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Pilot Demonstration of BAT/BEP in Kombolcha Textile Sh. Co. (ETHIOPIA) of projects "Capacity Strengthening and Technical Assistance for the Implementation of Stockholm Convention (SC) National Implementation plans (NIPs) in Africa LDCs of SADC and COMESA sub-regions".

Project Nos.: GF/RAF/11/008 (WBS 104063-1-04-01)

GF/RAF/11/012 (WBS 104065-1-04-01)

Contract No. 3000016261

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## ABBREVIATIONS AND ACRONYMS USED IN THE REPORT

ABAquarine Blue
AVAquarine Violet
BATBest Available Technologies
BEPBest Environmental Practices
COMESACommon Market for Eastern and southern Africa
DBDutex Blue
DDTDichloro Diphenyl Trichloroethane
ETPeffluent Treatment Plant
EREuromin Red
LDCLeast developed Countries
NIP
PBDDPoly Bromo Dibenzo Dioxin
PCDD Poly Chloro Dibenzo Dioxin
PCDFPoly Bromo Dibenzo Furan
PFOSPerfluorooctane Sulfonyl
POPPersistent Organic Pollutant
SADCSouth African Development Community
Sh. CoShare Company
TCDD
TCDF
TIDITextile Industry Development Institute
UNIDOUnited Nations Industrial Development
Organization

#### Abstract

As part of the implementation of the Stockholm convention the activities performed in Kombolcha textile Sh. Co based on the contract made between the United Nations Industrial development (UNIDO) and Textile Industry development Institute (TIDI) of Ethiopian Federal Democratic republic for the implementation of pilot demonstration of BAT/BEP in textile industries of projects "Capacity Strengthening and Technical Assistance for the Implementation of Stockholm Convention National SC) Implementation Plans (NIPs) in Africa LDCs of SADC and COMESA 3000016261 sub-regions" with contract No. identifies the chemicals and processes which possibly can be causes for the formation of dioxin precursors and then dioxin/furan emission.

The most common chloranil contained chemicals which lead to the formation of dioxin precursors that are currently in use by Kombolcha textile Sh. Co are pigment violet 23 and pigment blue 15.1. Another potential source of dioxins and furans in this large amount of sludge generated from factory is the the Effluent treatment plant (ETP) because large volume of water and being discharged the chemicals are to ETP due to the incompatibility of machines in the factory's laboratory and production section. As a summary and best available technology and environmental practices, the following recommendations are given for decreasing or eliminating the formation of PCDDs/Fs in the textile processes: 1- Training of staff on chemical and raw material management in relation to environmental pollution because this by and large can help improve proper handling and application of chemicals, minimize the introduction of chloranil containing chemicals to the process and also proper treatment of each process. 2- Substitute the chloranil containing chemicals

used in the dyeing and finishing process with those having low chloranil composition.

3- Solve the incompatibility between the machines in the factory's laboratory and production section and making use of the sludge from the ETP for manufacturing non load bearing construction materials.

Item No. 2 of the recommendations indicated above has direct relevance to the proposed pilot demonstration project and this recommendation is expected to be implemented as phase 3 of the pilot demonstration project activity.

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#### INTRODUCTION

With the objective of safeguarding human health and the environment from the effects of highly harmful chemicals that persist in the environment and affect the well-being of humans as well as wildlife, the Stockholm convention requires each member country to implement its obligations by eliminating or restricting the production and use of toxic persistent organic pollutants (POPs) like dioxins and furans. Ethiopia, as one of the member countries who signed the convention is committed to implement its obligation by for example implementing BAT/BEP Pilot Demonstration Project in Kombolcha Textile Factory.

The general objective of this pilot demonstration project is to build the countrie's capacities to implement the measures required to meet their obligations under the Stockholm convention, including POPs reduction measures and improve their capacities to achieve the sound management of chemicals and the specific objective is to reduce dioxin/furan emissions from the textile sector through the introduction of technological changes and substitution of chemicals such as chloranil that are for dyeing and alkaline extraction for currently in use finishing. This document will give a brief description of the

activities performed in Kombolcha textile Sh, co regarding the chemicals and processes in the dyeing and finishing sections but address in more detail only those steps which have relevance to the rlease of PCDD/PCDF.

The study conducted in the factory shows that very few chemicals (like pigment violet 23 and pigment blue 15.1) that are used in the printing section and the sludge generated from the effluent treatment plant (ETP) can be potential sources for the release of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDDs/Fs).

#### I. THE STOLKHOLM CONVENTION

The Stockholm Convention on Persistent Organic Pollutants is an international environmental treaty by different nations of the world adopted or signed in 2001 and entered into force in 2004 to address the chemical pollution due to persistent organic pollutants (POPs) and aiming to eliminate or restrict the production and use of these chemicals. It is a global treaty whose main objective is to safeguard human health and the environment from the effects of highly harmful chemicals that persist in the environment and affect the well-being of humans as well as wildlife.

The Convention has a range of control measures to reduce and, where feasible, eliminate the release of POPs, including emissions of unintentionally produced POPs such as dioxins and also aims to ensure the sound management of stockpiles and wastes that contain POPs.

Currently the convention has about 179 parties (178 states and the European Union) and each party is supposed to implement the obligations of the Convention, including eliminating or restricting the production and use of the intentionally produced POPs, prohibiting and eliminating production and use or import of POPs, conducting research, identifying areas contaminated with POPs, and providing financial support and incentives to implement theConvention.

#### II. PERSISTENT ORGANIC POLLUTANTS (POPs)

Following the boom in Industrialization and manufacturing of vast number of chemicals after World War II, when thousands of synthetic chemicals were introduced into commercial use many POPs were widely produced and used for different purposes. Most of these chemicals were proved to be beneficial in pest and disease control, crop production and industry. These same chemicals, however, have had unforeseen effects on human health and the environment. Most of these chemicals are halogenated; with aromatic some halogenated compounds, including polychlorinated diphenylethers, tetrachloro benzyltoluenes, brominated and fluorinated naphthalenes and biphenyls; and highly or fully chlorinated and fluorinated alkanes (cyclic, linear, branched).

Persistent organic pollutants (POPs) are toxic chemical substances which resist disintegration, accumulate in organisms, transferred by air, water and, via migrating biological species, across international borders. They can be deposited far from the location of their releasing, where they accumulate into the terrestrial and aquatic ecosystems and are very likely to have significant negative human health or environmental impacts close to, or far away from, their source. These chemicals are proved to adversely affect human health and the environment around the world because POPs generated in one country can and do affect people and wildlife far from where they are used and released. They persist for long periods of time in the environment and can accumulate and pass from one species to the next through the food chain.

Generally POPs include a wide range of chemicals which are originated from two major sources.

- (a) Intentionally produced chemicals currently or once used in agriculture, disease control, manufacturing, or industrial processes. Examples include PCBs, which have been useful in a variety of industrial applications (e.g., in electrical transformers and large capacitors, as hydraulic and heat exchange fluids, and as additives to paints and lubricants) and DDT, which is used to control mosquitoes that carry malaria.
- (b) Unintentionally produced chemicals, such as dioxins, that result from some industrial processes and from combustion (for example, municipal and medical waste incineration and backyard burning of trash).

Initially, in 2004, 12 different chemicals called "Dirty Dozen" were identified as major Persistent Organic Pollutants (POPs) and these include: Aaldrin, chlordane, dichlorodiphenyl

trichloroethane (DDT), dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (dioxins), polychlorinated dibenzofurans (furans)

These chemicals are in one form or another found in different parts of the world being used for different applications. Most of them are used in agriculture to control harmful effects caused by different insects and pests. Some are also used in industrial processes for specific activities.

More recently, in 2010, nine additional chemicals were introduced as Persistent Organic Pollutants (POPs) and are added to the above list. These are:

Chlordecone, Lindane, Hexabromobiphenyl, Pentachlorobenzene, Alpha hexachlorocyclohexane, Beta hexachlorocyclohexane, Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (PFOS), Tetrabromodiphenyl ether and pentabromodiphenylether ('commercial pentabromodiphenyl ether'), Hexabromodiphenyl ether and heptabromodiphenyl ether ('commercial octabromdiphenyl ether)

Regardless of their origin, structure and other properties all persistent organic pollutants have common features when it comes to pollution. Some of these properties are:

(a). Toxicity:- POPs are toxic chemicals that laboratory, field, and health studies have linked to certain adverse health effects in people and wildlife.

(b). Persistence:- POPs are highly stable chemicals that resist the natural processes of degradation. Once introduced into the environment, they are not easily

affected by environmental actions (temperature, pressure,...) and they can persist for a long time.

- (c). Long-Range Transport:- POPs released in one part of the world can travel far from their original source via wind, water, and, to a lesser extent, via-migratory species. Atmospheric transport is the main long-range transport pathway for POPs, especially for PCDDs/Fs, which are more volatile.
- (d). Bioaccumulation:- POPs are readily absorbed in fatty tissue and accumulate in the body fat of living organisms; these substances become more concentrated as they move up the food chain, especially into larger, longer-living organisms. i.e. when POPs found in small amounts at the bottom of the food chain accumulate, they can pose a significant hazard to predators that feed at the higher level of the food chain. That way even small releases of POPs can have significant impact on the living environment.
- In the Stockholm Convention Chloranil is indicated as source of dioxin and furans when it used in the dyeing and finishing process of textile.

<u>Chloranil</u>: - which is also known as 2,3,5,6-tetra chloro-p-Benzoquinone; 2,3,5,6-tetrachloro-1,4-Benzoquinone; 2,3,5,6-Tetra chloro-2,5-cyclohexadiene-1,4-dione; Tetrachloro quinone; Quinone Tetrachloride; Chloranil is a yellow to greenish crystalline powder with the molecular formula  $C_6Cl_4O_2$ .

Like the parent benzoquinone, chloranil is a planar molecule which is used as a fungicide and as an intermediate in the manufacture of dyes.

Chloranil is classified as a water insoluble disinfectant and is derived from phenol with potassium chloride and hydrochloric acid.

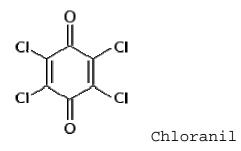
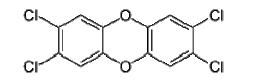


Figure 1. Molecular structure of Chloranil

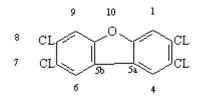
Chloroanil, more so than benzil, serves as a hydrogen acceptor. It is used for the aromatization reactions, such as the conversion of <u>cyclohexadienes</u> to the benzene derivatives and is a potential source for the formation of dioxins and furans.

Among the different kinds of Persistent organic pollutants (POPs) identified as very toxic to human health and the environment, the most toxic (carcinogens) are the commonly named dioxins and dioxin-like compounds. Dioxin is a term used to represent a group of chemical compounds with large number of isomers that are polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). There are about 75 isomers for polychlorinated dibenzo-p-dioxins (PCDDs) and about 135 isomers for polychlorinated dibenzofurans (PCDFs). These isomeric compounds are very similar in structure, differing only in the number and spatial arrangement of chlorine atoms in the this group, isomers with chlorine molecule. In atoms at positions 2,3,7,8 are especially toxic (carcinogens). For the polychlorinated dibenzodioxins (PCDDs) group 2,3,7,8tetrachlorodibenzodioxin (2,3,7,8-TCDD) with chlorine atoms at positions 2,3,7,8 is the most toxic. There are also brominated dioxins (PBDD/Fs), fluoro dioxins and mixed dioxins PXDD/Fs (X =

Cl, Br, F). PBDD/Fs are contaminants with properties similar to polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs), together with their persistence and toxicity. Fluorinated congeners of dioxins are taken to be less dangerous to humans and the environment due to their short half-life and low toxicity.



2,3,7,8 TCDD



2,3,7,8 TCDF

Figure 2. Molecular structure of the polychlorinated dibenzo-p-dioxins and dibenzofurans

#### III. SOURCES OF DIOXINS AND FURANS

Dioxins and furans have never been manufactured deliberately, except in small amounts for research purposes. They are rather unintentionally created in two major ways:

- By the processes used to manufacture some products like pesticides, preservatives, disinfectants, and other products.

- When some materials (chemical products, fuels, plastic, paper, different wastes and other substances) are burned at low temperatures.

#### (a) Dioxins and furans from manufacturing

Dioxins can be inadvertently formed during the manufacture of a group of chemicals called chlorophenols, and the products made from them. Chlorophenols have been widely used as preservatives, disinfectants, and also to keep industrial cooling waters free of nuisance organisms. Dioxins are mainly by products of industrial processes but can also result from natural processes, such as volcanic eruptions and forest fires. They are unwanted by products of a wide range of manufacturing processes including smelting, chlorine bleaching of different products and the manufacturing of some herbicides and pesticides.

Chlorinated compounds, specially chlorinated phenols and phenol derivatives have been proved to be the chief sources of PCDDs/PCDFs. A chlorophenol called 2,4,5-trichlorophenol is always contaminated with the most toxic kind of dioxin called 2,3,7,8-TCDD. Other chlorophenols also contain dioxins and

furans at different concentrations. Pentachlorophenols, for example which are used to preserve wood, contain relatively high levels of dioxins and furans, including many highly toxic kinds. Wood treatment facilities and sawmills have been significant sources of contamination, and wastes from their facilities are now treated as hazardous, or are proposed to be treated as such.

A more probable way by which Dioxin can be formed is proved to be the reaction of phenolic compounds with chlorine that leads to the formation of different dioxin precursors. It was proven that CDDs and CDFs could be ultimately produced from low temperature reactions between  $Cl_2$  and a phenolic precursor, combining to form a chlorinated precursor, followed by oxidation of the chlorinated precursors (catalyzed by a copper catalyst such as copper chloride) as shown below.

The initial step in forming dioxin is the formation of chlorine from HCl in the presence of oxygen (the Deacon process), as follows (Vogg et al., 1987; Bruce et al., 1991):

2HCl +  $\frac{1}{2}$  O<sub>2</sub>  $\longrightarrow$  H<sub>2</sub>O + Cl<sub>2</sub>

Phenolic compounds adsorbed on the fly ash surface are chlorinated to form the dioxin precursor, and the dioxin is formed as a product from the breakdown and molecular rearrangement of the precursor. The reaction is promoted by copper chloride acting as a catalyst (Vogg et al., 1987; Dickson and Karasek, 1987; Gullett et al., 1992):

Step 1:phenol +  $Cl_2$  ----> chlorophenol (dioxin precursor)Step 2:2-chlorophenol +  $\frac{1}{2}O_2$  \_\_\_\_\_ CuCl\_2-, dioxin + Cl2

In general the chemical industry is an important source of dioxins (PCDD/Fs) as by-products. PCDD/Fs are usually formed

during the synthesis of chlorophenols, chlorobenzenes, chlorobiphenyls, polyvinyl chloride, dyes, pigments, printing inks and halogenated pesticides.

Generation of PCDD/Fs from chemical manufacturing processes is favored if one or more of the following conditions are fulfilled.

- High temperatures (>150 °C);
- Alkaline conditions;
- Presence of chlorinated organic compounds;
- Presence of metal catalysts.

#### (b) Dioxins and furans from burning

In terms of dioxin release into the environment, uncontrolled waste incinerators (solid waste, hospital waste...) are often the worst culprits, due to incomplete burning. Long-term storage and improper disposal of PCB-based wastes with high levels of PCDDs/PCDFs may result in dioxin release into the environment and the contamination of human and animal food supplies.

Many sources of combustion produce the well known most toxic organic compounds called dioxins and furans. Incinerators of all kinds (municipal, industrial, and others) are significant sources for the formation of dioxins and furans. This has been proved as most of the products and wastes that are contaminated with dioxins and furans will produce larger amounts when burned. Dioxins and furans have been found both in the incinerator ash and in the gases and tiny particles escaping through stacks. Power plants, smelters, steel mills, and oil and wood stoves and furnaces all emit dioxins and furans.

Greater amounts of dioxins and furans are produced when material is burned inefficiently and at low temperatures. For example, the amounts of dioxins and furans formed during incineration can

be reduced by higher temperatures and more complete burning. Modern incinerators produce smaller amounts of dioxins and furans than older ones, and new technology is expected to reduce the amounts even further.

## IV. TEXTILE INDUSTRIES AS SOURCES OF DIOXIN/FURAN RELEASE (EMISSION)

Having a very long value chain the textile industry is one of the most complicated manufacturing sectors being fragmented and heterogeneous dominated by small and medium sized enterprises. It is composed of wide number of sub-sectors covering the entire production cycle from the production of raw materials to semiprocessed intermediate products and final/consumer products.

The complexity of the textile sector is so high to the extent of facing difficulties in finding a clear-cut classification among the different activities involved. As a result of the sector's complex nature it is also unlikely to point out a specific stage of textile process as a sole site where PCDD/Fs are released. The release of these chemicals in the textile industry is associated with different processes and nature of materials involved in one or more of the many steps carried out in the process of textile making.

In general the occurrence and release of PCDD/Fs from the Textile Industries is associated with the following factors:

1) PCDD/Fs containing chemicals from raw materials (cotton)

Pesticides such as pentachlorophenol, aldrin, dieldrin and others are known to be contaminated with PCDD/Fs. Since these chemicals are used as insecticides (biocides) for cotton and other crops, they inter to the textile process together with the raw material and contribute for the release of dioxins letting the textile industries to be potential sources of PCDD/Fs.

#### 2) Dyestuffs contaminated by PCDD/Fs

Different textile processes may utilize chlorinated chemicals contaminated by PCDD/Fs. As far as the release of dioxins in the textile industries is concerned, the chief sources are dioxazine and antraquinone dyes and pigments, produced from chloranil as intermediate product, and chloranil itself used as a catalyst in the production of dyes and pigments. PCDD/Fs are formed during the synthesis of chloranil from chlorinated phenols. Chloranil is formed as the final product of the chlorate-HCl oxidation of many aromatic compounds because of its great resistance to further oxidation. The application of sodium hypochlorite for bleaching purpose in the textile processes is also a potential source for the release of dioxins because pentachlorophenol, the contaminated most chemical with PCDD/Fs is proven to be found in the hypochlorite.

#### 3) Effluent water and sludge from the textile industries

Textile industries release large volumes of effluent water into the environment. The large volume of waste in the textile industry includes washing water from the preparation and continuous dyeing, alkaline waste from the preparation, and batch dye waste containing large amounts of salts, acids, or alkali and different kinds of dye stuffs and pigments.

The sludge left from the waste water has a complex nature containing heterogeneous mixtures of various organic and inorganic substances. Following a study of the potential sources of dioxins in sewage sludge, PCDD/Fs were detected in nearly all sewage sludges tested and it was concluded that the contribution of several textile products could account for the source of PCDD/Fs in many wastewater treatment plants.

#### V. KOMBOLCHA TEXTILE SHARE COMPANY

#### (i). Description and technology

Kombolcha Textile Share Company is one of the big integrated Textile factories in Ethiopia located in the town of Kombolcha, which is 376 Km north of Addis Abeba. The factory is located within easy access of main cotton - growing regions of the country such as the Awash valley and Gonder. The town of Kombolcha is connected to the port of Djibouti, 500kms east, via an all weather road, and Kombolcha Airport which is convenient for importing raw materials as well as for exports.

The factory was established in 1984 under the National Textile Corporation, and finally it was reorganized as a share company in 1998 with the following main objectives:

- To manufacture yarn and all kinds of grey & finished fabrics from cotton.
- To prepare goods for household use from cotton, yarn, and fabric products.
- To sell its products locally and mainly for export market.
- To engage generally in any other trade or business conducive to the attainment of its objectives.

The factory's products are made of 100% cotton and include woven dyed and printed cotton fabrics such as abujedid, mulmul, poplin, khaki, drill, twills, sheeting, terry towel, canvas, and also cotton yarn. In addition to the above mentioned items the fabrics different kinds of company produces and yarn in accordance with customer specifications and orders. The products of the company for export are mainly grey fabrics, bed sheets and terry towels. The current reliable export customers are KOTEMA of Geneva, Baoding, Tianpeng of China, Vitcon of Italy, Village Industry, Chemitex Belgium, Serofil of Italy, Textrade of Italy and Kopratexa of Germany. The company's products still enjoy acceptance in terms of quality and have greater demand in the domestic market. These days the company has made an expansion and installed a state of the art instruments in all processing mill which results in the increase of its installed production capacity to 14,848,934 meters of fabric per year. Recently the factory has an average actual production capacity of 7,218,516 meters of fabric per year. To realize this, the factory consumes an average of:

- 9,800Kg different dyes and pigments per year.
- 100,155Kg different chemicals per year.
- 2,424,749 literes of fuel
- 21,574,533 kw power
- 218, 063 m<sup>3</sup> of water

After dyeing and printing, significant amount of chemicals and dyestuffs are discharged to the effluent treatment plant in the form of waste water.

Textile industry involves wide range of raw materials, machineries and processes to engineer the required shape and properties of the final desired product. The following are lists of machineries installed and used in the dyeing and finishing sections in Kombolcha Textile Share Company.

S/n	Machine	Make &	Year	Nos.	Capacity*	Installed
		Model	of Mfg.	of m/c	Per m/c	load
1.	Singeing & desizing m/c	Reggian i	1982	1	25-100m/min	30kwh
2.	Scouring	Textima	1983	1	25-125m/min	27kwh
3.	Bleaching	Textima	1983	1	25-125m/min	27kwh
4.	Washing	Textima	1983	1	25-125m/min	68kwh
5.	Mercerizing	Textima	1982	1	12-63m/min	55kwh
6.	Cylinder Drier	OMEZ	1982	3	5-80m/min	29-55kwh
7.	Continuous Dyeing	Textima	1983	1	20-100m/min	143kwh
8.	Dyeing Jigger	OMEZ	1982	5	40m/min	-
9.	Bleaching m/c	Goller,		1	100m/min	
10.	Washing m/c	Goller		1	120m/min	
11.	Drying range	Goller		1	100m/min	
12.	Cold pad- batch	Benning er,Hola nd		1	6-60m/min	
13.	Soft flow dyeing m/c	Sclavo, Greek		1	350kg/hr	1 chamber
14.	Soft flow dyeing m/c	Sclavo, Greek		2	700kg/hr	2 chambers
15	Stenter	Textima	1982	2	8-60m/min	202kwh
16	Polymerizing m/c	Arjioli	1995	1	-	22kwh

17	Calendaring m/c	Comerio ercole	1982	1	10-100m/min	27.27kwh
18	Cloth Inspection m/c	Simat	1982	5	10-23m/min	22.2kwh
19	Doubling & Folding m/c	Simat	1982	2	60m/min	1.8kwh
20	Bale press/packin g m/c	Textima	1982	2	-	4kwh
21	Stenter	Monfort , Germany		1	150m/min	
22	Rotary Screen Printing, 6- c	Reggian i	1985	1	9-90m/min	-
23	Rotary Screen Printing, 8- c	Rijieco n, Italy		1	42m/min	

Table 1. List of machines installed in the dyeing and finishing sections of Kombolcha textile Sh. Co.

## (ii). Details of company/companies which currently supply chemicals to Kombolcha textile share company

Due to the variety and complexity of the chemicals, dye stuffs and other accessories requirement number of suppliers are involved in the supply chain. Not only the difference in the price of chemicals and dye stuffs which each supplier offers but also the un availability of the required chemicals and dye stuffs upon request has been a driving force for Kombolcha textile sh. Co. to deal with many and different suppliers. The list of suppliers given below includes suppliers with long period of experience in supplying and some are new requiring, evaluation of the listed suppliers' performance is a continuous & periodical activity to terminate based on criteria currently established by the factory.

S/N	OVERSEA SUPPLIERS OR PRODUCERS	LOCAL REPRESENTATIVE	MAIN SUPPLIES
01	GERMEX GMBH P.O.BOX:102306 20016 HAMBURG TEL:(040)331236 FAX:(040)338826 E-mail: <u>gerimex@aio.com</u> <u>GERMANY</u>	S.G TREADING P.O.BOX:34649 TEL:0116624187 FAX:011 553 9372 e-mail: <u>sgtreading@ethionet.et</u> ADDIS ABEBA	Spindle tape & rotary screen &film chemicals
02	DAISHO CO.LTD 3 <sup>rd</sup> floor building no. 11-16, 2-chome kawarayamachi CHUO-KU,OSAKA 542-0066 TEL:06-6768-1345 FAX:06-6768-1349 e- mail:dskue@gold.ocn.ne.jp JAPAN	S.G TREADING P.O.BOX:34649 TEL:0116624187 FAX:011 553 9372 e-mail: sgtreading@ethionet.et ADDIS ABEBA	chemical
03	SUNITA IMPEX PVT.LTD 36-A,BENTINCK STREET 1 <sup>ST</sup> FLOOR,KOLKATA-700069		chemical
04	DYSTAR BOEHME AFRICA(pvt)LTD P.O.BOX-1845 PIETERMARITZBERG-3200 27 SHEFILD ROAD, WILLOWTON PHONE-+27(0)33-3908170	SWIFT TRADING P.O.BOX 14540 PHONE: 011 615850 FAX: 011 61 4300 Email: <u>swift@telecom.net.et</u> ADDIS ABEB	Chemicals

	FAX 033-3902318		
	E-MAIL- swindon.ute@dystar.com		
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05	LAMBERTI SPA SEDE:VIA PIAVE 16-21041 ALBIZZATE PHONE-+39 0331-715-111 FAX-+39 0331 861 179 w.site: www.lamberti.com ITALY	NAZARETH INTERNATIONAL TREADING PVT.LTD PHONE : 011 FAX: P.O.BOX-62402	Day staff &chemicals Pigment
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Table 2. Details of Companies which currently supply chemicals to Kombolche Textile Sh. Co.

# (iii). Chloranil containing chemicals used in dyeing and <u>alkaline</u>

extraction for finishing in Kombolcha textile share company

Dyeing involves a chemical combination or a powerful physical affinity between the dye and the fibre of the fabric. In textile dyeing and finishing, extensive varieties of dyes and processes are used depending on the type of fabric and the end-product desired.

The input materials used in textile dyeing and finishing can include water, the fibre, yarn or cloth and different chemicals like organic acids, alkalis, bleaching agents, dyes, salts, stabilizers, surfactants and other auxiliary finishes. Dyeing is carried out in a jig or padding machine, in which the cloth is moved through a stationary dye solution prepared by dissolving the dyestuff powder in a suitable chemical and then diluting with water. After dyeing, the cloth is subjected to a finishing process. For this purpose Kombolcha textile Share Company uses variety of chemicals and dye stuffs it as manufactures wide range of products for local and foreign customers. Those chemicals used in dyeing and finishing sections of Kombolcha textile Share Company are:

1. Rantazol turquoise blue G 21%

2. Reactive NACY HE

3. Reactive Green

4. Reactive Black

5. Reactive Red 195 (HE)

6. Remazol brill Red 3BS

- 7. Rentazol turquoise Blue HE
- 8. Tolcative Blue P3R
- 9 .Tolcative bordseaux-B
- 10. Fabranthren olive MWNF-D
- 11. Dutex violet DAB
- 12. Flesco brittle Black
- 13. Bat Olive
- 14. Aquarine violet 4B
- 15. Phatalogen brilliant Blue
- 16. Aquarine Blue 3G
- 17. Aquarine Yellow 2GSM
- 18. Ophtical brightener
- 19. Cibanone Green BF MD
- 20. Cibanone Violet 2RB MD
- 21. Cibanone Orange RRTS
- 22. Cibanone Yellow
- 23. Solanthren brilliant Red IGG
- 24. Solanthren Yellow BR
- 25. Solanthren Brown BR
- 26. Anthrasol Violet ARR
- 27. Anthrasol Orange HR

- 28. Cibanol Orange RRTS
- 39. Indigosol Blue IBC granulated
- 30. Indigosol golden Yellow IRK
- 31 Indigosol Yellow IBR
- 32. Indigosol Grey IBC
- 33. Indigosol Olive Green IB
- 34. Indigosol Pink IR extra
- 35. Remazol Yellow GR
- 36. Remazol turquoise Blue
- 37. Remazol Grey ISG
- 38. Reactive Red 3BS
- 39. Reactive Orange CPB
- 40. Reactive Blue CA
- 41. Basilen Red MSB
- 42. Cibacron Red PB gran.
- 43. Cibacron Olive SMD
- 44. Cibacron Yellow FN 2R
- 45. Catacol turquoise Blue CA
- 46. Catacol Yellow A
- 47. Pigment Orange
- 48. Pigment Black

- 49. Euromine Yellow GSCONC
- 50. Euromine Red KBC
- 51. Indofix Blue 198
- 52. Ichofix golden Yellow HR
- 53. Reactive pigment Blue B
- 54. Pigment Blue KBC
- 55. Dutex Black
- 56. Imperon Orange
- 57. Neoprint N.Blue
- 58. Neoprint dark Brown
- 59. Pigment Turquoise
- 60. Setazol Yellow 3RI
- 61. Setazol Red 3BI

Among these chemicals those written in italics are known to be common sources or precursors for the formation of Dioxins and furans due to their chloranil content. The annual consumption and price of these chemicals is given in the following table.

Chloranil	Consumption		Total	Remark
containing	per year	Price per	Price	
Pigments	(kg)	Kg (Birr)	(Birr)	
Aquarine Violate				
4B	60	292.97	17578.5	
Impron orange KR	*	23.28		
Antrasol olive				
Green IB	*	175.35802		

Antrasol orange				
HR	*	232.40528		
Antrasol violate				
ARR	*	202.2274		
Remazol yellow				
GR	*	58.1928		
Setazol Red 3bs	*	59.9995		
Setazol Yellow				
3rs	*	51.332		
Euromin Red KBC	*	100.127		
Pigmacolor blue				
kbt	300	45.5545	13666.35	

Table 3. Chloranil containing chemicals and their annual consumption

\* These chemicals are found in very small quantities in Kombolcha Textile Sh.co and are not regularly used for production. They are only used very rarely upon some orders for local markets and no further purchase order is given for these chemicals.

## (iv). Type and quantity of alternative chemicals to substitute the chloranil based chemicals in the dyeing and alkaline extraction for finishing

Based on their properties and applications some chemicals (dye stuffs and pigments) can be substituted by others for different purposes. In the case of Kombolcha textile Sh.co the two commonly used chloranil containing pigments (aquarine violet and pigmacolor blue) can be substituted by those with less or no chloranil contents. As it is known that violet color can be obtained by mixing red and blue colors, a number of trials have been made to substitute aquarine violet with a mixture of euromin red and aquarine blue in Kombolcha textile Sh.co. The result is very encouraging that shades very closer to the one made with aquarine violet are obtained and even more better and similar shades can be made by using other pure red and blue reactive pigments or dyes. The main reason for the difference in the shades is believed to be due to the fact that euromin red and aquarine blue are not purely red and blue respectively but with some composition of other colors. The best option is thus to have the pure colors with no additional effects and prepare the derivatives accordingly.

For the case of the second chloranil containing pigment (pigmacolor blue) dutex blue was taken as best substitute and the shade made with dutex blue is nearly identical with that of pigmacolor blue and hence a one to one substitution can be made for these chemicals. The results of trials made to show the color matching between the chloranil containing pigments and their substitutes is shown in the following table.

The recipe of paste formulation is:

- Binder = 60gm/litre

- Emulsifier = 5gm/litre
- Thickener = 16gm/litre
- Fixing agent = 5gm/litre

This is common recipe for all cases. It is only the amount of pigments that varies depending on the required shade.

	Pigment used	Amount of	Shade
Trial		pigment(kg)	
No.			
	Aquarine	0.5	
0	violet		
	Total paste	100	100 X 100 100
	Euromine red	0.35	
1	Aquarine blue	0.1	
	Total paste	100	and the second second
	Euromine red	0.61	
	Aquarine blue	0.135	

2	Total paste	100	
	Euromine red	0.45	1000
	Aquarine blue	0.10	
3	Total paste	100	
	Euromine red	0.30	
4	Aquarine blue	0.15	
	Total paste	100	Sector States
	Euromine red	0.40	
5	Aquarine blue	0.10	
	Total paste	100	
	Euromine red	0.50	
6	Aquarine blue	0.135	
	Total paste	100	

Table 4. Trials for the substitution of aquarine violet with a mixture of euromine red and aquarine violet and pigmaccolor blue with dutex blue

Trial	Pigment used	Amount of	Shade
No.		pigment(kg)	
	Pigmacolor	1.5	
0	blue		
	Total paste	100	
1	Dutex blue	1.5	
	Total paste	100	Constant State

For the first part (substitution of aquarine violet with euromin red and aquarine blue) the last trial (trial 6) is found to be the best one (closer to the sample made with 0.5gm of aquarine violet). Using 70 gm(AV), 1500 meters of fabric is produced ..... (production section) But our sample was made using 0.5gm of AV 70qm(AV) = 1500meters0.5qm(AV) = ?X = 10.7 meters of fabric = 1626.4qm (1.6264kg) of fabric because 1meters of fabric = 152gm for this specific sample (design). This amount of fabric can be made with 0.635gm of ER and AB (0.5gm ER and 0.135gm AB) The proportion of ER and AB in the 0.635 mixture is 78.74% and 21.26% respectively. The quantity of aquarine violet required to produce 1ton of fabric can be calculated as: 1.6264kg fabric = 0.0005kg aquarine violet 1000 kg (lton) fabric = ? (x) X = 0.31 kg

Similarly the quantity of the substitutes (euromine red and aquarine blue) required to produce 1ton of fabric is: 1.6264kg fabric = 0.000635kg euromin red and aquarine blue 1000kg(1ton) fabric = ? (x) X = 0.39kg

In case of pigmacolor blue, this chemical can be fully substituted by dutex blue in one to one ratio. i.e. 1gm of pigmacolor blue is substituted by 1gm of dutex blue giving nearly identical shade and equal volume of product. Using 1kg of either chemicals 1025.05metres of fabric can be produced.

1025.05metres of fabric = 230kg of fabric because 1metre fabric = 225gm.(for a specific and commonly requested design) To produce 1ton of fabric using either chemical: 230kg fabric = 1kg of pigmacolor blue or dutex blue 1000kg (1ton) fabric = ? (x)

# X = 4.35 kg

In general the chemicals with no or very low concentrations of chloranil and other dioxin precursors and which can potentially substitute the chloranil containing chemicals and the difference in the annual budget while using the dioxin precursor chemicals or pigments and the alternative chemicals is shown in the following table.

	Consum	ption per	Price of	Total						Cost
Pigments	year		pigmen	Price of	Alternative chemicals	Consumpt	ion	Price of	Total	Difference
currently	Qty.of	Qty of	t PerKg	pigment	for chloranil based	per year		alternative	Price of	while
being	pigme	fabric	(Birr)	being	pigments	Qty.of	Qty of	chemical	chemica	using the
used	nt (kg)	(kg)		used		pigment	fabric	per Kg	ls (Birr)	alternative
				(Birr)		(kg)	(Kg)	(Birr)		(Birr)
Aquarine					Aquarine Blue (AB)	16.2		AB=137.2	2222.64	
Violate	60	195,840	292.97	17578.5	and Euromin red(ER)	60	195,840	ER=100.1	+	-9349.86
4B					inorder to substitute				6006.0 =	
					Aquarine Violate 4B				8228.64	
Pigma					Dutex blue (DB) in					
color blue	300	69,000	45.55	13,666.4	order to substitute	300	69,000	79.72	23,916.1	10,249.76
kbt					Pigmacolor blue					
Table 5	Altor	nativo	ahomiaa	la and	the difference in	່ວກການວ່ໄ	hudget	when us	na the	diovin

Table 5. Alternative chemicals and the difference in annual budget when using the dioxin precursor chemicals and the alternative ones

# (v). Technological changes and/modifications required as a result of the use of alternative chemicals

The textile finishing processes are typically not sources of PCDD/PCDF formation (Horstmann *et al.* 1993). Rather, the textile industry is considered to be a potential source for the release of PCDD/PCDF due to three basic reasons.

- Pesticides such as pentachlorophenol, known to be contaminated with PCDD/Fs, used as a biocide for cotton and enter the textile processes with raw materials (cotton);
- Dyestuffs and pigments contaminated by PCDD/Fs;
- Large volume of waste water from the textile finishing and other washing processes.

The techniques or methods for reduction or control of the formation of PCDDs/Fs from the textile processes should then be derived from these major causes. The best advisable approach to the release of PCDDs/Fs is not to use chemicals control contaminated with these POPs or at least to use chemicals whose contamination is smaller than the main dioxin precursors. In the case of Kombolcha textile Sh.co, different trials have been conducted to substitute the main chloranil containing pigments (pigment violet 23 and pigment blue 15.1) with chemicals having low degree of contamination with chloranil (pigment blue 15 plus euromin red and pigment blue 15.3). Better results than the results obtained can be achieved by using pure blue and red colors than aquarine blue and euromin red since the latter have additional effects of other colors. This may take time and making use of the pure colors which during the time of conducting our trials were not available can give a promising and better result than the one already achieved.

Another and even more effective option to substitute these chemicals is to use reactive dyes and pigments, which are a

class of highly coloured organic substances primarily used for tinting textiles, that attach themselves to their substrates by a chemical reaction that forms a covalent bond between the molecule of dye and that of the fibre. The dyestuff thus becomes a part of the fibre and is much less likely to be removed by washing than are dyestuffs that adhere by adsorption. They are water soluble that they can easily be removed in different forms and also environmental friendly in most cases. Though these reactive dyes/pigments and pure chemicals were not available in the nearby market locally at the time of this study, they are more expensive that their price is estimated to be around 30% higher than the existing chloranil containing chemicals and also more amount of binding agents will be required in some cases to improve their fastness properties.

However, the use of those proposed chemicals and also reactive dyes and pigments in place of the chloranil containing ones, like pigment violet and pigma color blue, is an inarguable option since these chemicals are reactive and can be converted in to different forms without causing an adverse impact on the environment.

As can be seen from their molecular formulas, the proposed chemicals do not have chlorine atoms in their molecules and this absence of chlorine can be taken as an advantage since chlorine is an important source for the formation of PCDDs/Fs.

No.	Chemical (pigment or dye	Molecular formula
	stuff)	
1	Pigment violet (violet 23)	$C_{34}H_{22}Cl_2N_4O_2$
2	Pigma color blue (Pigment blue	$C_{32}HxClyCuN_8$ , $x + y = 16$ ,
	15:1)	11 <= x <= 16, 0 <= y <= 5
3	Euromin red (Pigment red 57:1)	$C_{18}H_{14}N_2O_6S$
4	Aquarine blue (pigment blue	$C_{32}H_{16}CuN_8$
	15:3), $\beta$ type greenish	

-	Ducck Diuc	(proment	brue	15),	$C_{32}H_{16}CuN_8$	
	$\alpha$ type, reddish					

Table 6. Molecular formulas of chemicals to be substituted

Prior to the substitution of alternative chemicals, an intensive training should also be given to the staff on management of chemicals and raw materials in relation to environmental pollution.

Another important technological modification that should be made in Kombolcha textile Sh.co. is to solve the incompatibility between the old mini padder (Rapid Labortex) used in the laboratory and the new padder (Kusters dye pad) used in the production section. This is because these two machines are not compatible since the installment of the new machine in the production section and what is done in the laboratory cannot sometimes be duplicated to mass production and as a result there is uncontrolled system of using pigments and dye stuffs. This results in the consumption of large volume of pigments and dye stuffs which correspondingly increases the volume of waste water sludge. For this particular case, as best available and technique it is recommended to replace the old mini padder (Rapid Labortex) being used in the laboratory by a new one and which is compatible to the new padder (Kusters dye pad) used in the production section.

Managing the amount of printing paste discharged to the effluent treatment plant (ETP) after each printing activity is also another point of attention in Kombolcha textile Sh.co. This is because there is no mechanism of recovering the unused printing paste left in the hose between the paste preparation barrel and the printing machine. Rather this printing paste is washed away with water and discharged to the ETP there by increasing the pollution load and also the formation of

PCDDs/Fs. Minimizing the system volume therefore has major effects in reducing printing paste release to waste water. As Best available Technique it is recommended to minimize the volume of the printing paste supply system pipes so as to reduce printing paste losses in rotary-screen printing and recovery from the supply system itself. The detail of the recommended BAT/BEP for this section is given below (as ANNEX II)

Environmental pollution and release of POPs in textile industries is highly attributed to the large volume of waste in the textile industry which includes

washing water from the preparation and continuous dyeing, alkaline waste from the preparation, and batch dye and printing waste containing large amounts dye stuffs and pigments, salts, acids, or alkali.

In the case of Kombolcha textile Sh.co., the combined textile effluent from dyeing and printing clusters is treated in common effluent treatment plant where the biological treatment of the wastewater leads to the generation of chemical sludqe in voluminous quantities. About 8000 kg/year of sludge is produced in this factory and this sludge is kept in an open air surface which in the long run can lead to the contamination of soil, surface and ground waters. Currently the best advisable and recommended technique for disposal of solid sludge is to use the sludge for production of non-load bearing construction materials (bricks). This bricks can be used for different purposes like decorating green areas and other non constructional purposes. A demonstration work to show that the solid sludge from the ETP can be used for making such non-load bearing bricks has been conducted in the factory and the detail is given below.

# Material and method

#### Collection of chemical sludge sample

The sample sludge was collected from the open air land where the sludge after waste water treatment plant of kombolcha textile Sh. Co. is collected.

# Characterization of sludge

Characterization of sludge was done for common phisico chemical parameters and heavy metals. The test result for the phisico chemical properties and heavy metal of the sludge from kombolcha textile Share Company is given below:

No	parameter	value
1	PH	7.02
2	Organic carbon (%)	24.66
3	Available (MgK <sub>2</sub> O)	641.86
4	Available $p(MgP_2O_5)$	336.61
5	Exchangeable sodium%	1.26
6	Cu(Mg/Kg)	36.2
7	Fe(Mg/Kg)	42.9
8	Mn(Mg/Kg)	25.74
9	Zn(Mg/Kg)	5.65

Table 7: The phisico chemical characterization of sludge generated from kombolcha textile share company

# Solidification stabilization experiment

The sludge with high moisture content was heated in a hot air oven for 48 hrs at 110  $^{\circ}$ c. After drying the sludge was powdered manually with mortar and then was passed through 215 micro sieves. The hollow block 20\*20\*40 size was used for this purpose and a mixture of (dry sludge, cement), sand and gravel at 1:2:4 ratio were mixed manually and then water was poured until the mixture was uniform and then made to the desired design of bricks and were subjected to 28 days of water curing. The sludge cement ratio was varied from 20% - 40% sludge and 80% - 60% cement for different samples. Those samples made of 30% : 70% sludge cement ratio were found to be strong enough to be used as non-load bearing construction purposes.

# Result and discussion

The solidified bricks were evaluated for physical engineering property compressive strength. The compressive strength of 40% and 30% sludge replacement for cement after 28 days of curing was 0.36N/mm<sup>2</sup> and 0.55 N/mm<sup>2</sup> respectively and the control samples with only cement was 2.3 N/mm<sup>2</sup>. This shows that if the work is done in a well controlled process full filling all the necessary conditions for each parameter (temperature, time, sand and gravel grade) bricks which are more stronger than those already made and satisfy the maximum standard (strength requirement) for non-load bearing construction purposes can be produced. The brick samples made by mixing the sludge from Kombolcha textile Sh. Co with cement, sand and gravel as a first trial are shown below.







40% : 60% sludge 30% : 70% sludge 35% : 65% sludge cement ratio Cement ratio cement ratio Figure 4. Bricks made of sludge and cement in Kombolcha Textile Sh. Co.

From this trial it is possible to conclude that the use of Textile ETP sludge up to a maximum of 30% substitution for cement may be possible in the manufacture of non-structural building materials. The use of Textile ETP sludge in these applications could serve as an alternative solution to disposal for reducing the emission of dioxine/furans from the already used chloranil containing dyes and pigments inside the sludge.

# Cross-media effects

Since there is no any kind of air emissions that might be released from the brick and the process of brick making, it is unlikely that the Chloranil containing dyes and pigments from the sludge within the brick can be transported long distances and cause environmental problems.

# Applicability

By making use of the sludge from the factory's ETP to produce non load bearing construction materials (bricks) as best method for disposing of sludge there is a potential to reuse the sludge instead of damping in an open land. However to implement this technique effectively the Factory does not have an instrument called filter press to segregate the solid sludge cakes immediately after secondary clarifier. Thus to practically implement the above BAT/BEP suggestion the company should have at least one filter press so as to make readymade sludge cakes for simple production of Bricks and also a mill to grind the dry sludge. (VI). COLLECT BASE LINE DATA ON DIOXIN/FURAN RELEASE FROM KOMBOLCHA TEXTILE Sh.Co THAT ARE USEFUL TO COMPARE THE RATE OF REDUCTION OF DIOXIN/FURAN EMISSION FROM THE FACTORY BEFORE AND AFTER INTRODUCTION OF THE PRINCIPLES OF BAT/BEP.

# (a) - Collecting and compiling data from the Factory

The methodologies used to collect data from Kombolcha Textile Sh.co were:

- Document review
- On site visit in all working sections of the factory
- Experimental tests

Using the above methods valuable and detail information was obtained on the following points.

- Raw materials, products and by-products of the factory
- Chemicals and accessories used
- Chemical storage areas
- Handling and management of chemicals and other raw materials
- Dyeing and finishing activities
- Waste fraction /sludge /contaminated sites

#### Description

In all the above cases it was observed that there was poor handling and management of raw materials, chemicals and also sludge disposal that may cause contamination of different sites with dioxin precursors like pesticides and PCDD/PCDF containing dyes and pigments at different levels.

In the textile production chain, the finishing processes are typically not sources of PCDD/PCDF formation (Horstmann et al. 1993). Rather, the use of PCDD/PCDF-containing dyes and pigments and the use in some countries of PCDD/PCDF-contaminated fungicides to treat unfinished raw materials such as cotton appear to be the sources of the detected PCDD/PCDF.

New formation of PCDD/PCDF may occur in the textile production chain where effluents are treated and sludge is being removed and incinerated.

Chemicals known to be contaminated with PCDD/PCDF are used for the two purposes and include the chemicals listed below (European Commission 2003b):

Defoliant or fungicide: Pentachlorophenol and 2,4,6 trichlorophenyl 4'-nitrophenyl ether<sup>1</sup> (Chloronitrofen);

Dyes: Chloranil-based dioxazine and phthalocyanine-based dyes.

Results from the analysis of textiles of various origin and fibers gave strong indications that pentachlorophenol has been and perhaps still is being used as a biocide on raw materials, especially on cotton. The PCDD/PCDF pattern clearly revealed that it was the major source of the PCDD/PCDF in the textiles.

Another potential source for the formation of PCDD/PCDFs is the large volume of waste water generated from the Textile industries. There are several steps in the textile production chain where wastewaters generate sludge that is incinerated: for example, from wastewater containing pigment printing paste and different dye stuffs. As with any incineration process, PCDD/PCDF can be formed since this sludge contains relatively high contents of chloride as well as organically bound chlorine.

Of the 635,000 metric tons of dyes produced annually worldwide, about 10-15 % of the dye is disposed of in effluents from dyeing operations. However, dyes in wastewater may be chemically bound to fabric fibers.

Based on the analyses of 16 samples from Germany, the mean PCDD/PCDF concentration found in finished cotton products were at 0.21±0.10 ng IDTEQ/kg with a median of 0.20 ng IDTEQ/kg (Horstmann 1994) and these results were confirmed by random sample analyses of raw and preDtreated cotton arriving at the Hamburg harbor, which contained 0.03D0.2 ng IDTEQ/kg (Hutzinger et al. 1995). (UNEP Standard Toolkit for Identification and Quantification of releases of Dioxins, Furan and other unintentional POPs, January 2013, Annex 50).

PCDDs/PCDFs have been detected in air emissions, wastewater and wastewater treatment sludge from textile mills. However, currently available data are not sufficient to support the derivation of emission factors for these vectors.

# (b)-Reference data on dioxin/furan total release

The annual releases for all vectors of a source or a source category are calculated as follows: Source Strength (Dioxin Emissions per year) = Emission Factor x

#### "Activity Rate"

The PCDD/PCDF emission is expressed in grams TEQ per year. According to the above equation, the annual **Source Strength** is

calculated by multiplying the release of PCDD/PCDF (e.g., in µg -TEQ) per unit of feed material processed or product produced (e.g., ton or liter) = the **Emission Factor** - by the amount of feed material processed or product produced (tons or liters per year) = the **Activity Rate**. In general this has been found to be the best way of relating releases to processes and making estimates for unmeasured sources. (Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases, December 2005)

Activity rates are values in unit per year of product manufactured ( e.g., steel, textiles, cement,etc.) or feed material processed (e.g., hazardous waste, coal, diesel fuel, etc.), or annual quantities of material released (e.g., liters of wastewater, kilograms or tons of sludge generated, etc.).

Emission factor(from UNEP toolkit)	0.21 $\mu$ g TEQ/ton
Total fabrics (in terms of tons of Bleached, dyed and printed fabric)/ year	2,029,082 tones
Total fabrics (in terms of tons of printed fabric)/ year	178,500 tones

Table8: Emission factor for dioxin/furan release (UNEP toolkit)

Product	Type of	Annual	Annual	Baseline
ion	Chemical used	Consumption	Production,(	emission
units		(Kg)	ton)	
Bleachi	Hydrogen	52,500	975,582	
ng	peroxide			
	Caustic soda	109,200		
Dyeing	Dyestuff	45,500	875,000	*

# (c)-Baseline emission data (Estimated) from each process

Printin	Pigment	52,500	178,500	37.5	mg
g	Thickner	17,500		TEQ	
	Binder	70,000			
	Other	100,155			
	chemicals				

Table 9: Base line emission data collected from dyeing and finishing sections of Kombolcha Textile Sh.co

An estimation of the quantity of dioxins/furans emissions from Kombolcha Textile factory shows that a total amount of 37.5 mg TEQ of Dioxin/Furan is emitted annually from a total production of 178,500 tones of printed fabrics.

\* Although there are few number of dyestuffs with some potential of contamination with dioxin precursors it was impossible to take the quantity consumed and estimate the dioxin/furan release because there is large difference between the amount of dyestuffs used in the laboratory and the one in mass production which is resulted from the incompatibility of the mini-pader used in the laboratory and the dyeing machine in the production section. Different amount of dyes are used every time in the production section with trial and error methods.

# VII. CONCLUSION

The textile industry comprising fragmented and complex processes is known to consume large volume of different chemicals among which some are of serious environmental concerns as being sources of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Kombolcha textile Sh. Co. as one of the largest integrated factories in Ethiopia also uses

variety of chemicals (dyestuffs and pigments) for finishing and dyeing activities. Among the large number of chemicals which the factory uses, very few chemicals are found under the chloranil containing classification of dioxin precursors or chemicals of which only two chemicals (pigment violet or violet 23 and pigmacolor blue or pigment blue 15.3) are the common application of such dioxin precursor chemicals ones. The according to Stockholm convention should be avoided by replacing these chemicals with environmentally friendly ones as already demonstrated in this research work. In addition to substituting these chemicals another environmental issue that needs high attention to act upon is the disposal of solid waste (sludge) generated from the factory's effluent treatment plant (ETP). Different studies show that the sludge from textile effluents being concentrated with different chemicals from the dyeing and finishing activities can be a potential source of dioxin/furan emission specially when incinerated. With regard to this issue the best advisable safe way of disposal these days is to use the sludge for manufacturing non load bearing construction materials (bricks) by mixing with cement, sand and gravel. The trial work which is conducted inside the factory to demonstrate this fact is very encouraging and this technique must be well exercised in the factory because it is the safest and sustainable method of disposal.

# VIII. Recommendations

Based on the findings from the study in kombolcha Textile Sh. Co. the following actions are recommended as best available

techniques and environmental practices for minimizing or eliminating the formation of 2,3,7,8-TCDD/TCDF in the dyeing and finishing activities of textile processes.

- 1. Reduction of the application of chloranil containing chemicals or substituting them with chemicals having no or less composition of chloranil or other dioxin precursors.
- 2. Process control monitoring and optimization: To be able to reduce different pollutants simultaneously and to maintain low releases, improved process control is required. It has been found that in kombolcha textile Sh. Co. large volume of printing and dyeing chemicals are washed and discharged to the factory's effluent treatment plant (ETP) and increase the pollution load in general and dioxin/furan emission in particular. This was happened because of the incompatibility of the mini padder (Rapid Labortex) used in the laboratory and the new padder (Kusters dye pad) used in the production section. Solving this problem can by large reduce the amount of water and chemicals discharged to the ETP and then the pollution load due to these chemicals.
- 3. Training of personnel: Training of staff can be a very cost-effective way of reducing discharges of toxic substances because it results in prevention of introducing harmful substances to the process at the very beginning including raw materials specification, inspection, management of chemicals and raw materials for precursor materials and also control of processes to minimize effluent discharges.
- 4. Making use of the sludge from the factory's ETP to manufacture non load bearing construction materials.
- 5. Research and development: The factory must conduct intensive and continuous research on the substitution of

dioxin precursors with other chemicals which are not only free from chloranil but also can give good quality products.

6. Investment: It is clear that sufficient amount of resource has to be allocated while improving and/developing a system and thus Kombolcha Textile Sh. Co has to acquire the necessary investment for the practical implementation of the proposed BAT/BEP exercises (substitution of chemicals, optimizing the use of chemicals through acquiring compatible mini padder with the Kusters dye pad, conduct staff training and also acquiring the necessary instrument to convert the sludge to non load bearing construction materials).

#### IX. ANNEXES

<u>ANNEX I:</u> Contract agreement between the United nations development Organization (UNIDO) and the textile Industry Development Institute (TIDI) of Federal democratic republic of Ethiopia.

#### UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

# GENERAL CONDITIONS OF CONTRACT

#### Artile1- Confidential Nature of Documents

All drawings photographs, mosaics, plans, maps, reports, recommendations, estimates, documents and all other data complied by or received by the contractor under this contract shall be the property of UNIDO, shall be treated as confidential shall be delivered only to UNIDO's authorized officials on completion pf the work under this contract: their contents shall not be made known by the contractor, without the written consent of UNIDO, to any person other than the personnel of the contractor performing services under the contract. The obligations of this paragraph do not lapse upon satisfactory completion of the work under this contract or termination of this contract, including termination by UNIDO.

#### Article 2 - Independent contractor

The contractor shall have the legal status of an independent contractor, Any person assigned by the contractor to perform services under this contract shall remain in the employment of the contactor. The contractor's personnel and subcontractors shall not be considered in any respect as being the employees or agent of UNIDO or the United Nations. Without restricting the generality of the foregoing, UNIDO shall not be liable for any claims and demands, loss, costs, damages, actions, suit or other proceedings, brought or prosecuted in any manner base upon, occasioned by or attributable to the employment relationship between any person assigned by the contractor to perform services under this contract and the contractor. Unless otherwise provided for in this contract, UNIDO shall be liable for claims of any kind in connection with the performance of such services. The contractor and his employees shall conform to all applicable laws, regulations and ordinances promulgated by legally constituted authorities' of the government.

### Article 3 - The Contractor's Responsibility for Employees

The contractor shall supervise and be fully responsible for the work performed by and the professional and technical competence of his employees and shall select, for work under this contract, reliable individuals who will perform effectively in the implementation of the contract, comply with the laws of the government, respect the local customs and conform to a high standard of moral and ethical conduct.

#### Article 4 -Assignment of personnel

The contractor shall not assign any personnel other than those referred to in this contract for the performance of work in the field without the prior written approval of UNIDO. Prior to assigning any other personnel for the performance of work in the field, the contractor shall submit to UNIDO for its consideration the curriculum vitae of any person the contractor proposes to assign for such service.

# Article 5- Removal of Personnel

Upon written request by UNIDO, the contractor shall withdraw from the field any personnel provided under this contract and shall replace such personnel by other acceptable to UNIDO, if UNIDO so requests. All costs and additional expenses resulting from the replacement, for whatever reason, of any of the contractor's personnel shall be for the account of the contractor. Such withdrawal shall no be considered as termination in part or in total of this contract under the provisions of paragraph 12 "Termination" hereafter.

#### Article 6- Assignment

The contactor shall no assign, transfer, pledge or make other disposition of this contract of any part therefore or of any of the contractor's rights, claims or obligations under this contract except with the prior written consent of UNIDO.

# Article 7- Sub-contracting

In the event the contractor requires the service of sub-contractors, the contractor shall obtain the prior the prior written approval and clearance of UNIDO for all sub-contractors. UNIDO's approval of a subcontractor shall not relive the Contractor of any of his obligation under this contract, and the terms of any sub-contract shall be subject to and in conformity with the provisions of this contract.

#### Article 8- UNIDO Privileges and Immunities

Nothing in or relating to this contract shall be deemed a waiver of any of the privileges and immunities of UNIDO.

#### Article 9 -Non-employment of UNIDO Staff Members

The contractor shall not while this contract is in effect, employ or consider the employment of UNIDO staff members without the prior written approval of UNIDO.

#### Article 10- Language, Weights and Measures

Unless otherwise specified in the contract the English language shall be used by the contractor in all written communications to UNIDO with respect to the services to be rendered and all documents procures or prepared by the contractor pertaining to the work. The metric system of weights and measures shall be used by the contractor and estimates of quantities involved shall be made and recorded in metric units, except when otherwise specified in the contract.

#### Article 11- Force Majeure

Force Majeure as used herein shall mean acts of God, laws or regulations, industrial disturbances, acts of the public enemy. Civil disturbances, explosions and any other similar event of equivalent force no caused by nor within the control of both party and which neither party is able to overcome. As soon as possible after the occurrence of any event constituting Force Majeure and if the Contractor is thereby rendered unable, wholly or in part to perform its obligations and meet its responsibilities under this contract the contractor shall give notice and full particulars shall give notice and full particulars therefore in writing to UNIDO. In this event, the following provisions shall apply:

- a. The obligations and responsibilities of the contractor under this contract shall be suspended to the extent of its inability to perform them and for a log as such inability continues. During such suspension and in respect of work suspended, the contractor shall be entitled only to reimbursement by UNIDO, against appropriate vouchers of the essential costs of maintenance of any of the contractor's equipment and of per diem of the contractor's personnel rendered idle by such suspension.
- b. The contractor shall within fifteen (15) days of the occurrence of the Force Majeure, submit a statement to UNIDO of estimated expenditures for the duration of the period of suspension
- c. The term of this contract shall be extended for a period equal to the period of suspension taking, however, into account any special conditions which may cause the time for completion of the work to be different from the period of suspension.
- d. If the contractor is rendered permanently unable, wholly or in part, by reason of force Majeure to perform its obligations and meet its responsibilities under this contract, UNIDO shall have the right to terminate this contract on the same terms and conditions as are provided for in paragraph 12 "Termination" except that the period of notice may be seven (7) days instead of thirty (30) days.

e. For the purpose of the preceding sub-paragraph (d), UNIDO may consider the contractor permanently unable to perform in case of any period of suspension in excess of ninety (90) days. Any such period ninety (90) days of less shall be deemed temporary inability to perform.

#### Article 12- Termination

UNIDO may terminate this contract in whole or in part and at any time, upon thirty (30) day's notice of termination to the contractor. The initiation of arbitral proceedings in accordance with paragraph 16, "Arbitration", below shall not be deemed a termination of this In the event such termination is not caused by contract. the contractor's negligence of fault, UNIDO shall be liable to the contractor for payment in respect of work already accomplished, for the cost of repatriation of the contractor's personnel, for necessary terminal expenses of the contractor, and for the cost of such urgent work as is essential and as the contractor is asked by UNIDO to complete The Contractor shall keep expenses at a minimum and shall not undertaken any forward commitment from the date or receipt of UNIDO's notice of termination.

#### Article 13- Bankruptcy

Should the contractor be adjudged bankrupt or be liquidated of become insolvent, or should the contractor make a general assignment for the benefit of its creditors, or should a receive be appointed on account of the contractor's insolvency, UNIDO may. without prejudice to any other right or remedy it may have under the terms of this contract, terminate this contract forthwith by giving the contractor written notice of such termination. The contractor shall immediately inform UNIDO of the occurrence of any of the above events.

#### Article 14- Insurance and Liabilities to Third parties

a. The contractor shall provide and thereafter maintain insurance against all risks in respect of its property and any equipment used for the execution of this contract.

- b. The contractor shall provide and thereafter maintain all appropriate workmen's compensation insurance, or its equivalent, with respect to its employees to cover claims for personal injury or death in connection with this contract
- c. The contractor shall also provide and thereafter maintain liability insurance in an adequate amount to cover third party claims for death or bodily injury, or loss of or damage to property, arising from or in connection with the provision of services under this contract or the operation of any vehicles, boars airplanes or other equipment owned or leased by the contractor or its agents, servants, employees or sub-contractors performing work or services in connection with this contract
- d. The contractor shall, upon request provide UNIDO with satisfactory evidence of the insurance required under this Article.
- e. Any amount not insured or not recovered from the insurers shall be borne by the contractor.
- f. If the contractor fails to effect and keep in force any of the insurances required under the contract, the and in any such case UNIDO may, at its option, hold the contractor in default in accordance with the contract or effect and keep in force any such insurances and pay any premium as may be necessary for that purpose and from time to time deduct the amount so paid from any monies due to the contractor, or recover the same as a debt due from the contractor.

# Article 15- Indemnification

The contractor shall indemnify, hold and save harmless and defend at its own expense UNIDO, its officers agents servants and employees from and against all suits, claims demands and liability of any nature or kind, including costs and expenses, arising directly out of acts, of omissions, negligence of misconduct the contractor. This requirement shall extend to claims or liabilities in the nature of workmen's compensation and to claims or liabilities arising out of the use of patented inventions or devices. The obligations under this paragraph do not lapse upon termination of this contract. The

indemnity provide under this Article 15 shall be limited to the fees due to be paid to the contractor for the services under this contract.

#### Article 16- Settlement of Disputes

a. Amicable Settlement

The parties shall use their best efforts to settle amicably any dispute, controversy or claim arising out of, or relating to this contract of the breach, termination or invalidity thereof. Where the parties wish to seek such and amicable settlement through conciliation the conciliation shall take place in accordance with the UNCITRAL Conciliation Rules then obtaining or according to such other procedure as may be agreed between the parties.

#### b. Arbitration

Unless any such dispute, controversy or claim between the parties arising out of or relating to this contract or the breach, termination or invalidity thereof is settled amicably under there preceding paragraph of this Article within sixty (60) days after receipt by one party of the other party's request for such amicable settlement, such dispute controversy or claim shall be referred by either party to arbitration in accordance with the UNCITRAL arbitration rules the obtaining, including its provisions on applicable law. The arbitral tribunal shall have no authority to award punitive damage. The parties shall be bound by any arbitration award rendered as a result of such arbitration as the final adjudication of any such dispute. It is understood, however, that the provisions of this paragraphs shall not constitute nor imply the waiver by UNIDO of its privileges and immunites.

# Article 17- Conflict of Interest

No employee of the Contractor assigned to perform work under this contract shall engage, directly or indirectly, either in his own name or through the agency of another person, in any business, profession or occupation in the country of the government nor shall he make loans to or investments in any business, profession or occupation in the said country.

#### Article 18- Obligations

In connection with the performance of its services under this contract, the contractor shall neither seek nor accept instructions from any authority external to UNIDI. The contractor shall refrain from any action which may adversely affect UNIDO and shall fulfill its commitments with full regard for the interests of UNIDO, Unless authorized in writing by UNIDO, the contractor shall not advertise or other wise make public the fact that it is performing or has performed services for UNIDO. Also, the contractor shall not, in many manner whatsoever, use the name, emblem or official seal of the United Nations or of UNIDO or any abbreviation of the name of the United Nations in connection with its business or otherwise. The contractor is required to exercise utmost discretion in all matters relating to this contract. Unless required in connection with the performance of its work under this contract or where specifically authorized by UNIDO, the contractor shall not communicate at any time to any person, government or authority external to UNIDO any information which has not been made public and which is known to it by reason of its association with UNIDO. The contractor shall not, at any time, use such information to private advantage. These obligations do not lapse upon satisfactory completion of the work under this contract or termination of this contract, including termination by UNIDO.

#### Article 19 - Title Rights

(a) The united Nations Or UINDO, as the case may be, shall be entitled to all property rights including but not limited to patents, copyrights and trade marks with regard to material which bears a direct relation to or results from the services provided to the united Nations or UNIDO by the contractor under this contract. At the request of UNIDO, the contractor shall take all necessary steps. Prepare and process all necessary documents and assist in securing such property rights and transferring them to the United Nation and UNIDO in compliance with the requirements of the applicable law. The contractor shall have the right to use any material which bears a direct relation to, or results from the services provided to the united Nations or UNIDO by the contractor under this contract for academic teaching and research purposes.

(b) Title to any equipment and supplies which may be furnished by UNIDO shall rest with the United nation or UNIDO as the case may be and any such equipment and supplies shall be returned to UNIDO at the conclusion of this contract or when no longer needed by the contractor. Such equipment and supplies, when returned to UNIDO, shall be in the same condition as when delivered by UNIDO to the contractor, subject to normal wea and tear.

# Article 20 -Facilities privileges and Immunities of contractor and contractor's personnel

UNIDO agrees to use its best efforts to obtain for the contractor and his personnel (except government nationals employed locally) to the extent granted by the governments to UNIDO staff members, such facilities, privileges and immunities as the government has agreed to grant to contractors and to their personnel performing services for united Nations Development Programme within country. the Such facilities, privileges and immunities shall include exemption from or reimbursement of cost of any taxes, duties, fees or levies which may imposed in the country on salaries or wages earned by be the contractor's foreign personnel in connection with the execution of the work under this contract and on any equipment, materials and supplies which the contractor may bring into the country in connection with the work under this contract or which, after having been brought into the country, may be subsequently withdrawn there from. A copy of the relevant provisions concerning facilities, privileges and immunities which UNIDO Shall Seek to obtain is attached to and made a part of this contract (Annex B).

# Article 21- Waiver of facilities, Privileges and Immunities

Any provision whether in an agreements, plan of operation or any other instrument, to which the recipient government is a party and by which the recipient government confers benefits upon the contractor and his personnel in the form of facilities, privileges, immunities or exemptions by reason of his performance of services for UNIDO under this contract may be waived by the UNIDO where, in its opinion, the facility, Privilege of immunity would impede the course of justice and can be waived without prejudice to the successful completion of the work under this contract of to the interest of the United Nations Development Programme or UNIDO.

#### Article 22- Encumbrances/liens

The contractor shall not cause or permit any lien, attachment or other encumbrance by person to be placed on file or to remain on file in any public office of on file with UNIDO against any monies due or to become due for any work done or materials furnished under this contract, or by reason of any other claim or demand against the contractor.

#### Article 23- Tax Exemption

a. In accordance with section 7 of the convention on the privileges and Immunities of the United Nations and Section 9 of the convention on the privileges and Immunities of specialize agencies which are applicable to UNIDO by virtue of Article 21 of its constitution, UNIDO is exempt from all direct taxed, except charges for public utility services and is exempt from customs duties and charges or a similar nature in respect of articles imported or exported for its official use. In the event any governmental authority refuses to recognize UNIDO's exemption from such taxed duties or charges the contractor shall immediately consult with UNIDO to determine a mutually acceptable procedure. b. According, the contractor authorizes UNIDO to deduct from the contractor's invoice any amount representing such taxed, duties or charges, unless the contractor has consulted with UNIDO before the payment therof and UNIDO has, in each instance specifically authorized the contractor to pay such taxes duties or charges under protest. In that event the contractor shall provide uNIDO with written evidence that payment of such taxes, duties or charges has been made and appropriately authorized.

# Article 24 -Child labor

- a. The contractor represents and warrants that neither him, nor any of his suppliers is engaged in any practice inconsistent with the right set forth in the convention on the rights of the child, including Article 32 thereof, which inter alia requires that a child shall be protected from performing any work that is likely to be hazardous or to interfere with the chil's educations or to be harmful to the child's health or physical mental, spiritual, moral or social development
- b. Any breach of this representation and warranty shall entitle UNIDO to terminate this contract immediately upon notice to the contractor, without any liability for termination charges or any other liability of any kind of UNIDO.

### Article 25- Mines

a. The contractor represents and warrants that neither him nor any of his suppliers is actively and directly engaged in patent activities, development, assembly, production trade or manufacture of mines or in such activities in respect of components primarily utilized in the manufacture of mines or in such activities in respect or components primarily utilized in the manufacture of mines. The term "Minies" mean those device defined in Article2, paragraphs 1,4 and 5 of Protocol II annexed to the convention on prohibitions and restrictions on the use of certain conventional wapons which May be Deemed to be Excessively Injurious or to have in discrminate effects of 1980. b. Any breach of this representation and warranty shall entitle UNIDO to terminate this contract immediately upon notice to the contractor, without any liability for termination charges or any other liability of any kind of UNIDO.

# ANNEX II

Recovery of printing paste from supply system in rotary screen printing machines

# Description

This technique allows the recovery of the printing paste remaining in the supply system in rotary screen printing machines at the end of each run. Before filling the system, a ball is inserted in the squeegee and then transported by the incoming paste to its end. After finishing a print run, the ball is pressed back by controlled air pressure, pumping the printing paste in the supply system back into the drum for re-use. The technique is illustrated in the figure below, showing the

ball during the phase in which the pump is transporting the paste back to the drum.

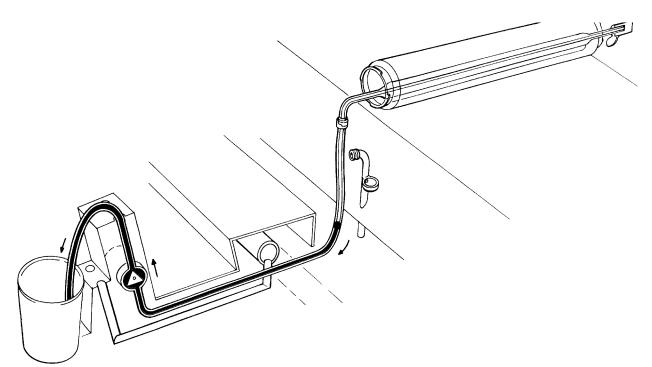


Figure 3. Recovery of printing paste from the paste supply system by back-pumping an inserted ball [179, UBA, 2001] with reference to "Stork, 2001"

# Main achieved environmental benefits

Printing paste losses are reduced drastically. In textiles, for instance, at a printing width of 162 cm, the loss is reduced from 4.3 kg (in the case of a non-optimized printing paste supply system) to 0.6 kg.

Rotary screen printing machines have up to 20 supply systems, although in practice, for fashion patterns, 7 - 10 different printing pastes are common. Therefore, the 3.7 kg of printing paste saved per supply system have to be multiplied by 7 - 10. Water pollution can thus be minimized considerably.

To achieve maximum benefit from this measure, modern printing machines with minimum volume feed systems should be used

#### Operational data

The described technique is successfully applied in textile finishing mills, especially in combination with recycling of the recovered printing paste.

# Applicability

The technique is applicable to new installations (new rotary screen printing machines). Certain existing machines can be retrofitted. There is only one supplier for this technique (Stork Brabant B.V., NL-5830 AA Boxmeer). All their machines newer than the so-called RD-III (that is RDIV and all subsequent models) can be retrofitted with the described system.

As mentioned earlier the technique is applied in textile finishing mills (for flat fabrics). In principle this system can also work for carpets, but it is not applied for various reasons. Probably the main reason is related to the type of thickeners most commonly used in carpet printing pastes. These are based on guar-gum, which is quite inexpensive, but has a limited shelf-life and therefore cannot be stored for long time before re-use (it is biodegradable and the

growth of bacteria and other organisms such as yeasts, rapidly destroy the viscosity).

#### Economics

Investment for retrofitting this recovery system to a rotary screen printing machine with 12 new squeegees and pipes (for a printing width of 185 cm) is about EUR 42000. The next table shows the savings achievable in the reference mill. Number of changes of printing pastes per day= 8 Number of working days per year= 250 Average number of printing pastes per design= 7 Saving of printing paste per supply system= 3.7 kg Price of printing paste= 0.6 euros/kg Saving per year= 31080 euros/yr Source: [179, UBA, 2001] Table 7. Calculation of savings achievable in a typical textile mill by installing the referenced printing paste recovery system Driving force for implementation

Severe waste water problems and the need to reduce printing paste losses for economic and environmental reasons have been the main driving forces.

**ANNEX III:** Detail of Filter press and its working principle

A belt filter is compact in size and fairly reliable. With a belt filter there is a continuous feed of sludge and a continuous discharge of sludge cake and filtrate. Belt filters usually start by allowing the sludge to rest on a porous belt for some draining using gravity prior to being pressed.

Before sludge can be placed in a belt filter, or other dewatering device, it typically requires chemical conditioning, such as the addition of polymer.

Polymers act as a bridge that connects solids particles by creating larger particles that trap additional solids within its mass. Polymers can be added directly to the feed line and mixed in the line using a Venturi-type restriction in the line or be mixed in a separate mixing chamber.

Dosages must be optimized to ensure proper dewatering. Improper dosages can lead to a sludge cake that is too wet and also to washout, which is characterized by large volumes of water carrying into the dewatering zone and overrunning the sides of the belt.

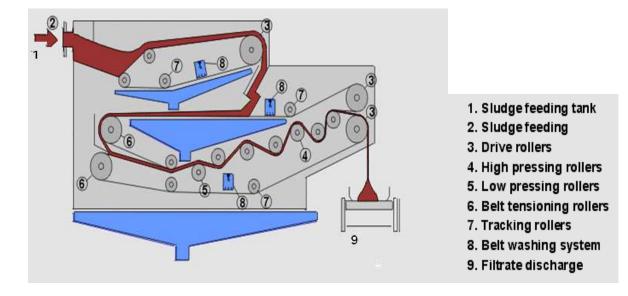


Figure 5. Diagram of a belt filter

# Economics

Though, this is dependent on the Factories brick requirement for non-structural purpose ,it is a good opportunity the factory to minimize the cost of buying normal bricks for decorating the companies green areas . In addition, it is a cheaper and environmentally friendly way of managing solid wastes as compared to land filling and incineration.

# Driving force for implementing this technique

Prevention of environmental pollution due to the sludge generated from the factory and safe way of disposing it are the driving forces.