFACTURING WOVEN MILLS

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This document includes a draft emission scenario document (ESD) on textile manufacturing wool mills, submitted by Canada. This document is intended to provide additional information about the published ESD on Textile Finishing Industry [ENV/JM/MONO(2004)12].

Emission Scenario Document for Woven Fabric Dyeing and Finishing Mills

Prepared for

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1 – INTRODUCTION

The purpose of this emission scenario document (ESD) is to provide a realistic worst-case emission scenario for chemicals used at woven fabric dyeing and finishing mills. The information about the processes and chemicals used is derived from a field study, literature data, and several reports from the European Union and the U.S. The emission estimation methods given in this ESD are based on those developed by the Organization for Economic Cooperation and Development with parameter defaults reflecting Canadian operations.

2 – CANADIAN WOVEN FABRIC WET PROCESSING SECTOR

The textile industry can be divided into dry processing and wet processing from a standpoint of water usage (USEPA, 1996). The dry processing uses small amounts of water and contributes insignificant load to wastewater generation. On the other hand, the wet processing involves many operations which consume large quantities of water and is, therefore, the primary source of the textile industry wastewater.

In Canada, the wet processing sector consisted of the following six types of mills according to the Environment Canada's 1997/98 survey (Environment Canada, 1998):

- knit fabric dyeing and finishing mills
- woven fabric dyeing and finishing mills
- wool dyeing and finishing mills
- stock/yarn dyeing and finishing mills
- carpet dyeing and finishing mills
- non-woven fabric dyeing and finishing mills

The Canadian wet processing textile mills are concentrated in the provinces of Quebec and Ontario. As given in Table 1, 134 mills out of the total of 145 were located in the two provinces (Crechem Technologies Inc., 1998). The remaining 11 mills are located in New Brunswick, Nova Scotia, Prince Edward Island, and British Columbia.

Table 1 – Distribution of Canadian Wet Processing Textile Mills

Type	Knit	Woven	Stock/Yarn	Carpet	Wool	Non-woven	Unclassified	Total
Quebec	36	25	8	5	5	0	5	84
Ontario	24	9	5	2	0	7	3	50
New Brunswick	0	2	0	0	1	0	1	3
Nova Scotia	2	2	0	1	0	0	0	5
Prince Edward Island	0	0	0	0	1	0	0	1
Manitoba	0	0	0	0	0	0	0	0
Alberta	0	0	0	0	0	0	0	0
British Columbia	1	0	0	0	1	0	0	2
Total	63	38	13	8	8	7	8	145

Source: Crechem Technologies Inc., 1998

Woven fabric dyeing and finishing mills were a major part of the Canadian wet processing sector, placed second to knit fabric mills. As given in Table 2, they accounted for 26% of the total mills, 21% of the fabric processed by the wet processing sector, and 31% of the wastewater generated (Crechem Technology Inc., 2000).

Table 2 – Woven Fabric Mills in Canadian Wet Processing Sector

	Number of Mills	Quantity of Fabric Processed	Quantity of Wastewater Generated
Woven Mills	38	66.9 million kg/yr	32,500 m ³ /d
Industry Total	145	319.7 million kg/yr	103,700 m ³ /d
Industry Share	26.2%	20.9%	31.3%

Source: Crechem Technologies Inc., 2000.

3 – WOVEN FABRIC WET PROCESSING OPERATIONS

3.1 – Process Description

Figure 1 shows a typical process for woven fabric dyeing and finishing mills. It consists of three sections: 1) preparation; 2) dyeing and printing; and 3) finishing. Water and wastewater treatment are commonly integral parts of a woven mill.

3.1.1 - Preparation

In the preparation section, incoming raw materials are pretreated to remove impurities and colour in order to make them suitable for dyeing and finishing (USEPA, 1978;

Farnfield, 1975). The raw materials are known as woven greige goods which are woven fabrics coming out of a loom without any treatment.

Singeing is often the first step in the preparation which is a dry operation to remove protruding ends of fibres (Joseph, 1981). It does not involve the use of chemicals and water. In the singeing operation the woven fabric is opened to full width and fed onto a storage scray. It then enters a singer and passes through open flames or hot metal plates. The operation gives the fabric a clear, smooth, and uniform surface.

The singeing operation is followed by desizing which removes sizing materials. The sizing materials are specific chemicals, such as starch, polyvinyl alcohol (PVA) and carboxymethyl cellulose (CMC), which are applied to yarns before weaving in order to furnish protection to warps (Olson, 1983; Chen, 1989). The sizing materials form a surface coating which is stiff and hard. They must be removed as early as possible in a wet processing mill.

In the desizing operation a desize water bath is used to receive the fabric coming out of the singer (Joseph, 1981). Desizing materials such as enzymes are added to the bath in order to dissolve the sizing agents. The fabric is then fed into a washer and moves through a series of loops and rollers to remove the desizing materials and the dissolved sizing agents.

The desized fabric is scoured to remove natural and acquired impurities with scouring agents (Chen, 1989; Joseph, 1981; USEPA, 1996). Soaps or synthetic detergents with alkaline builders are common scouring agents. In the scouring operation, the fabric from the previous washer is fed into a caustic saturator where a sodium hydroxide solution is prepared with addition of wetting agents and emulsifiers. The saturated fabric is then fed into a J-box through which impurities are removed by retaining the fabric for a period of time. The fabric is finally fed into washers to remove the caustic solution and other agents.

Mercerizing is performed to add luster to the fabric, to improve dyeing characteristics and to increase strength (Joseph, 1981). It subjects the fabric to a solution of sodium hydroxide and feeds it between rolls to ensure uniform penetration of the solution as well as to remove excess solution. The spent caustic solution is removed from the fabric by washing and the sodium hydroxide is recovered for reuse. Neutralizing chemicals may also be used during the washing to prevent any possible damage to the fabric by the mercerizing chemicals.

The fabric is bleached to prepare it for dyeing and printing (USEPA, 1996, 1978; Joseph, 1981; Chen, 1989). Cotton fabrics are bleached white, whereas synthetic fabrics are bleached for stain removal or for a desired translucent bluish-white colour. In the bleaching operation the fabric is first saturated with bleaching agent, activator, stabilizer, and other necessary chemicals. It is then subjected to elevated temperatures for a specified period of time to complete the bleaching action. Finally, the bleached fabric is thoroughly rinsed and dried.

3.1.2 – Dyeing and Printing

Dyeing can be carried out either in batches or continuously (Chen, 1989; USEPA, 1996). In a batch operation, as in the case of jet or jig dyeing, preparation of a dye solution, application of a dye to fabrics, and washing of dyed fabrics are performed in a single vessel in a sequential manner and do not interfere with one another. Continuous dyeing, on the other hand, integrates the above steps into a line of operations and the fabric being dyed is continuously fed through a range which is a continuous machine used for dyeing a large quantity of textile materials and consists of compartments for wetting-out, dyeing, after-treatments, washing, and rinsing (Hollen and Saddler, 1973).

In the dyeing operation the fabric is first loaded into a dyeing machine and then brought to equilibrium or near equilibrium with a dye solution (Carr, 1995). Because dyes have an affinity for the fibre, dye molecules migrate from the dye solution into the fibre over a period ranging from minutes to hours. The migration of dye molecules can be accelerated and optimized by introducing auxiliary chemicals to the dye bath and by controlling dyebath conditions (mainly temperature). As the dyeing is completed, the fabric is rinsed to remove unfixed dyes and spent chemicals and dried to prepare for printing.

Textile printing involves localized dyeing processes in which a dye or pigment solution or dispersion is applied to the fabric in a design (Carr, 1995). The colouring matters (dyes or pigments) involved are the same as those used for dyeing. Two methods are generally employed in fabric printing (Chen, 1989; USEPA, 1978). The first one is roller printing which is accomplished by applying the print paste to an etched or engraved roller and transferring the design to the fabric by contact with the roller. The second method is screen printing which transfers the print paste to the fabric through openings of a specially designed screen.

After printing, the fabric is subjected to steaming, aging, or other treatment to fix the colour and/or pattern onto the fabric. Steaming and aging are two similar treatments; the former is to specifically expose printed fabric to hot steam (Hall, 1975) and the latter is to generally expose it to a hot moist atmosphere (Farnfield, 1975). The printed fabric is then washed and rinsed to remove any residual dyes.

3.1.3 – Finishing

The dyed and/or printed fabric is further subjected to wet finishing which involves the use of a variety of finishing agents in a solution to improve the appearance, texture, and performance of the fabric (USEPA, 1996, 1978; Chen, 1989). It employs a padding machine which passes the fabric through a finishing solution between two padding rolls. The rolls facilitate the transfer of the finishing agents from the solution to the fabric surface and at the same time remove excess liquid. The fabric is then sent to a steaming

or washing machine to remove residual chemicals and dried in a dryer to cure the finishes onto the fabric.

The fabric is further subjected to dry finishing which does not involve the use of water. The dry finishing utilizes mechanical means to cause physical changes to the fabric and the methods employed include optical finishing, brushing and napping, softening, shearing, and compacting.

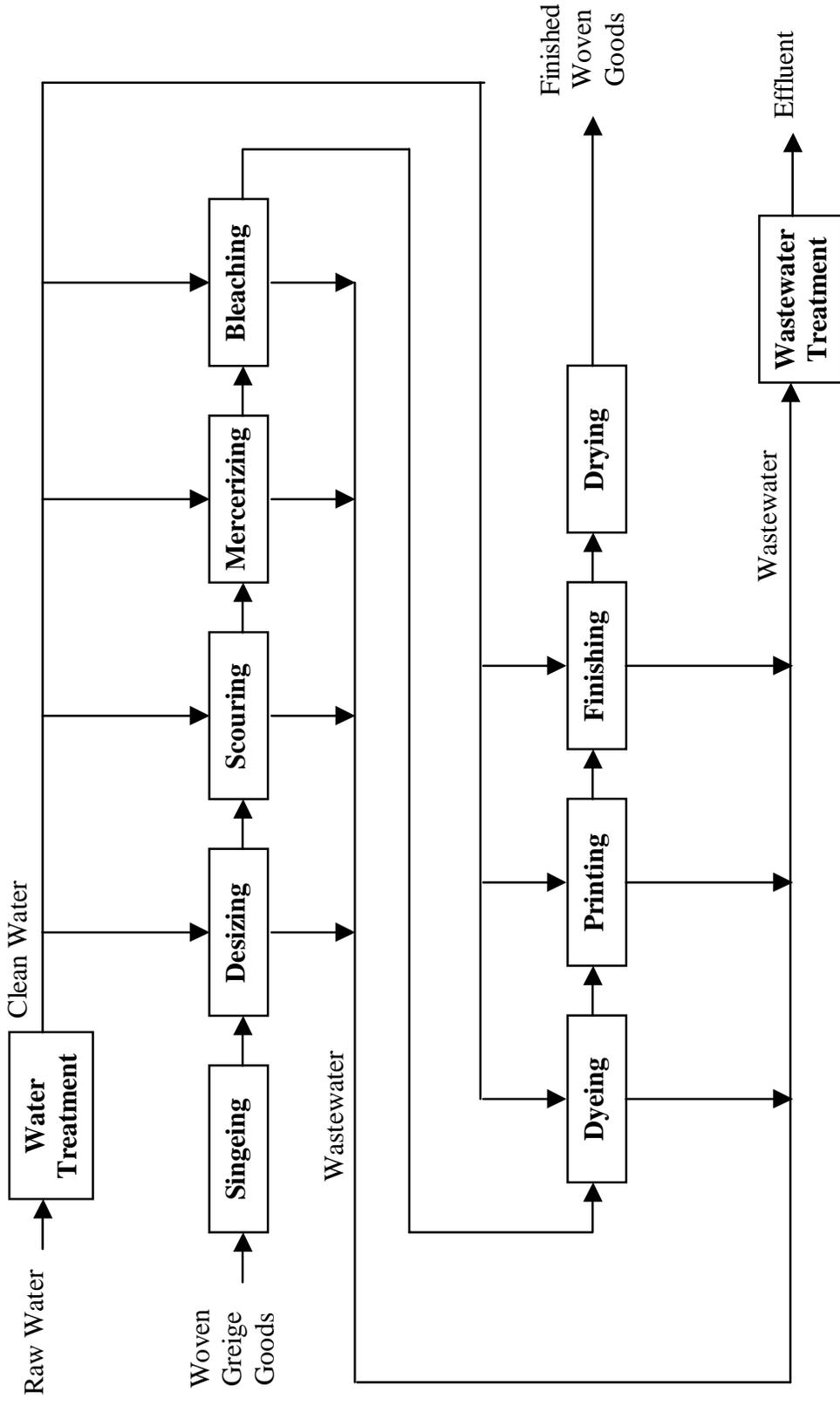


Figure 1 - Typical Process for Woven Fabric Dyeing and Finishing Mills

3.2 – Chemical Use

Chemicals used at woven fabric wet processing mills may be classified into the following categories (Crechem Technologies Inc., 2003):

- 1) Surfactants
- 2) Dyes and pigments
- 3) Dye carriers and auxiliaries
- 4) Desizing agents
- 5) Solvents
- 6) Phosphates
- 7) Bleaching agents and assistants
- 8) Salts
- 9) Alkalis
- 10) Acids
- 11) Buffering agents
- 12) Thickeners
- 13) Chelating agents
- 14) Biocides
- 15) Cleaners
- 16) Chemicals for boiler and cooling water treatment
- 17) Chemicals for water treatment
- 18) Chemicals for wastewater treatment

3.2.1 – Chemicals Used in Desizing

Enzymes are by far the most commonly used desizing agents (Nettles, 1983). Solvents such as Varsol® may also be employed to facilitate a desizing operation. Starches, polymers, and natural gums, which are water-insoluble substances applied during a sizing operation, are converted to water-soluble compounds and then removed.

3.2.2 – Chemicals Used in Scouring

Chemicals employed in scouring can be divided into seven groups (Olson, 1983). The first group contains only caustic soda with which water-insoluble natural oils and waxes react in the presence of water to form water-soluble soaps which are easily removed.

The second group includes soaps and detergents which emulsify oils and waxes (Olson, 1983). In a general sense, soaps and detergents are very similar in terms of chemistry, and the basic principles underlying their action are the same (Carr, 1995). Detergents are, however, much more effective in their action, and their chemical structures can be substantially altered to achieve a variety of effects in a way that is not possible with simple soap molecules.

The third group consists of surfactants which reduce water surface tension and water-oil interfacial tension (Olson, 1983).

The fourth group consists of chelating agents, also known as sequestering agents (Nettles, 1983; Olson, 1983). As important textile auxiliaries, they are used to block active sites of heavy metal ions and, therefore, prevent them from entering undesired reactions.

The fifth group includes penetrants which assist other chemicals to penetrate into the lignin mass of cellulosic materials (Olson, 1983). Sodium silicate is a common penetrant.

The sixth group includes builders which increase the activity or the effect of soaps and detergents (Olson, 1983). Builders are generally salts such as borates, silicates, phosphates, sodium chloride, sodium sulphate, etc.

The seventh and final group consists of solvents which are frequently used in conjunction with detergents in order to dissolve and, therefore, remove more water-insoluble fats and waxes (Olson, 1983).

3.2.3 – Chemicals Used in Bleaching

Chemicals used in bleaching can be organized into five groups (Olson, 1983). The first group consists of bleaching agents which react with colouring matter present in fabrics. Bleaching agents can be further broken down to oxidative and reductive agents (Nettles, 1983). Hydrogen peroxide is a typical oxidative bleaching agent and sulphur dioxide is a typical reductive agent.

The second group consists of buffering agents which are used to control the pH level of a bleaching bath. Buffering agents are either alkalis or acids (Nettles, 1983).

The third group consists of surfactants which reduce water surface tension as well as water-oil interfacial tension. Surfactants may be anionic, nonionic, cationic, amphoteric, or blends of all four types (Nettles, 1983). The most common bleaching surfactants appear to be the anionic type including sulphate, phosphate, carboxymethylate, and methyltaurine. Also in common usage are the nonionic types including ethoxylated primary alcohols, ethoxylated secondary alcohols, mercaptan thioethers, and ethoxylated fatty acids.

The fourth group consists of fluorescent whitening agents which are used to improve the whiteness of textile materials (Adanur, 1995; Nettles, 1983). Fluorescent whitening agents, also known as optical brighteners, function by absorbing ultraviolet light and reflecting it in the blue-white spectrum, thereby exerting an intensifying effect on whiteness.

The fifth group consists of a variety of additives which are used to facilitate bleaching. They include defoamers, antiredeposition agents, sequestrants, etc. Stabilizers such as sodium silicate and sodium nitrate are also included in this group (UK Environmental Agency, 1997).

3.2.4 – Chemicals Used in Mercerizing

Chemicals used in mercerizing are divided into two groups. The first group includes alkalis used as mercerizing agents which adds lustre to fabric, improves dyeing characteristics and increases fabric strength (Joseph, 1981). The second group includes neutralizing agents which are applied after mercerizing to remove residual alkali which may otherwise cause fibre crocking and poor dye fixation. Sodium hydroxide is by far the most commonly used mercerizing agent, but liquid ammonia is also used in the operation (Carr, 1995; Adanur, 1995).

3.2.5 – Chemicals Used in Dyeing

Dyes, salts, dye carriers, and many auxiliaries are used in dyeing. Auxiliaries include buffering agents, acids/alkalis, dye-bath lubricants, dispersing agents, chelating agents, anti-redeposition agents, etc. (USEPA, 1996, p.179-183).

Use of reductive agents is also found in dyeing (Smith, 1988). They help remove surface dye from fabric (after-clearing) and from dyeing machines. In addition, they function as antichlor agents to destroy residual chlorine from hypochlorite, chlorite bleaching or stripping prior to dyeing which uses potentially chlorine-sensitive dyes.

3.2.6 – Chemicals Used in Printing

Pigments or dyes, and various auxiliaries are used in printing. Auxiliaries include thickeners, binders, reductants, etc. Thickeners are used in printing to ensure the printed design is precisely located with clean defined edges (Carr, 1995). Many polysaccharides derived from starch-containing plants, seaweeds yielding alginates, plant gums, and cellulose derivatives, particularly cellulose ethers, are used as thickeners in textile printing. They have been developed to substitute for kerosene (USEPA, 1996, p.198). Common binders are acrylic copolymers which allow for 100% fixation of prints. Reductants are used in discharge printing which involves destroying an existing dye in pre-dyed fabrics to replace it with another or to let the ground shade shine through (Cognis, Div. of Henkel Canada, www.cognis.com).

3.2.7 – Chemicals Used in Chemical Finishing

Chemical finishing involves the application of a wide range of chemicals to improve and enhance various properties of a fabric (Chen, 1989). These chemicals are classified into the following groups:

- Abrasion-resistant finishes that improve the resistance of fabrics to abrasion damage.
- Absorbent finishes that increase the moisture-holding power and speed up the drying action of textile.

- Antislip finishes that keep yarns in their proper position in fabrics and reduce seam fraying.
- Antistatic finishes that reduce the static charge of fabrics.
- Antiseptic finishes that control the spread of disease and reduce the danger of infection following injury; help inhibit the development of unpleasant odours from perspiration and other soil in fibrous structures; and reduce damage to fabrics from mildew-producing fungi and rot-producing bacteria.
- Flame retardants that reduce the flammability, charring, or afterglow of fabrics.
- Mothproofing finishes that are applied to fibres, especially wool and wool blends, to prevent damage by moths and carpet beetles.
- Waterproof and water-repellent finishes that coat or seal fabrics so that water does not pass through them.
- Stain- and soil-resistant finishes that prevent stain and soil from penetrating fibres.
- Soil-release finishes that provide a hydrophilic surface attracting water and permitting it to lift off soil or coat fibres so that soil never penetrates.
- Durable-press finishes that enable fabrics to retain an attractive appearance during wear and to return their original smooth surface and shape after laundering.

4 – RELEASE ESTIMATION

Environmental releases from woven fabric wet processing are divided into: 1) wastewater; 2) air emissions; and 3) solid waste. The chemical nature of each group from individual operations is summarized in Table 3 (USEPA, 1997, p.43).

Table 3 – Environmental Releases from Woven Fabric Wet Processing

Process	Wastewater	Air Emissions	Solid Waste
Desizing	BOD from water-soluble sizes; synthetic size; lubricants; biocides; antistatic compounds	volatile organic compounds	packaging waste; fiber lint; yarn waste; cleaning materials, such as wipes, rags, and filters; cleaning and maintenance wastes containing solvents
Scouring	disinfectants and insecticide residues; NaOH; detergents, fats; oils; pectin; wax; knitting lubricants; spin finishes; spent solvents	volatile organic compounds	little or no residual waste generated
Bleaching	hydrogen peroxide, sodium silicate or organic stabilizer; high pH	little or no air emissions generated	little or no residual waste generated
Singeing	little or no wastewater	small amounts of exhaust	little or no residual waste

Process	Wastewater	Air Emissions	Solid Waste
	generated	gases from burners	generated
Mercerizing	high pH; NaOH	little or no air emissions generated	little or no residual waste generated
Dyeing	metals; salt; surfactants; toxics; organic processing assistants; cationic materials; color; BOD; COD; sulphide; acidity/alkalinity; spent solvents	volatile organic compounds	little or no residual waste generated
Printing	suspended solids; urea; solvents; color; metals; heat; BOD; foam	solvents, acetic acid from drying and curing oven emissions; combustion gases; particulate matter	little or no residual waste generated
Finishing	BOD; COD; suspended solids; toxics; spent solvents	volatile organic compounds; contaminants in purchased chemicals; formaldehyde vapours; combustion gases; particulate matter	fabric scraps and trimmings; packaging waste

Source: USEPA, 1997, p.43

4.1 – Wastewater

The Health Canada 2003 field study found that the principal source of wastewater for woven mills was spent processing baths and rinse water from scouring, desizing, bleaching and dyeing (Crechem Technologies Inc., 2003). Residual finishes and coatings, cleaning of finish liquor troughs, printing equipment cleaning, and chemical container cleaning also contributed to the pollutant load of wastewater.

On average, woven fabric wet processing mills in Canada generated 177 litres of wastewater per kg of woven fabric processed according to the Environment Canada 1997/98 survey (Environment Canada, 1998). This is higher than the water use data from the U.S which was reported in the range of 5-508 L/kg with an average of 113 L/kg for woven mills (USEPA, 1996). In general, the wastewater generated can be assumed to be equal in volume to the water used. Table 4 provides water use data on an operation basis.

Table 4 – Water Use by Different Operations and Dyeing Methods in U.S.

Section	Operation or Method	Water Consumption		Liquor Ratio
		gallon/lb	L/kg	kg of water/kg of fabric
Preparation	Singeing	nil	nil	
	Desizing	0.3-2.4	2.5-20	
	Scouring	2.3-5.1	19-43	
	Continuous bleaching	0.3-14.9	2.5-124	
	Mercerizing	0.12	1.0	
Dyeing	Continuous	20	167	1:1
	Beam	20	167	10:1
	Beck	28	233	17:1
	Jet	24	200	12:1

Section	Operation or Method	Water Consumption		Liquor Ratio
		gallon/lb	L/kg	kg of water/kg of fabric
	Jig	12	100	5:1
	Paddle	35	292	40:1
	Skein	30	250	17:1
	Stock	20	167	12:1
	Pad-batch	2	17	
	Indigo dyeing	1-6	8-50	
Printing	Printing	3	25	
	After-washing	13.2	110	
Finishing	Chemical	0.6	5.0	
	Mechanical	nil	nil	

Sources: USEPA, 1996; Smith, 1988

Textile mill effluent is characterized by high concentrations of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), and other toxic chemicals. Provided in Table 5 are typical pollutant loads of raw textile mill effluents from woven mills processing cotton and synthetic blends in the UK (UK Environment Agency, 1997).

Table 5 – Characteristics of Raw Textile Mill Effluent from Woven Mills in UK

Pollutant	Units	Value
BOD	mg/L	550-650
Total Suspended Solids or TSS	mg/L	185-300
COD	mg/L	850-1200
Colour	ADMI*	325
pH		7-11

*American Dye Manufacturers Institute
Source: UK Environment Agency, 1997

The quantity of chemicals released to wastewater depends upon their fixation rates. In typical dyeing and printing operations, 50-100% of dyes are fixed on fibres and the remainder is discarded in the form of spent dyebaths and/or wastewater from subsequent textile washing (USEPA, 1997). Summarized in Table 6 are fixation rates of various dyes along with their application methods and typical substrates.

Table 6 – Fixation Rates of Dyes

Dye Class	Application Method	Typical Substrate	Fixation Rate
Acid	Exhaust/Beck/Continuous	wool, nylon	80-93%
Basic	Exhaust/Beck	acrylic, some polyesters	97-98%
Direct	Exhaust/Beck/Continuous	cotton, rayon, other cellulotics	70-95%

Disperse	High-temperature exhaust, Continuous	polyester, acetate, other synthetics	80-92%
Reactive	Exhaust/Beck/Cold pad batch/ Continuous	cotton, other cellulose, wool	50-80%
Sulphur	Continuous	cotton, other cellulose	60-70%
Vat	Exhaust/Package/Continuous	cotton, other cellulose	80-95%

Source: USEPA, 1997, p.35

4.2 – Solid Waste

The Health Canada 2003 field study found that small quantities of solid waste were generated from woven mills (Crechem Technologies Inc., 2003). These included packaging materials (paper bags, boxes and drums), off-spec fabric products, and sludge collected during wastewater screening. They were either recycled or landfilled.

The same study also found several hazardous waste materials from woven mills (Crechem Technologies Inc., 2003). They included: 1) spent dye liquor; 2) residual finishes; 3) residual print paste; and 4) oil removed during scouring operations. These waste materials were collected into drums or tanks and disposed of by third-party service companies.

4.3 – Air Emissions

The Health Canada 2003 field study indicated that air emissions occurred in many operations (Crechem Technologies Inc., 2003). Volatile substances were vented to the atmosphere from finishing, coating, and printing operations. Since many wet processing operations such as scouring, desizing, bleaching, and dyeing were carried out in open tanks, the air emission of volatile organic compounds was inevitable. Air emissions were also observed when dyed fabric materials were dried using tenter frames.

5 – EMISSION SCENARIOS

5.1 – Fate of Chemical Agents

Described in Figure 2 is the fate of a chemical agent used at a facility. The agent is shipped to the facility using one or more types of containers. It is then unloaded or unpackaged and transferred to the production process. The agent leaves the facility via the following routes:

- Container residue that remains in containers after unloading or unpackaging and ends up in wastewater or is disposed of by other means.
- Process residue that remains in process vessels and transfer pipelines and also ends up in wastewater or is disposed of by other means.
- Liquid loss that enters wastewater streams during normal applications.
- Air emission that occurs if the agent contains volatile components.
- Reaction loss that occurs if the agent undergoes chemical reactions during its use.
- Product retention that accounts for a portion of the agent fixed onto finished products.

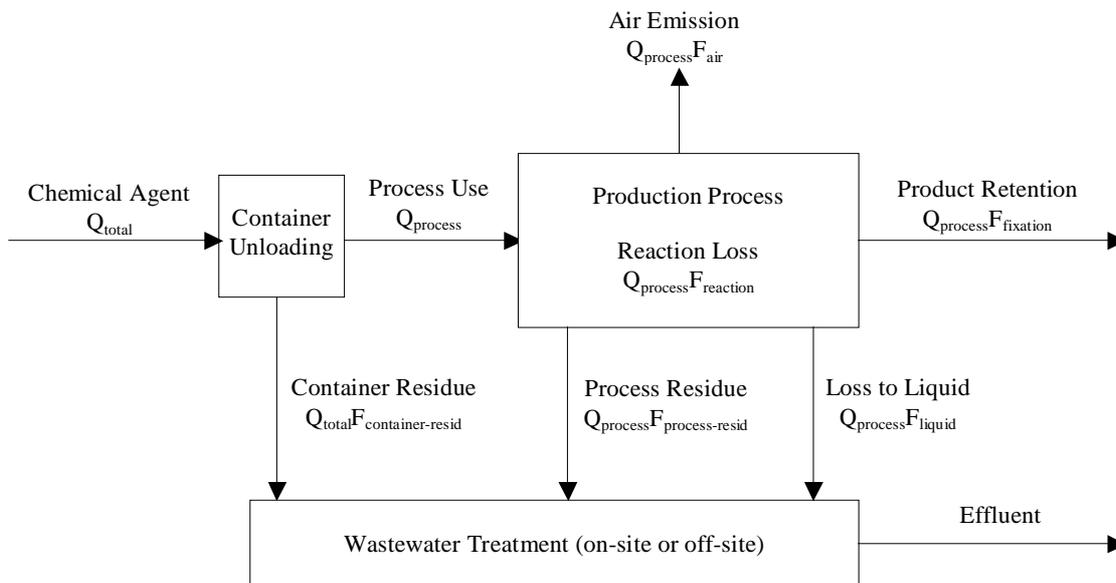


Figure 2 – Fate of a Chemical Agent Used at a Facility

Various wet operations were identified for woven mills in a field study conducted for Health Canada (Crechem Technologies Inc., 2003). These operations included desizing, scouring, bleaching, dyeing, coating, and wet finishing.

5.2 – General Approach to Aqueous Emission Estimation

A general approach to aqueous emission estimation was recommended by the Organization for Economic Cooperation and Development in 2000 in a publication entitled "Guidance Document on Emission Scenario Documents" (OECD, 2000). The approach is based on the fixation of chemical agents onto finished products and can be described by the following equation assuming no air emission and reaction loss:

$$E_{water} = \frac{Q_{product} Q_{agent} C_{substance} (1 - F_{fixation})}{T_{operation}}$$

The equation includes a set of input variables on the right and one output variable on the left. The definitions and value types of these variables are provided in Table 7.

Table 7 – Input and Output Variables of Aqueous Emission Estimation Equation

Variable		Symbol	Units	Value Type
Output	Aqueous emission of a substance in chemical agent	E_{water}	kg/d	Calculated
Input	Annual production	Q_{product}	tonne/yr	User input without default available
	Chemical agent use rate	Q_{agent}	kg/tonne	Provided with default which can be modified by users
	Substance concentration in chemical agent	$C_{\text{substance}}$	%	
	Fixation rate (fraction of chemical agent retained by product)	F_{fixation}	%	
	Annual operation days	$T_{\text{operation}}$	d/yr	

Source: OECD, 2000.

5.3 – Emission Estimation Calculations

5.3.1 – Emission to Wastewater

The emission to wastewater from a knit mill can be estimated according to a scheme described in Figure 2. The scheme is based on a spreadsheet formula used by the USEPA for exposure estimation. The emission consists of three portions: 1) liquid loss; 2) container residue; and 3) process residue. Liquid loss is incurred when a fraction of a chemical agent is not retained by finished products and enters wastewater, while container and process residues are common losses resulting from chemical handling and transferring. The following equation can be used for the aqueous emission estimation:

$$\begin{aligned}
 E_{\text{water}} &= \text{liquid loss} + \text{container residue} + \text{process residue} \\
 &= \frac{Q_{\text{total}} C_{\text{substance}}}{T_{\text{operation}}} (1 - F_{\text{container-resid}} - F_{\text{process-resid}}) (1 - F_{\text{air}} - F_{\text{reaction}} - F_{\text{fixation}}) + \\
 &\quad \frac{Q_{\text{total}} C_{\text{substance}}}{T_{\text{operation}}} F_{\text{container-resid}} + \frac{Q_{\text{total}} C_{\text{substance}}}{T_{\text{operation}}} F_{\text{process-resid}}
 \end{aligned}$$

where

- E_{water} : daily aqueous emission of a substance in chemical agent, kg/d
- Q_{total} : total chemical agent received by or shipped to a facility, kg/yr
- $C_{\text{substance}}$: substance concentration in chemical agent, %
- $F_{\text{container-resid}}$: container residue as percentage of total chemical agent received by or shipped to a facility, %
- $F_{\text{process-resid}}$: process residue as percentage of total chemical agent received by or shipped to a facility, %
- F_{air} : air emission as percentage of chemical agent used in production process,

F_{reaction} :	% reaction loss as percentage of chemical agent used in production process,
F_{fixation} :	% fixation rate, i.e., fraction of chemical agent retained by finished products, %
$T_{\text{operation}}$:	annual operation days, d/yr

5.3.2 – Total Chemical Agent

The total amount of a chemical agent received by or shipped to a facility can be estimated from the use rate of the agent if it is not provided directly.

$$Q_{\text{total}} = \frac{Q_{\text{product}} Q_{\text{agent}}}{(1 - F_{\text{container-resid}} - F_{\text{process-resid}})}$$

where

Q_{total} :	total chemical agent received by or shipped to a facility, kg/yr
$F_{\text{container-resid}}$:	container residue as percentage of total chemical agent received by or shipped to a facility, %
$F_{\text{process-resid}}$:	process residue as percentage of total chemical agent received by or shipped to a facility, %
Q_{product} :	annual woven fabric production, tonne/yr
Q_{agent} :	chemical agent use rate based on product mass, kg/tonne

5.3.3 – Air Emission

The fraction of a substance in a chemical agent emitted to the atmosphere is defined as

$$F_{\text{air}} = \frac{E_{\text{air}}}{Q_{\text{use}}} \times 100\%$$

where

F_{air} :	fraction of a substance in a chemical agent released to air, %
E_{air} :	quantity of a substance in a chemical agent released to air, kg/d
Q_{use} :	quantity of a substance in a chemical agent used in production process, kg/d

The air emission of a target substance can be estimated from a reference substance based on vapour pressure if the two substances are involved in the same operations (USEPA, 2000).

$$F_{\text{air}} = F_{\text{air-ref}} \frac{P_{\text{air}}}{P_{\text{air-ref}}}$$

where

- F_{air} : fraction of a target substance released to air, %
- $F_{\text{air-ref}}$: fraction of a reference substance released to air, %
- P_{air} : vapour pressure of a target substance, Pa
- $P_{\text{air-ref}}$: vapour pressure of a reference substance, Pa

A reference substance should be volatile so that its air release reaches a sufficient quantity, while at the same time, it should be found in aqueous discharge to ensure reasonable partitioning between water and air. To simplify calculations it is necessary to assume that the reference substance is not retained by finished products and is released to air and water only. Under these conditions, the air emission of the reference substance can be estimated by the equation.

$$F_{\text{air-ref}} = \frac{E_{\text{air-ref}}}{E_{\text{air-ref}} + E_{\text{water-ref}}}$$

where

- $E_{\text{air-ref}}$: quantity of reference substance released to air, kg/d
- $E_{\text{water-ref}}$: quantity of reference substance released to water, kg/d

5.3.4 – Reaction Loss

The loss due to chemical reactions is substance specific. In general, it is assumed at zero, i.e., the substance in question does not undergo chemical transformation. Some substances may, however, change chemically and need to be evaluated from the data available.

5.4 – Parameter Defaults

5.4.1 – Container Residues

Container residues result from chemical unloading and its quantity depends primarily upon the type of containers used. Listed in Table 8 are container residue defaults used by the USEPA for exposure estimation. Drums and totes (semi-bulk) are common container types used by the textile industry. It is recommended that a value of 3.0% instead of 4.0% be used to estimate liquid drum residue for Canadian facilities.

Table 8 – Container Residue Defaults

Container Type	Residue as % of Total Quantity Received	
	Dry	Liquid
Bag	0.1	0.2
Keg	0.3	0.6
Drum	1.0	4.0
Semi-bulk	0.1	0.5
Bulk	0.1	0.2

Source: USEPA spreadsheet exposure estimation, 2004

5.4.2 – Process Residue

Process residue results from the use of process vessels and transfer pipelines. Listed in Table 9 are process residue defaults used by the USEPA for exposure estimation.

Table 9 – Process Residue Defaults

Process Hardware	Residue as % of Total Quantity Received	
	Dry	Liquid
General	0.1	1.0
Batch vessel	0.2	1.0
Transfer pipeline	0.1	1.0

Source: USEPA Spreadsheet Exposure Estimation, 2004

5.4.3 – Air Emission

The fraction of a substance in a chemical agent released to air depends upon its volatility. Its default is zero assuming the substance is a non-volatile compound. The value for a volatile substance may be estimated using emission factors or engineering calculations.

5.4.4 – Reaction Loss

The default for reaction loss is zero assuming no chemical reaction takes place as a chemical agent is used in production processes.

5.4.5 – Annual Woven Fabric Production

The annual wool fabric production widely varied from mill to mill. The figure ranged from 88 tonne/yr for a small mill with 10 employees to 17,000 tonne/yr for a large mill with 600 employees (Environment Canada, 1998). The average production was estimated at 1,760 tonne/yr.

5.4.6 – Annual Operation Days

The value for annual operation days ($T_{\text{operation}}$) was in the range of 235-250 d/yr for woven mills according to a field study conducted for Health Canada (Crechem Technologies Inc., 2003). The value of 250 d/yr can be used as a default.

5.4.7 – Use Rate, Active Substance Concentration and Fixation Rate

The use rate and fixation rate for chemical agents used at woven mills were determined in a field study conducted for Health Canada (Crechem Technologies, 2003). These figures are presented in Table 10 and can be used as defaults. The active substance concentration was not determined in the study, but can be assumed to be 100% by default. It should be noted that the fixation rate for dyes is based on USEPA data (USEPA, 1997, p.35).

Table 10 – Use Rate and Fixation Rate for Chemical Agents Used at Woven Mills

Chemical Agent	Use Rate (kg/tonne)		Fixation Rate (%)	
	Default	Range	Default	Range
Surfactants	285	no data	0	0
Acid dyes	14.5	no data	87 ¹	80-93 ¹
Basic dyes	0.6	no data	98 ¹	97-98 ¹
Direct dyes	0	no data	83 ¹	70-95 ¹
Disperse dyes	3.1	no data	86 ¹	80-92 ¹
Reactive dyes	2.4	no data	65 ¹	50-80 ¹
Sulphur dyes	0	no data	65 ¹	60-70 ¹
Vat dyes	0.6	no data	88 ¹	80-95 ¹
Premetallized dyes	0	no data	97 ¹	95-98 ¹
Dye carriers and auxiliaries	44.3	no data	0	0
Desizing agents	9.2	no data	0	0
Solvents	2.9	no data	0	0
Phosphates	1.0	no data	0	0
Bleaching agents	2.1	no data	0	0
Salts	9.2	no data	0	0
Alkalis	57.0	no data	0	0
Acids	18.4	no data	0	0
Buffering agents	9.0	no data	0	0
Sequestering agents	5.7	no data	0	0
Finishing agents	118	no data	90	90
Coatings	212	no data	90	90
Biocides	0.33	no data	0	0
Chemicals for boilers and cooling water	2.1	no data	0	

Source: Crechem Technologies Inc., 2003

¹Data used by USEPA (1997, p.35)

GLOSSARY

Aging – a treatment method with which printed fabric is exposed to a hot moist atmosphere.

Bleaching – a wet processing operation to improve the whiteness of textile materials by removing natural colouring and/or extraneous substances.

Chemical finishing – use of chemical agents to improve the appearance, texture and performance of fabric, same as wet finishing.

Desizing – a wet processing operation to remove stiffening materials from yarns or fabrics.

Dry finishing – use of mechanical means to cause physical changes to fabric.

Finishing – use of chemical or mechanical means to modify the property of fabric.

Knitting – use of needles to form a series of interlocking loops from a yarn or from a set of yarns.

Mercerizing – a wet processing operation to increase the tensile strength, luster, dye affinity and abrasion resistance of a fabric.

Preparation – any wet processing operation, such as scouring, desizing, bleaching, mercerizing, etc., to prepare yarn or fabric for dyeing and finishing.

Printing – localized dyeing process in which a dye or pigment solution or dispersion is applied to fabrics.

Range – a continuous machine used for dyeing a large quantity of textile materials and consists of compartments for wetting-out, dyeing, after-treatment, washing and rinsing.

Scouring – a wet processing operation to remove natural fats, waxes, proteins, and other constituents, as well as dirt, oil, and other impurities.

Singeing – a dry operation to remove protruding ends of fibres from woven fabrics by passing through open flames or hot metal plates.

Size – a sizing agent, i.e., a stiffening material applied to yarns prior to weaving to increase their abrasion resistance.

Sizing – a wet processing operation to apply stiffening materials to yarns or fabrics to increase their abrasion resistance.

Steaming – a treatment method with which printed fabric is exposed to hot steam.

Wet finishing – use of a variety of agents in a solution to improve the appearance, texture, and performance of fabric.

ABBREVIATIONS

ADMI – American Dye Manufacture Institute

BOD – Biochemical oxygen demand

COD – Chemical oxygen demand

ESD – Emission scenario document

TSS – Total suspended solids

UK – United Kingdom

USEPA – United States Environmental Protection Agency

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